Conformational Characteristics and Crystalline Order in Poly(2-methyl-1,3-propane glycol terephthalate)

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ABSTRACT: Poly(2-methyl-1,3-propane glycol terephthalate) was obtained by a transesterification condensation reaction of 2-methyl-1,3-propanediol and dimethyl terephthalate. The polymer has an intrinsic viscosity of 0.73 dL/g in chloroform, and its glass-transition temperature is 55 °C. The mean-square dipole moment of the chains per repeating unit, measured in dioxane solutions at several temperatures in the interval 20−60 °C, yields values of 4.17−4.07 D^2. Rotational isomeric state calculations of the polarity of the chains suggest that the gauche population about $OCH_2-CH(CH_3)-CH_2O$ bonds are disfavored with respect to that about the same bonds in poly(3-methyloxetane) $[-OCH_2-CH(CH_3)-CH_2^-]_n$. The polymer crystallized from dilute solutions develops crystalline order although the chains are random stereochemical copolymers.

Introduction

Some polyesters prepared by condensation of terephthalic acid and symmetric aliphatic glycols, with the repeating unit $-OC(O)C_6H_4C(O)O(CH_2)_x-$, are polymers of great commercial interest.[1,2] These polymers develop crystalline order and display the even−odd melting effect, and their melting temperatures decrease as the number of methylene groups in the glycol residue increases.[3−5] Substitution of a methylene group of the glycol residue by an ether group may either suppress the ability to crystallize or decrease the melting temperature of the resulting polymer. It is worth noting that poly(diethylene glycol terephthalate) (PDET), with the repeating unit $-OC(O)C_6H_4C(O)O[(CH_2)_2O]_2^-$, does not crystallize from the melt, although it does from very dilute solutions.[6] This behavior has been attributed to the high preference for gauche states of the CH_2-CH_2 bonds, which favor coiled conformations of the repeating unit at the expense of more extended conformations involved in the development of crystalline order.[7−9] Moreover, the relative closeness of the melting temperature of PDET (≈90° C) to the glass-transition temperature (≈20° C) causes the crystallization process to take place in a relatively high-viscosity medium, thus hindering or impeding the development of crystalline order. Crystallization of PDET from dilute solutions is a consequence of the low viscosity of the crystallization medium that diminishes the transport energy involved in the crystallization process. The preference for gauche states of the CH_2-CH_2 bonds of poly(ethylene terephthalate) (PET) is presumably responsible for the relatively low crystallization rate of this polymer from the melt. The crystallization behavior of PET makes it feasible to not only obtain this polymer in the amorphous state by quenching from the melt but also to prepare PET with the desired degree of crystallinity by controlling the crystallization rate.[1,2] As a consequence of the possibility offered by some polyesters containing the terephthaloyl moiety in the acid residue to prepare them in both the amorphous and the crystalline states, these polymers have been used to study how the crystalline entities affect the mechanical and dielectric responses of molecular chains to perturbation fields by comparing the relaxation behavior of semicrystalline polyesters with that of the same polymers in the amorphous state.[10]

The physical properties of polymers depend not only on their conformational characteristics but also on the intermolecular interactions. Although these interactions in polyesters mainly occur between the dipoles associated with the ester residues of neighboring chains, intramolecular dipolar correlations govern the overall polarity of the isolated chains. Dipolar correlations depend on the relative populations of cis and trans conformations of the terephthaloyl residue as well as on the dipolar correlations between the ester residues of two consecutive repeating units.[7] Obviously, the latter correlations decrease as both the length and flexibility of the glycol residue of the polyesters increase.

There are relatively few experimental studies relating the conformational properties of polyesters to their chemical structure.[7−9,11,12] This fact is a consequence of the relatively low molecular weights reached in polycondensation reactions, which in most cases impedes the determination of the unperturbed dimensions of the chains. On the other hand, the insolubility of most polyesters in nonpolar solvents precludes the experimental measurement of the polarity of isolated chains.[13]

This work focuses on the measurement of the mean-square dipole moment of poly(2-methyl-1,3-propane glycol terephthalate) (PTMT), an amorphous polymer readily soluble in dioxane. The dipole moments of the chains are interpreted in terms of the rotational isomeric state model, and by comparing theoretical and experimental results, the values of the conformational energies associated with the rotational states about the $OCH_2-CH(CH_3)-CH_2O$ bonds are obtained. Preliminary results also are reported showing the capability of PTMT to develop crystalline order.

Experimental Procedure

Synthesis of Poly(2-methyl-1,3-propane glycol terephthalate). Dimethyl terephthalate was purified by recrystallization from methanol, whereas 2-methyl-1,3-propane diol (Aldrich) was dried with calcium hydride and further distilled under reduced pressure. The polymer was obtained by a transesterification condensation reaction of 2-methyl-1,3-propanediol (0.13 mol) and dimethyl terephthalate, under stirring,

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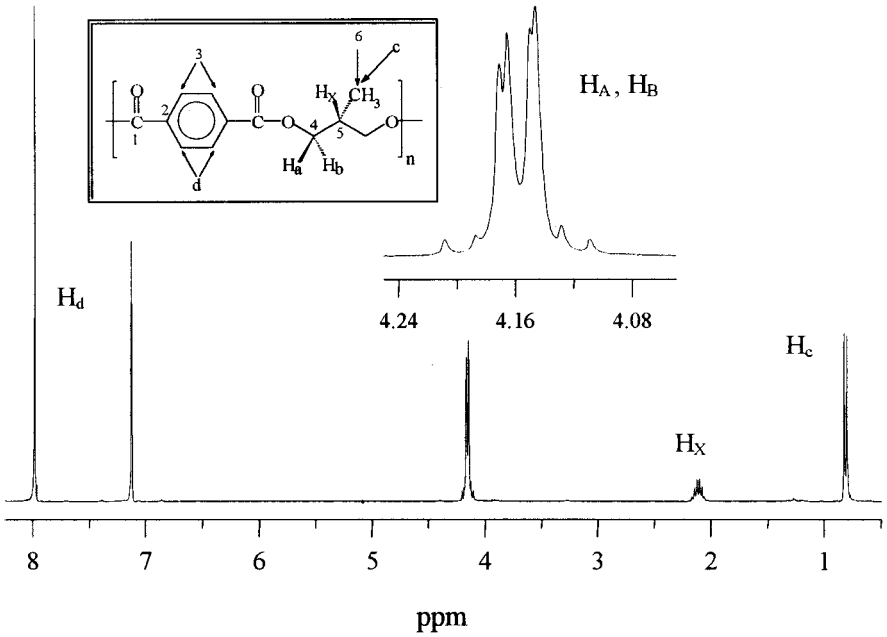

Figure 1. ^{1}H NMR spectrum of PTMT in C_6D_6 at 60 °C; H_{AB} 4.16 (ABX), H_c 0.84 (d), H_d (8.01), H_x 2.14 (m).

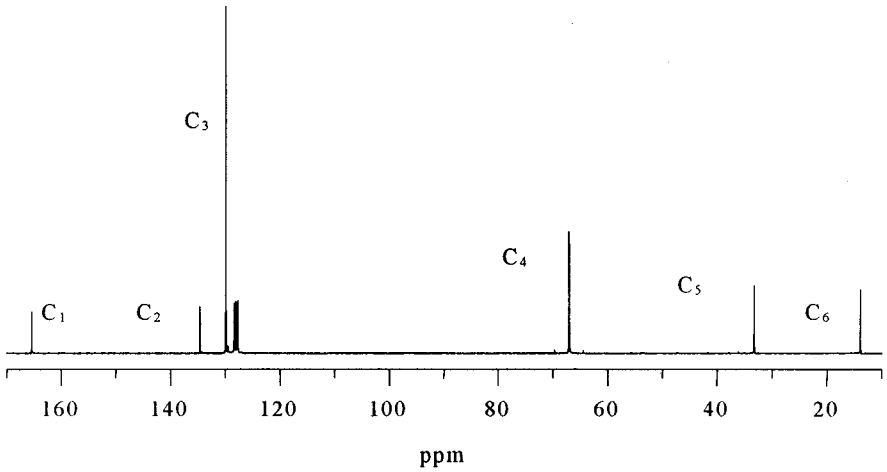

Figure 2. ^{13}C NMR spectrum of PTMT in C_6D_6: C_1 165.4 (167.0), C_2 134.5 (134.8), C_3 129.8 (129.6), C_4 67.0 (69.4), C_5 33.1 (31.2), C_6 13.8 (12.5) (The numbers associated with the carbon atoms are indicated in the insert of Figure 1).

in the presence of isopropyl titanate, which acts as catalyst. The first step of the reaction proceeded at 180−200 °C for 17 h, in a nitrogen atmosphere, whereas in the second step, the temperature was increased to 270 °C and the reaction was carried out in high vacuum. The polyester was dissolved in chloroform and precipitated several times with methanol to eliminate the possible presence of alicyclic and cyclic oligomers. Finally, the polymer was dried overnight in high vacuum at 100 °C.

Characterization Poly(2-methyl-1,3-propane glycol terephthalate). The molecular size of the polymer was characterized with a GPC apparatus (Waters 150C) coupled with a viscometer (Viscotek, 150 R), obtaining 0.73 dL/g for the intrinsic viscosity, and the values of M_n, M_w, and M_p (the molecular weight corresponding to the peak of the GPC chromatogram) were, respectively, 22 000, 53 000, and 45 000.

The glass-transition temperature of the polyester was measured with a Perkin-Elmer DSC-7 calorimeter at a heating rate of 10° C/min. The value of T_g, taken at the onset of the departure of the endotherm from the baseline in the glassy region, was 55° C.

The polymer was characterized by ^{1}H and ^{13}C spectroscopy in deuterated benzene at 60 °C, using tetramethylsilane (TMS) as a reference. The spectra obtained, shown in Figures 1 and 2, indicate the purity of the chains.

Polymer X-ray diffraction patterns were obtained with a Philips X-ray diffractometer using nickel-filtered Cu Kα radiation.

Dielectric Measurements. Dioxane (Panreac) was successively refluxed over potassium hydroxide and methyl isocyanate to eliminate the presence of aldehydes and alcohols. Freshly purified dioxane was used to prepare solutions of PTMT with the weight fraction, w, of polyester lying in the interval 3.3×10^{-3}−1.1×10^{-2} The dielectric permittivity of the solutions was measured with a capacitance bridge (General Radio, type 1640 A). The measurements were performed at 10 kHz with a three terminal cylindrical cell. The increments of the values of the index of refraction of the solutions with respect to that of the solvent were measured with a differential refractometer (Chromatix Inc.).

Because of the high molecular weight of the chains, end group effects on the polarity of the chains were neglected, and the mean-square dipole moment of PTMT chains per repeating unit was calculated by means of the equation of Guggenheim and Smith[14,15]

$$\frac{\langle \mu^2 \rangle}{x} = \frac{27 k_B T M_0}{4\pi\rho N_A (\epsilon_1 + 2)^2} \lim_{w \to 0} \left[\left(\frac{\partial \epsilon}{\partial w} \right) - 2 n_1 \left(\frac{\partial n}{\partial w} \right) \right] \qquad (1)$$

where $\langle \mu^2 \rangle / x$ is the mean-square dipole moment per repeating

Table 1. Experimental Values of the Mean-Square Dipole Moment per Repeating Unit, $\langle\mu^2\rangle/x$, and the Dipole Correlation Coefficient, g, of Poly(2-methyl-1,3-propane glycol terephthalate) at Different Temperatures

T, °C	$d\epsilon/dw$	$2n_1 dn/dw$	$\langle\mu^2\rangle/x$, D^2	g
20	2.48	0.18	4.17	0.58
30	2.46	0.18	4.24	0.59
40	2.28	0.18	4.07	0.57
50	2.20	0.18	4.07	0.57

unit of the chains, k_B and N_A are, respectively, the Boltzmann constant and Avogadro's number, T is the absolute temperature, M_0 is the molecular weight of the repeating unit, ρ is the density of the solvent, and n is the index of refraction of the solution (the subindex 1 refers to the corresponding magnitudes for the solvent).

Results

The derivatives $d\epsilon/dw$ and dn/dw in eq 1 are, respectively, proportional to the total and the electronic polarizations of the chains. The values of $d\epsilon/dw$ were obtained from the isotherms showing the concentration dependence of the increments of the dielectric permittivity of the solutions with respect to that of the solvent. The plots are straight lines whose slopes give the values of $d\epsilon/dw$ represented in the second column of Table 1. In the same way, the value of dn/dw at 20° C was obtained from the slope of the plot Δn ($=n - n_1$) against the weight fraction of polymer in the solutions; it was assumed that dn/dw does not change with temperature, an assumption that will not change significantly the values of $\langle\mu^2\rangle$ due to the relatively low value of dn/dw in comparison with that of $d\epsilon/dw$. The pertinent results at the temperatures of interest are shown in the third column of Table 1.

The values of the mean-square dipole moment per repeating unit, $\langle\mu^2\rangle/x$, were calculated from the values of $d\epsilon/dw$ and dn/dw given in Table 1, in conjunction with eq 1. The corresponding results are shown in the fourth column of this table. The uncertainty of these results was estimated to be ±2.5%.

The polarity of the chains is customarily expressed in terms of the intramolecular correlation coefficient, g. The value of this parameter for high-molecular-weight PTMT is given by

$$g = \frac{\langle\mu^2\rangle}{2m_E^2} \qquad (2)$$

where m_E is the dipole moment associated with the ester group. The value of m_E was taken to be 1.89 D, the dipole moment reported for methyl benzoate.[16] The contribution to the polarity of the chains of the other bonds was considered to be negligible. The polarity of the chains expressed in terms of g is given in the fifth column of Table 1.

Theoretical Calculations

A schematic representation of the repeating unit of PTMT in the all-trans conformation is shown in Figure 3. As indicated above, the dipole moment of the ester group is 1.89 D, and its direction makes an angle of 123° with the $C^{ar}-C(O)$ bond.[17] The supplements of the skeletal bond angles used in the theoretical calculations of the mean-square dipole moments were 68°, with the exception of the $<C^{ar}C(O)O$ and the $<C(O)OCH_2$ angles, whose values were taken to be 66° and 67°, respectively.

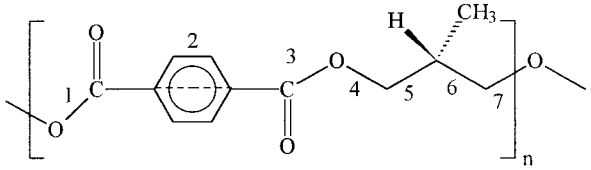

Figure 3. Structural unit of PTMT in all-trans conformation.

The large torsional potential opposing rotation about the ester C(O)−O bonds of the repeating unit renders overwhelming preferences of these bonds for the planar trans conformations.[11,18,19] Therefore, bonds of type 1 and 3 were considered to be restricted to the trans state. On the other hand, because coplanarity favors overlapping between the double bonds of the carbonyl and the phenyl groups,[18] the terephthaloyl residue is restricted to trans and cis conformations, and consequently, the rotational states about the virtual bond of type 2 are 0° and 180°. Moreover, the interactions between the carbonyl groups of the terephthaloyl residue are relatively small so that the cis conformation about the virtual (O)-C*−C*(O) bond has an energy, E_γ, only 80 cal mol^{-1} above that of the alternative trans.[17] The rotational angles about bonds of type 4 in Figure 3 are located at 0° ± 104°. The rotational states of positive sign about these bonds have an energy, $E_{\sigma k}$, 0.4 kcal mol^{-1} above that of the alternative trans states; g^- states, however, give rise to strong repulsive interactions between the methyl and the carbonyl groups.[11] The energy of these states is $E_{\sigma k} + E_\omega$, where $E_\omega = 1.4$ kcal mol^{-1} is the second-order energy between the carbonyl and the methylene groups. Gauche states of positive sign (+120°) about bonds of type 5 place the oxygen atom between the methyl and the methylene groups causing stronger repulsive interactions than those of the alternative gauche states (−120°), where the methyl group is located in the plane and the methylene group is out of the plane; that is, they interchange their locations. The energy associated with the g^+ and the g^- rotational states will be denoted as $E_{\sigma\beta}$ and $E_{\sigma\alpha}$, respectively, and it is expected that $E_{\sigma\beta} > E_{\sigma\alpha}$. Although the critical interpretation of the dipole moments of poly(3-methyloxetane),[20] $[-OCH_2-CH(CH_3)-CH_2-]_n$, suggests that $g^\pm$ conformations about $OCH_2-CH(CH_3)-CH_2O$ should have an energy lower than that of the corresponding trans states; the different nature of the oxygen of the ester and the ether group may alter these results. In view of the lack of information about the conformational energies of these types of structures, their values were obtained from the theoretical calculation of g as a function of these energies and further comparison with the experimental value of the dipole correlation coefficient. Symmetry considerations dictate that the conformational energies associated with g^+ and g^- states about bonds of type 6 will be similar to those of g^- and g^+ states about bonds of type 5. In the same way, the energies of g^+ and g^- states about both bonds of type 7 of the repeating unit correspond, respectively, to those of g^- and g^+ states about bonds of type 4 (see the statistical weight matrices of eq 4).

Rotational states of different sign about two consecutive bonds, which give rise to second-order interactions between a methylene (or methyl) group and the carbonyl group, have an energy, E_w, of ca. 1.4 kcal mol^{-1} above that of the tt states. Rotations of type g^-g^+ about bonds 5 and 6 produce second-order interactions between two oxygen atoms separated for four bonds, and the energy,

$E_{w'}$, of these states is ca. 0.6 kcal mol^{-1} above that of the alternative tt states.[12]

The statistical weight matrices corresponding to bonds 1−7 of the repeating unit of PTMT are the following:

$$\mathbf{U}_1 = [1] \qquad \mathbf{U}_2 = [1\ \gamma] \qquad \mathbf{U}_3 = \begin{bmatrix}1\\1\end{bmatrix}$$

$$\mathbf{U}_4 = [1\ \sigma_k\ \omega\sigma_k] \quad (3)$$

$$\mathbf{U}_5 = \begin{bmatrix}1 & \sigma_\beta & \sigma_\alpha\\ 1 & \omega\sigma_\beta & \omega\sigma_\alpha\\ 1 & \omega\sigma_\beta & \sigma_\alpha\end{bmatrix} \qquad \mathbf{U}_6 = \begin{bmatrix}1 & \sigma_\alpha & \sigma_\beta\\ 1 & \sigma_\alpha & \omega'\sigma_\beta\\ 1 & \omega'\sigma_\alpha & \sigma_\beta\end{bmatrix}$$

$$\mathbf{U}_7 = \begin{bmatrix}1 & \omega\sigma_k & \sigma_k\\ 1 & \sigma_k & \omega\sigma_k\\ 1 & \omega\sigma_k & \omega\sigma_k\end{bmatrix} \quad (4)$$

where the statistical weights of the matrices are Boltzmann factors or exponentials of the conformational energies. A simple operation of symmetry performed on matrices $\mathbf{U_4}-\mathbf{U_7}$ allows for the formulation of the statistical weight matrices when the methyl group of the repeating unit in Figure 3 is on the other side of the plane. However, the polarity of PTMT is insensitive to the stereoregularity of the chains, and consequently, the calculations were made assuming that the methyl group is always located in the position shown in Figure 3.

In the all-trans conformations, the dipoles flanking the terephthaloyl residue of the repeating unit are located in an almost antiparallel direction, and as a consequence, this conformation has the lowest polarity of all of the conformations to which the chain has accessibility. Therefore, departure from the planar trans conformation by rotation about the skeletal bonds increases the dipole moments of PTMT. Preliminary calculations showed that the set of conformational energies $E_{\sigma\alpha} = -0.1$ kcal mol^{-1} and $E_{\sigma\beta} = 0.2$ kcal mol^{-1} give a reasonably good account of the experimental results. Consequently, the evolution of g with the rotational populations along the chains was followed using the following main set of conformational energies: $E_\gamma = 0.080$, $E_{\sigma\alpha} = -0.1$, $E_{\sigma\beta} = 0.2$, $E_{\sigma k1} = 0.4$, $E_{\sigma k2} = 1.4$, $E_\omega = 1.4$ and $E_{\omega'} = 0.6$ kcal mol^{-1}.

The variation of the dipolar correlation coefficient g with E_γ is shown in Figure 4, where it can be seen that in changing this conformational energy from +1 to −1 kcal mol^{-1} the dipolar correlation increases from 0.21 to 0.86. The increase of the polarity of the chains as E_γ decreases reflects the fact that the lower the energy, the higher the fraction of cis conformation of the terephthaloyl residue in which the dipoles flanking it are nearly in parallel direction. As E_γ increases, the population of the terephthaloyl residue in which the dipoles are in the antiparallel direction increases and hence the value of g decreases.

Rotations of the same sign about two consecutive $CH_2-CH(CH_3)-CH_2$ bonds increases the antiparallelism between the dipoles of the two consecutive ester groups flanking the glycol residue. Consequently, the value of g should decrease as both $E_{\sigma\alpha}$ and $E_{\sigma\beta}$ decrease. This behavior is reflected in Figure 4, where it can be seen that g increases from 0.51 to 0.61 when $E_{\sigma\alpha}$ increases from −1 to +1 kcal mol^{-1}. On the other hand, in changing $E_{\sigma\beta}$ from +1 to −1 kcal mol^{-1}, the dipolar correlation coefficient varies from 0.59 to 0.52.

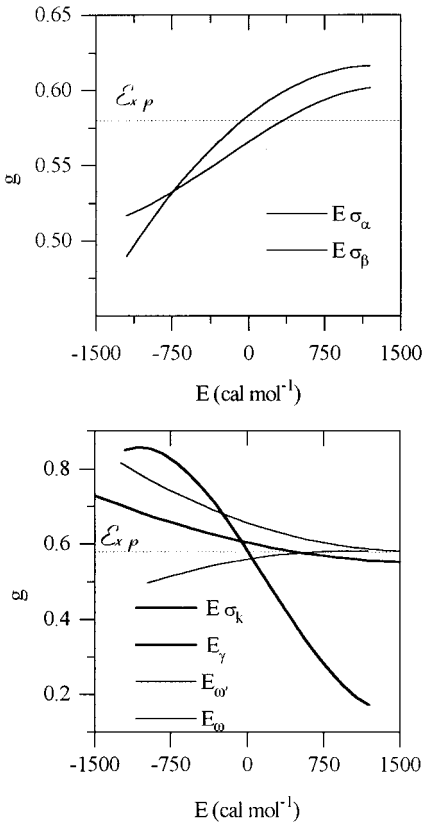

Figure 4. Dependence of the dipolar autocorrelation coefficient on the conformational energies indicated.

The polarity of the chains is rather sensitive to $E_{\sigma k}$, as shown in Figure 4, where it can be seen that the value of g decreases as this conformational energy increases. Thus, the dipolar correlation coefficient varies from 0.70 to 0.55 when $E_{\sigma k}$ increases from −1.25 to +1.25 kcal mol^{-1}. The dipolar correlation coefficient is slightly sensitive to the second-order conformational energy $E_{\omega'}$. However, g shows a moderate dependence on E_ω, as can be seen in Figure 4, where the variation of the dipolar ratio with this second-order energy is shown. The high values reached by g for $E_\omega < 0$, which differ significantly from the experimental results, support the relatively high value reported in the literature for this second-order energy.

The computational results indicate that the main set of conformational energies gives a good account of the experimental results if a value of 0.4 kcal mol^{-1} instead of 0.2 kcal mol^{-1} is used for $E_{\sigma\beta}$. In this case, the calculated value of g at 20° C is 0.58, in very good agreement with the experimental result. The calculations suggest that the temperature coefficient of the dipole moment of the chains, expressed in terms of $d\ln\langle\mu^2\rangle/dT$, is slightly positive ($1.4 \times 10^{-4}$ K^{-1}). Although the experimental temperature coefficient seems to be negative, reliable conclusions concerning the true value of this quantity cannot be reached from the present results. It should be stressed that small errors of only a few tenths of percent in the determination of the dielectric permittivity can severely alter the value and even the sign of $d\ln\langle\mu^2\rangle/dT$. Therefore, the dipolar correlation coefficient, rather that its temperature coefficient, should be used in the critical interpretation of the polarity of the chains as a function of their chemical structure.

Discussion

Earlier studies[8] have shown that the population of gauche states about OCH_2-CH_2O bonds, which gives rise to first-order O···O interactions, is strongly influenced by the environment of the bonds. Thus, whereas the energy of gauche states about CH_2-CH_2 bonds in polyoxyethylene is ca. 0.5 kcal mol^{-1} below that of the alternative trans states,[21] the same states about CH_2-CH_2 bonds, which give rise to first-order interactions between an oxygen atom of an ether group and an oxygen atom of an ester group, as occurs in PDET, have an energy ca. 0.8 kcal mol^{-1} below that of the corresponding trans states.[8]

Apparently, the fraction of gauche states about CH_2-CH_2 bonds is not affected by the ester group when these states give rise to first-order CH_2···O interactions. Actually, the energy of gauche states about $OCH_2-CH_2-CH_2O$ bonds in polyoxytrimethylene is ca. 0.1 kcal mol^{-1} below that of the alternative trans states,[21] similar to that obtained for the same states in poly(ditrimethylene glycol terephthatate)[12] However, if the energy of gauche states about $OCH_2-CH(CH_3)-CH_2O$ bonds in poly(3-methyloxetane) (P3MO) is taken as a basis of comparison, one finds that the ester group affects the rotational population about these bonds. Actually, a careful analysis of the polarity of the latter polymer indicates[20] values of $E_{\sigma\alpha}$ and $E_{\sigma\beta}$ about 0.5 and 0.2 kcal mol^{-1}, respectively, below those of the alternative trans states, significantly lower than −0.1 and 0.4 kcal mol^{-1}, respectively, the results obtained for these parameters in the present analysis. Accordingly, the ester groups seems to decrease the gauche population about C−C bonds in PTMT in comparison with that of similar bonds in P3MO.

As shown in Figure 4, the dipolar correlation coefficient is only slightly sensitive to the second-order interactions $E_{\omega'}$ and E_{ω} for positive values of these quantities. Coiling of the repeating unit in itself is strongly dependent on the values of $E_{\omega'}$, and consequently, the molecular dimensions rather than the polarity of the chains should show a strong dependence on the value of this parameter.

Owing to the insolubility of most polyesters in nonpolar organic solvents, experimental results concerning the polarity of these chains are scarce. Only the polyesters with ether groups in the glycol residue present sufficient solubility in suitable solvents so that their dipole moments can be measured. It is expected that the dipoles separated by the glycol residue in polyesters with general structure $-OC(O)C_6H_4C(O)O(CH_2)_x^-$ are uncorrelated for values of $x \geq 5$. Therefore, the polarity of these chains would come near to that of a freely jointed chain were it not for the terephthaloyl residue, which only permits the cis and trans conformation, and consequently, the dipoles flanking it can only be in nearly parallel and nearly antiparallel directions. This is one of the greatest differences between aromatic and aliphatic polyesters as far as their polarity is concerned. Actually, the dipoles of aliphatic polyesters with general structure $-OC(O)(C_2H_2)_xC(O)O(CH_2)_y$ are nearly uncorrelated when x and y are larger than 5, and as a result, their dipolar correlation will be close to unity.

The fact that PTMT dissolved in hot toluene and then precipitated as a powder standing in the solution overnight at room temperature prompted us to look at its physical properties. Owing to the asymmetry of the glycol residue, PTMT chains are stereochemically random copolymers comprised by racemic diads (with the methyl groups are located at the same side of the plane) and meso diads (with the methyl groups located at alternating sides of the plane). At first sight, the stereoirregularity of the chains should impede the development of three-dimensional order in this polymer. However, the calorimetric curve of PTMT powder shows two thermal transitions: one located around 50 °C, associated with the glass transition, followed by an endothermic peak whose maximum lies in the interval 73−82 °C, depending on the annealing time. It should be noted that the thermogram of the polymer cooled from the melt shows only the glass−rubber transition. This behavior is reflected in Figure 5, where the thermograms corresponding to the sample precipitated from dilute solution (first run), together with the cooling cycle (second run), followed by another heating cycle (third run) are shown.

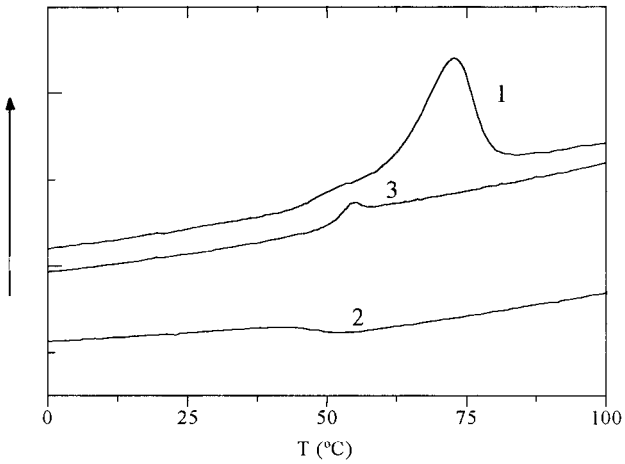

Figure 5. DSC thermograms obtained in different conditions: (1) heating of the sample precipitated from toluene solution; (2) cooling of the sample from the melt, and (3) further heating.

Table 2. Glass-Transition and Melting Temperatures of PET, PTT, PBT, and PTMT

polymer	T_g, °C	T_m, °C
PET	69	265
PTT	35	235
PTMT	55	73−82
PBT	22	232

In Table 2, the values of the glass-transition, T_g, and melting temperatures, T_m, of PTMT are compared with those corresponding to PET,[22] poly(trimethylene glycol terephthalate) (PTT), and poly(butylene glycol terephthalate) (PBT). The values of T_g corresponding to the symmetric polyesters in the amorphous state, decrease as the number of methylene groups, x, in the repeating unit increases. This behavior is a consequence of the fact that the methylene groups favor the chain mobility and, as a result, T_g drops as x increases. The presence of a methyl group in PTMT decreases the molecular mobility of the chains compared to PTT, thus raising the glass-transition temperature of this polymer nearly 20 °C above that of PTT.

A significant drop occurs in the melting temperature of PTT when a hydrogen atom located in the central methylene group of the repeating unit of this polymer is substituted for a methyl group. Because the contribution of the conformational entropy to the melting entropy is higher in PTT than it is in PTMT, the low value of the melting temperature of the latter polymer

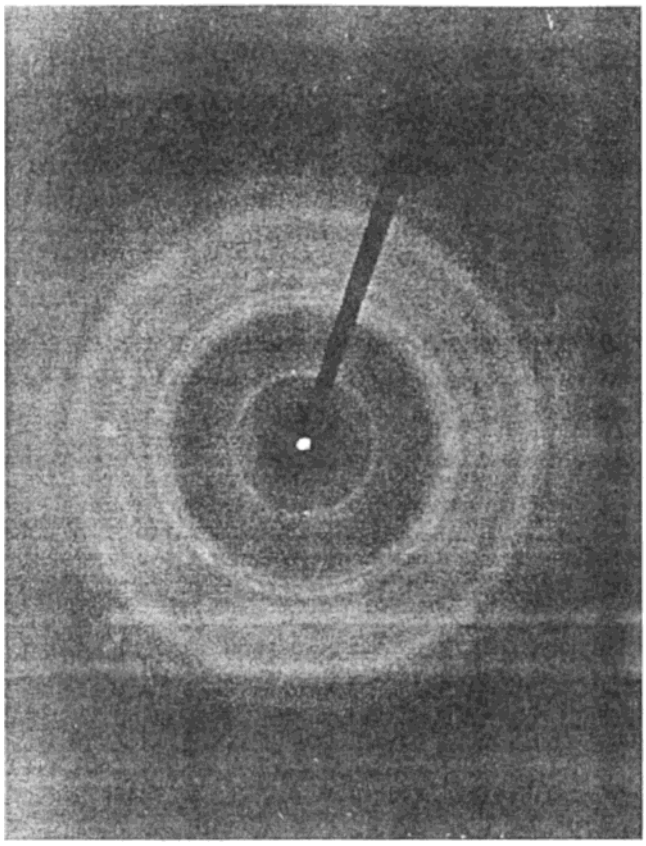

Figure 6. X-ray diffractogram of PTMT powder precipitated from toluene solution by cooling.

must be attributed to its comparatively small melting enthalpy.

The X-ray diffractogram of PTMT in the powder form, shown in Figure 6, has at least seven rings. The inner ring is well-defined and thin, whereas the others are broader, displaying some spotty grains. The broadness of the rings suggests poorly defined interplanar distances. Oriented samples cannot be obtained from the polymer because the melt does not develop crystalline order in a reasonable time interval. By assuming that the inner reflection corresponds to the repeating distance of the structural unit and, consequently, to the *c* axis, the interplanar distance obtained from the first ring is 11.1 Å. The fact that this value is somewhat lower than that corresponding to the repeating unit in the all-trans conformation, 12.3 Å, suggests that some of the $CH_2-CH(CH)_3$ bonds of the glycol residue may be in the gauche conformation. In connection with this, one should consider that in a planar all-trans conformation, the consecutive phenyl groups of polyterephthalates with an odd number of methylene groups in the structural unit have opposed directions and, consequently, repetition along the chain axis takes place every two structural units. Accordingly, the inner reflection in Figure 6 presumably corresponds to a second order of a ghost first-order reflection;[23] the sharpness of this reflection indicates a large coherence length along the *c* axis.

The texture of the powder grains observed by polarized light microscopy with crossed polarizers appears dark. However, after shearing the powder between two crystals, domains with strong birefringence appear. This behavior is similar to that of a liquid crystal. Because it was not possible to prepare oriented samples because the closeness of the glass−rubber to the melting temperature prevents the development of crystallinity order in uniaxially stretched PTMT films, one cannot conclude whether the powder has bi- or tridimensional order. At present, some promising efforts are being made to circumvent this difficulty, and the results obtained will be published later.

The determination of the thermodynamic melting enthalpy for semicrystalline polymers is customarily obtained from the depression of the melting temperature by diluents using Flory's relationship[24]

$$\frac{\frac{1}{T_m}-\frac{1}{T^0_m}}{v_1}=\frac{V_u}{V_1}\frac{R}{\Delta H_u}\left(1-\frac{BV_1}{R}\frac{v_1}{T_m}\right) \qquad (5)$$

where $T_m{}^0$ and T_m are the melting temperatures of the pure polymer and the polymer−diluent mixture, respectively, v_1 is the volume fraction of diluent, ΔH_u is the heat of fusion per repeating unit, R is the gas constant, V_u/V_1 is the ratio of the molar volume of the polymer unit and that of the diluent, respectively, and B is the interaction parameter for the polymer−diluent pair. The thermodynamic melting enthalpy of PTMT cannot be obtained using eq 5 because the polymer only crystallizes from dilute solutions. The apparent melting enthalpy obtained from the area of the melting peak lies in the range 6.2−10.6 cal mol^{-1}, depending on the annealing time. The fact that these values are nearly one-half of those corresponding to poly(ethylene terephthalate) suggests a relatively high degree of order in the PTMT precipitated from dilute toluene solutions. Both the X-ray diffraction patterns and the calorimetric thermograms of PTMT indicate that the low level of stereochemical regularity of these chains is not a hindrance to the development of some type of crystalline order. In consonance with this, it is important to indicate that there are experimental results[25] suggesting that the development of crystallinity is compatible with poorly regular and repetitive crystal lattices, as indicated by the fact that the varied sequence of chemical groups along protein chains does not prevent them from being packed in a basically regular fashion.

Conclusions

A critical analysis of the dipole moments of poly(2-methyl-1,3-propane glycol terephthalate) indicates that g^+ and g^- states about $CH_2-CH(CH_3)-CH_2$ bonds of the glycol residue have higher energy than that of the corresponding states about similar bonds in poly(3-methyloxetane) $[-O-CH_2-CH(CH_3)-CH_2^-]$, taking as reference the alternative trans states.

Poly(2-methyl-1,3-propane glycol terephthalate) precipitated from very dilute solutions by cooling develops some type of order although this polyester is a random stereochemical copolymer. The conformational characteristics of the polymer suggest that the chains are loosely packed in the crystal. Therefore, enthalpy rather than the entropy is responsible for the low value of the melting temperature of semicrystalline PTMT in comparison with that of poly(trimethylene glycol terephthalate). The closeness of T_g to T_m prevents the possibility of preparing uniaxially stretched crystalline films of PTMT whose X-rays diffractogram patterns would shed light on the kind of order that appears in the polyester in powder form.

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