Influence of the Spacer on the Thermotropic and Conformational Properties of Poly[oxybis(trimethylene) p,p'-bibenzoate] and Poly(heptamethylene p,p'-bibenzoate)

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ABSTRACT: The effect of the ether group of the spacer of poly[oxybis(trimethylene) p,p'-bibenzoate] (PDTMB) on the thermotropic behavior of this polyester has been analyzed by comparing the properties of PDTMB with those of poly(heptamethylene p,p'-bibenzoate) (P7MB), the analogue polybibenzoate with an all-methylene spacer. The ability to develop three-dimensional order from the mesophase is greatly diminished by the presence of the oxygen atom. Moreover, P7MB exhibits a monotropic behavior as the crystal, on heating, is transformed directly into the isotropic melt, while PDTMB appears to be a "regular" thermotropic polymer. The oxygen atom, however, seems to have almost no influence on the stability of the mesophase, and both polyesters present similar thermodynamic parameters for the liquid crystalline phase. Moreover, theoretical studies were carried out on the two polymers to estimate the angular correlations between two successive mesogenic groups, chain sequence extension and mean-square dipole moment distributions, and internal energies associated with the different conformers in the melt. Very similar quantities have been found for both polybibenzoates regarding these conformational characteristics that can affect the formation and stability of the respective mesophases.

Introduction

The introduction of flexible aliphatic units as spacers in the main chain is a widely used method of reducing the high melting points of all-aromatic, rodlike polyesters.[1,2] The amount of that reduction depends not only on the length of the spacer (with the usual even–odd effect) but also on the presence of ether linkages, usually provided by the use of ethylene oxide oligomers.

Several works have been published concerning the thermotropic liquid crystal character of polyesters derived from bibenzoic acid.[3-6] Specifically, the influence of oxygen atoms in the spacer on the thermotropic ability of poly(triethylene glycol p,p'-bibenzoate) (PTEB) has been studied[6] by comparing the properties of this polymer with those of poly(octamethylene p,p'-bibenzoate) (P8MB), the analogue with an all-methylene spacer. The effect of the ether groups in the spacer of PTEB is reflected on the lowering of the transition temperatures and on the ability to develop three-dimensional structures, as well as on the change of the type of mesophase formed.[6] Moreover, several conformational parameters are also sensitive to the presence of oxygen atoms.

Less use has been made of spacers derived from oxyalkylene oligomers with an odd number of carbons. However, some preliminary results have been reported on the effect of the ether group of poly[oxybis(trimethylene) p,p'-bibenzoate] (PDTMB) on the thermotropic properties of this polyester.[7] The ability of developing a three-dimensional phase is greatly inhibited in this polymer. On the contrary, the properties of the mesophase of PDTMB are very similar to those of poly(heptamethylene p,p'-bibenzoate) (P7MB), the analogue polyester with an all-methylene spacer.[7,8]

The aim of this work is to offer more insight into the influence of the oxygen atoms on the development of liquid crystalline order by means of a comparative study of the phase diagrams of PDTMB and P7MB, using thermodynamic and kinetic considerations. Conformational characteristics that can affect the formation and stability of the liquid crystalline phase of these two polybibenzoates are also studied by statistical mechanics procedures.

Experimental Section

Poly[oxybis(trimethylene) p,p'-bibenzoate] and poly(heptamethylene p,p'-bibenzoate) were synthesized by transesterification of diethyl p,p'-bibenzoate and the corresponding diols as previously described,[7,8] using isopropyl titanate as catalyst. The two polybibenzoates were purified by precipitating into methanol their solutions in chloroform. The values of the intrinsic viscosity, measured at 25 °C in chloroform, are 1.05 and 1.03 dL g^{-1} for PDTMB and P7MB, respectively.

^{13}C NMR measurements were performed in a Varian XL-300 spectrometer in solutions of deuterated chloroform at room temperature. The corresponding spectra, together with the assignment of the different signals, are shown in Figures 1 and 2. Both the calculated[9] and experimental chemical shifts are presented in Table I.

PDTMB, freshly cooled from the isotropic melt (200 °C), was annealed at 70 °C. The thermal transitions of this sample were determined with a Perkin-Elmer DSC7 calorimeter at a rate of 20 °C/min. X-ray diffraction patterns of unoriented samples were obtained by using a Geiger counter X-ray diffractometer from Philips Co. Wide-angle X-ray diffraction photographs of a PDTMB sample freshly cooled from the melt and stretched to a draw ratio of about 10:1 were also taken in a flat camera with a sample–film distance of 60 mm. In all the cases, nickel-filtered Cu Kα radiation was used.

Results

Phase Behavior. Some aspects of the phase behavior of PDTMB and P7MB have been previously reported.[7,8] The main conclusions were that, on cooling, the mesophase of P7MB is rapidly transformed into a three-dimensional crystal. On the contrary, the liquid crystalline phase of PDTMB is stable at any temperature (below its isotropization point) at the time scale of the DSC measurements. However, at very long times the mesophase of PDTMB is also able to undergo the transformation to three-dimensional order. This behavior can be seen in Figure 3, where the thermogram of a sample of this polybibenzoate annealed at 70 °C during 24 days is shown. Actually, the annealed sample presents two endotherms: one occurs at

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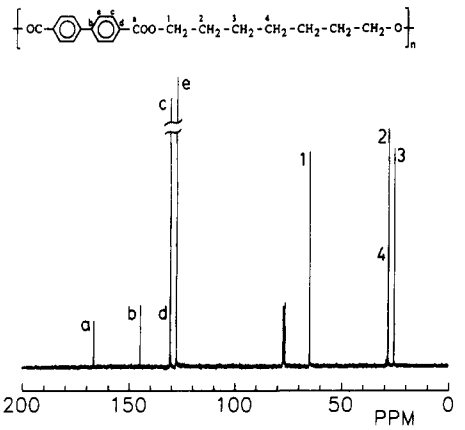

Figure 1. ^{13}C NMR spectrum of P7MB in deuterated chloroform at room temperature.

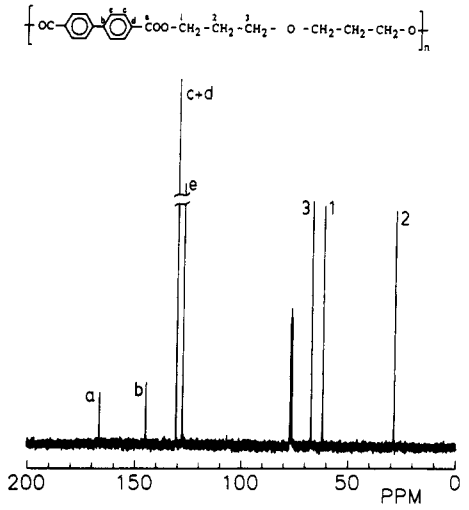

Figure 2. ^{13}C NMR spectrum of PDTMB in deuterated chloroform at room temperature.

Table I
Assignments of Carbon Signals (See Figures 1 and 2) and Their Experimental and Calculated Chemical Shifts (ppm) in the ^{13}C NMR Spectra of the Polyesters

	P7MB		PDTMB	
carbon atom	exp[a]	calc[b]	exp[a]	calc[b]
a	166.3	166.8	166.2	166.8
b	144.3	145.9	144.3	145.9
c	130.1	130.2	130.2	130.2
d	129.9	129.6	130.2	129.6
e	127.2	127.4	127.2	127.4
1	65.1	67.9	62.4	64.2
2	28.6	29.9	29.4	30.6
3	25.9	26.5	67.6	66.4
4	28.9	29.7		

[a] Solvent was deuterated chloroform. [b] According to ref 9.

about 101 °C, with an enthalpy of 17 J/g (1.39 kcal per mole of repeating unit), corresponding to the transformation of the crystal into the mesophase, and the other is just the transition from the mesophase to the isotropic state. The second run of this experiment, also represented in Figure 3, only shows the endotherm corresponding to the isotropization of the mesophase. The X-ray diffractograms presented in Figure 4 indicate that the first endotherm of the annealed sample comes from a three-dimensional crystal. Thus, the top diagram in Figure 4 is very similar to that of the crystal of P7MB,[8] with the difference of a smaller crystallinity for PDTMB, as deduced from the relative importance of the amorphous halo underneath the crystalline diffractions. The diffractograms corresponding to the isotropic state (obtained[7]

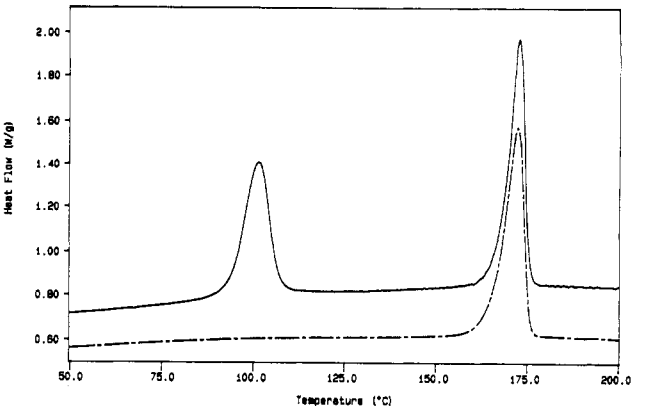

Figure 3. DSC curves of a sample of PDTMB annealed at 70 °C during 24 days (upper) and the subsequent second run (lower).

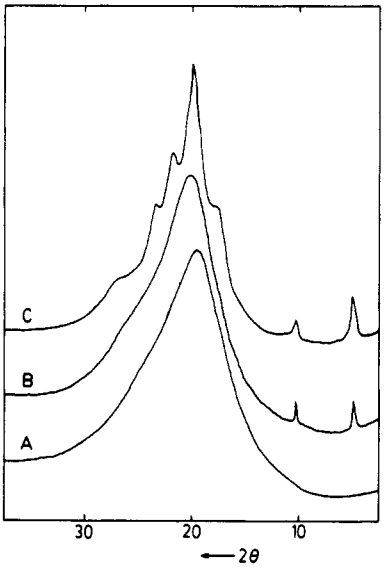

Figure 4. X-ray diffractograms of different samples of PDTMB: (A) isotropic melt (diagram obtained[7] at 192 °C); (B) liquid crystalline state (sample freshly cooled from the melt to room temperature); (C) three-dimensional crystal (sample annealed at 70 °C, diagram obtained at room temperature). Noise has been suppressed.

at 192 °C) and to the mesophase (a sample of PDTMB freshly cooled from the melt to room temperature) are also presented in Figure 4.

In order to identify the mesophase of PDTMB, X-ray diffractometric experiments were performed. Figure 5a shows the diffractogram corresponding to an isotropic sample of this polymer after melting at 200 °C and cooling to room temperature. The picture shows three rings: a sharp inner reflection, a barely visible second order, and a diffuse outer halo. These features are characteristic of a smectic mesophase. The wide-angle broad outer ring corresponds to $2\theta = 20.1°$ and an intermolecular spacing of 4.4 Å, whereas the sharp inner ring corresponds to a spacing of 16.8 Å with a second order at 8.4 Å. The locations of the mesogenic groups in the mesophase can be normal to the plane of the layer as in the smectic S_A or they form an angle with the plane of the layer as in smectic S_C. In the first case the thickness of the smectic layer, d, is close to the length, l, of the repeating smectogenic group, and in the second case d and l are related by the cosine of the tilt angle. The nature of the mesophase can be determined from the analysis of the X-ray diffraction diagrams of the oriented polymer. The most important feature of the diffraction of a stretched sample of PDTMB (Figure 5b) is that the observed inner reflection is located in the meridional position with the

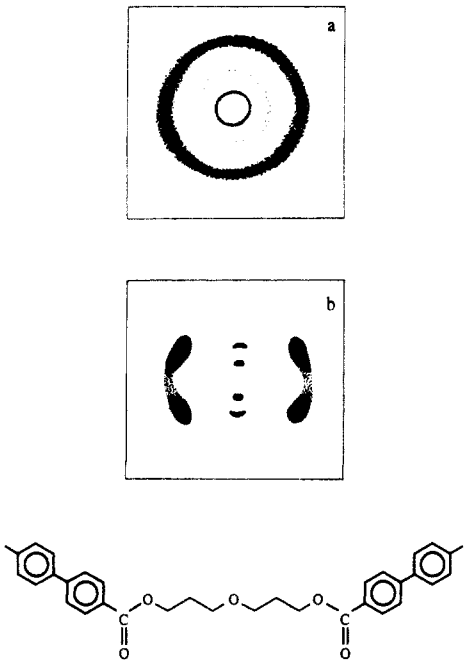

Figure 5. WAXD photographs of PDTMB: (a) unoriented sample; (b) stretched specimen. The structure represents the extended-chain conformation of PDTMB.

same layer spacing as that in the nonstretched sample. Moreover, at least two orders of this reflection are also observed on the meridian. The appearance of these reflections on the meridional line reveals that the layers of the mesophase are perpendicular to the stretching direction. This behavior can be attributed to the presence of a smectic S_A mesophase, similarly to the case of a sample of P7MB with a comparable thermal history.[5] Similar diffractions are displayed for the mesophase of this polymer, with a layer spacing d = 17.6 Å, indicating that the replacement of an oxygen atom for a methylene group in the middle of the chain increases the distance between layers in 0.8 Å.

The diffraction pattern of stretched PDTMB presents a broad outer halo with an interesting characteristic: it shows a minimum of intensity on the equatorial line that is split into two intense maxima lying above and below the equator. The maximum of intensity is displayed at an angle of about 27–30° from the equator. Consequently, both maxima are forming an angle of around 60° (Figure 5b). This peculiar behavior was previously reported[10] for poly(pentamethylene p,p'-bibenzoate) and seems to be general for the polybibenzoate series with an odd number of methylene groups in the spacer. From our results, this characteristic seems to be independent of the presence or not of oxygen atoms in the flexible spacer, and it is attributed to the tilt angle between the mesogenic groups and the fiber axis. Therefore, the diffraction results show (a) the smectic nature of the mesomorphic structure and (b) that the chain and the smectic plane are perpendicular but the fiber axis and the bibenzoate group are forming an angle close to 30° (structure depicted in Figure 5).

There is another important difference between P7MB and PDTMB. As was shown before,[8] the crystal of P7MB exhibits a monotropic transformation into the isotropic state, and the mesophase is not detected on heating. This mesophase, however, can be observed on cooling from the melt prior to its transformation into the crystal, and the thermodynamic parameters of the smectic phase can be determined by holding the temperature in a region where its transformation into the crystal is very slow and subsequently recording the DSC thermogram.[8] On the contrary, the results of this work show that PDTMB presents a "regular" thermotropic behavior, since the crystal of this polymer on heating leads to the mesophase prior to its isotropization (on cooling from the isotropic state, only the mesophase is detected by DSC, due to the extremely long times required for its transformation into the crystal).

The thermodynamic parameters of the different transformations displayed by P7MB and PDTMB are collected in Table II. The corresponding phase diagrams can be obtained from these values by estimating the free energies of the various phases. The free energy of the melt could be calculated from the data of specific heats at temperatures high enough to prevent any transformation and extrapolating to low temperatures. In the absence of these values, the phase diagrams can be constructed in relation to that state by determining the corresponding free energy differences. The usual approximation[11,12] for the free energy of fusion, ΔF_u, of a polymer melting at T_m with an enthalpy of fusion ΔH_u is given by the following expression:

$$\Delta F_u = \Delta H_u(T_m - T)T/Tm^2 \quad (1)$$

The use of this equation is limited by several facts. First, it is only a good approximation in a wide temperature range only if the difference in heat capacity between the supercooled liquid and the ordered phase is not considerably temperature dependent.[12] Second, the numbers in Table II represent actual values and not equilibrium values (this is especially important for the crystal, because very small differences, if any, are expected for the isotropization parameters). Moreover, the orientational order of the mesophase may change considerably as a function of temperature. Nevertheless, the free energy diagrams determined from eq 1 can be used at least for semiquantitative purposes. The corresponding diagrams for P7MB and PDTMB, using the values in Table II, are shown in Figures 6 and 7. The monotropic transition of the crystal in P7MB is characterized by the crossing of the curves corresponding to the crystal and to the mesophase at a temperature higher than the isotropization point, contrary to the case of PDTMB.

It is obvious that although the more stable phase will be that one with the lowest free energy, kinetic considerations will also affect the formation of a certain phase. Thus, the mesophase of PDTMB can be kept at temperatures where the crystal is more stable without detecting any transformation for several days. Moreover, a given phase can be frozen below the glass transition temperature, T_g. The value of this temperatue is 17 °C for PDTMB[7] and 41 °C for P7MB.[13] Therefore, PDTMB can be maintained forever as a liquid crystal below its T_g. In the case of P7MB, if rather drastic quenching conditions are applied to the molten polymer, the crystal formation can be almost completely avoided, and samples with a very small crystallinity[14] (of the order of 10%) remain unchanged at room temperature, due to the higher value of its T_g. All these considerations are very important for the interpretation of the mechanical properties of the samples, which are strongly dependent on the crystal content.

Angular Correlations between Two Successive Mesogenic Groups. Development of liquid crystalline order in thermotropic polymers must be strongly influenced by the angular correlation between two successive mesogenic cores in the melt which, in turn, must depend on the conformational flexibility of the spacer. Thus, nematic order will require fairly small correlation angles, whereas smectic order might also be compatible with larger correlation angles. Earlier studies[15] have shown that the

Table II
Thermodynamic Parameters of the Transitions between the Crystal (c), Smectic (s), and Isotropic (i) Phases and Experimental and Calculated Spacings of the Two Polyesters

	T/°C					ΔH/(kcal mol^{-1})				ΔS/(cal mol^{-1} K^{-1})					
	c→i	s→i	i→s	s→c	c→s	c→i	s→i	s→c	c→s	c→i	s→i	s→c	c→s	l_{exp}/Å	l^a_{calc}/Å
PDTMB		172	154		101		1.55		1.39		3.5		3.7	16.8	21.2
P7MB	168	160	135	95		2.60	1.50	1.10		5.9	3.5	3.0		17.6	21.5

[a] Assuming all-trans conformation.

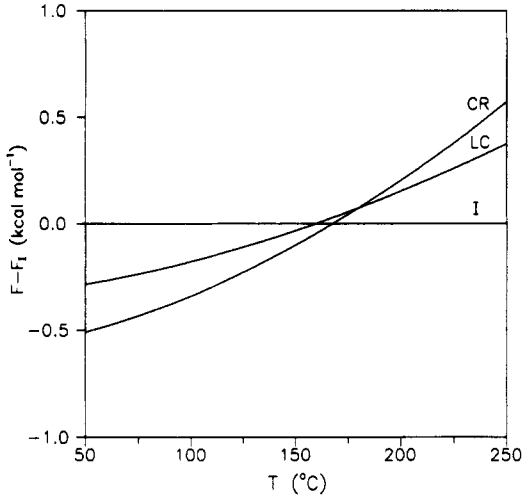

Figure 6. Free energy diagram of P7MB.

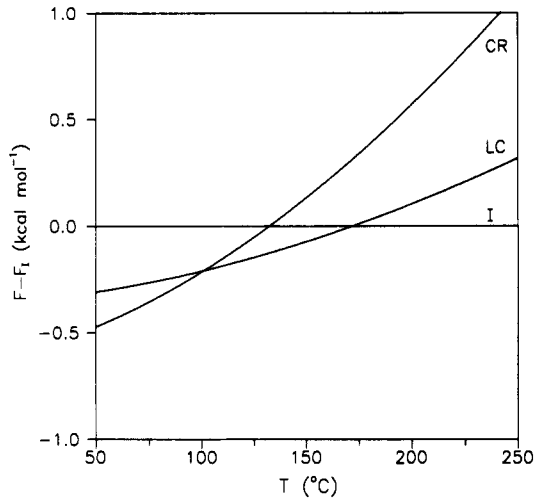

Figure 7. Free energy diagram of PDTMB.

orientational correlation of two successive rigid groups in polymers with polymethylene spacers depends on the even–odd character of the spacer.

To investigate how the alignment of two successive mesogenic groups in the thermotropic polyesters used in this study is altered by changing the central methylene group in a heptamethylene spacer for an ether group, the integral distribution for the angular correlation of two successive groups was calculated for P7MB and PDTMB. Conformational energies of the rotational isomers of the latter polymer were determined from the critical interpretation of the unperturbed dimensions and dipole moments of PDTMB using the skeletal bond lengths and skeletal bond angles indicated in Table III. Whereas the O–C*O* bond of the ester group is restricted to trans states,[16] the energy minima about the O–CH_2 bond of this group are located[17] at 0,±104°; furthermore, the rotational angles about the O–CH_2 ether bonds and CH_2–CH_2 bonds were assumed[18] to be 0,±100° and 0,±120°, respectively. There is a wealth of information that suggests that gauche

Table III
Geometrical Parameters

bond length/Å	skeletal bond angle/deg
C*–C_6H_4–C_6H_4–C* = 10.2[a]	C^{ph}–C*–O = 114
C*–O = 1.35	C*–O–CH_2 = 113
CH_2–CH_2 = 1.53	CH_2–CH_2–O = 110
CH_2–O = 1.43	CH_2–O–CH_2 = 110

[a] Virtual bond.

states about CH_2–O bonds of the ester group have an energy of 0.4 kcal mol^{-1} above that of the alternative trans states; this energy is significantly lower than the relative energy of 0.9 kcal mol^{-1} associated[16,18] with gauche states about O–CH_2 bonds of the ether group. Gauche states about CH_2–CH_2 bonds that produce first-order CH_2···O interactions have an energy of nearly 0.3 kcal mol^{-1} below that of the alternative trans states.[18,19] Rotations of different sign about two consecutive bonds are forbidden except in those bonds that produce second-order C*O*···O and CH_2···O interactions whose energies were considered to be 2 and 0.6 kcal mol^{-1}, respectively.[16]

Rotational angles about CH_2–O bonds of the ester group of P7MB were also assumed to be located at 0,±104°, whereas these angles were assumed to be 0,±120° for the CH_2–CH_2 bonds of the spacer. As in polyethylene, gauche states about CH_2–CH_2 bonds have an energy of 0.5 kcal mol^{-1} above that of the corresponding trans states.[16] Second-order interactions CH_2···CH_2 produced by rotations of different sign about two consecutive bonds of the spacer amount to 2 kcal mol^{-1} with respect to the tt states.[16]

The differential distribution curves for the angular correlation of the mesogenic groups of PDTMB and P7MB were obtained in the form of a histogram by generating all possible conformations and their statistical weights for the repeating units of these polymers at their respective transition temperatures, 172 and 160 °C. Furthermore, the sum of the statistical weights of the conformers with correlation angles of two successive mesogenic groups lying in the interval $\theta_m - 1°$ and $\theta_m + 1°$, where θ_m is an integer value, were obtained for each polymer and normalized with respect to the sum of the statistical weight of all the conformers. The integral distribution curves, $P(\theta)$, for the angular correlations of the rigid cores of PDTMB and P7MB were determined from the respective distribution curves, and the results obtained are shown in Figure 8. The curve corresponding to P7MB exhibits a wide plateau extending from nearly 70 to 160°, so that most of the angles between successive mesogenic groups lie in narrow intervals. Thus about 76% of all the conformers have correlation angles between 63 and 75°; this percentage drops to 21% for the angles between 171 and 180°. Although PDTMB exhibits an integral distribution curve $P(\theta)$ somewhat more irregular than P7MB, relatively large percentages of conformers for which the angles between two successive rigid cores lie within narrow intervals also exist in this polymer; for example, 69% of the conformers have correlation angles between 67 and 91°; moreover, a small fraction of conformers in this polymer have correlation angles lying in the range 37–57°.

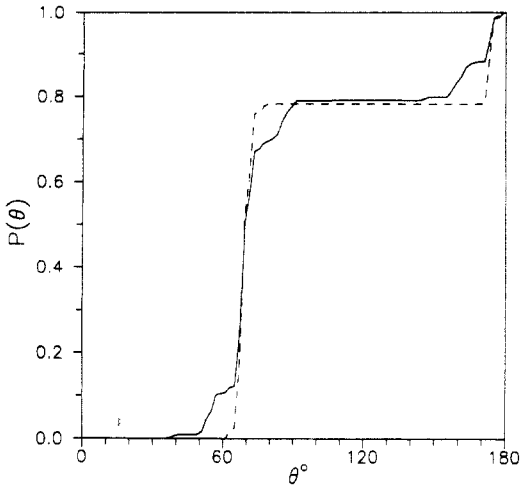

Figure 8. Integrated distribution curves for the angle θ defined by two successive mesogenic groups calculated for PDTMB (continuous line) and P7MB (broken line).

Chain Sequence Extension and Mean-Square Dipole Moment Distributions. Formation of smectic mesophases discriminates the conformations of the repeating unit whose end-to-end distances comply with the layers thickness. Contrary to what occurs in three-dimensional order, it is expected that more than a single conformation will meet the requirements necessary for mesophase order development. The all-trans conformations will not certainly intervene in the mesophases formation of PDTMB and P7MB since their end-to-end distances amount to 21.2 and 21.5 Å, respectively, values that are significantly larger than the experimental thicknesses found for the mesophases of these polymers, which amount to 16.8 and 17.6 Å, respectively. To find the population of conformers in the melt at the transition temperatures (172 and 160 °C respectively for PDTMB and P7MB) whose spatial extensions are compatible with the experimental smectic layer thickness, the differential distributions of the repeating unit extensions were obtained in the form of histograms by calculating the conformers for which their end-to-end distance lies in the range $l_m - 0.5$ Å and $l_m + 0.5$ Å, l_m being an integer value. Calculations were performed following the procedure described before to determine the differential distributions of angular correlations.

Histograms showing the conformer fractions as a function of the repeating unit extension of PDTMB and P7MB are shown in Figures 9a, and 10a, respectively. The distribution for PDTMB is asymmetric with a relatively large tail of compact conformations. The histogram exhibits a prominent maximum centered at $l_m = 17$ Å; moreover, the fact that the fraction of conformers with extensions lying in the interval $l_m = 17 \pm 0.5$ amounts to 0.178 suggests that a significant proportion of conformers in the isotropic state have extensions that comply with the thickness of the smectic layers (16.8 Å). The distribution histogram for P7MB presents the same features as that for PDTMB, in the sense that it is also asymmetric and exhibits a significant fraction of conformers whose spatial extensions lie in the vicinity of the thickness (17.6 Å) of the smectic phase measured for this polymer.

Calculations of the average energies associated with the conformers whose spatial extensions lie in the interval $l_m \pm 0.5$ are shown for PDTMB and P7MB in Figures 9d and 10d, respectively. In both cases the most compact conformations exhibit the highest energy. However, the energy tends to decrease in P7MB as l_m increases, presumably as a consequence of the fact that the amount of low-energy trans states in the conformers increases. This is not the case for PDTMB because gauche → trans transitions about CH_2–CH_2O bonds involve an increase in energy. Therefore the dependence of $\langle E \rangle$ on l_m does not follow a definite trend in this polymer. It should be pointed

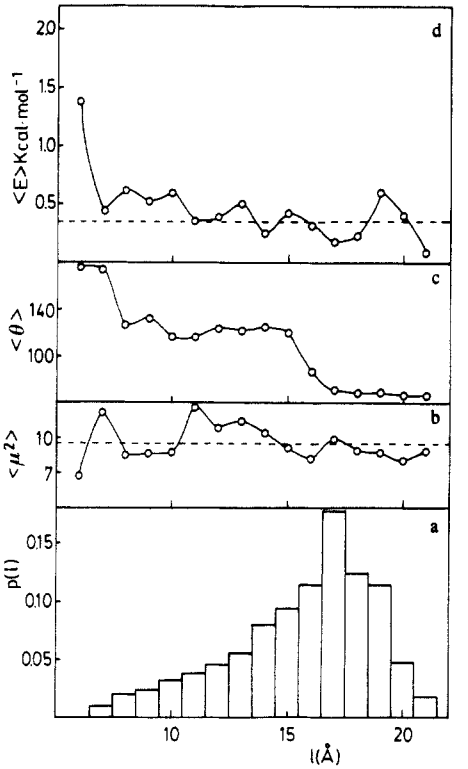

Figure 9. Distribution of chain extensions (a), mean-square dipole moments (b), average angles (c), and internal energy (d) as a function of the extension for PDTMB (the broken lines correspond to the average dipole moment and energy of all the conformers).

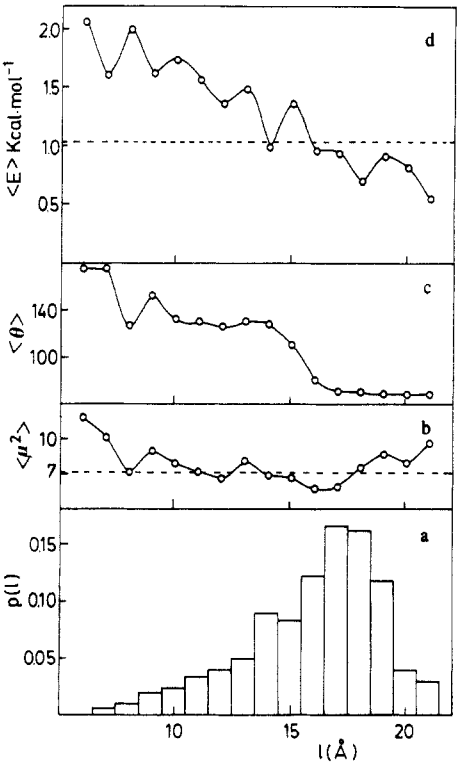

Figure 10. Distribution of chain extensions (a), mean-square dipole moments (b), average angles (c), and internal energy (d) as a function of the extension for P7MB (the broken lines correspond to the average dipole moment and energy of all the conformers).

out, however, that the average energy of the conformers with spatial extensions compatible with the thickness of the smectic layers is lower than the average energy of all conformers in both polymers.

The average values of the correlation angles between two successive mesogenic groups for the conformers of each l_m interval are given in Figures 9c and 10c for PDTMB and P7MB, respectively. The most coiled conformations form angles of nearly 180° in both polymers for $l_m < 8$ Å; then the correlation angle decreases and its value remains practically constant above 100° until l_m reaches a value of nearly 15 Å. A significant decrease in the value of $\langle\theta\rangle$ can be seen in the intervals $15 < l_m < 17$ Å and $14 < l_m < 17$ for PDTMB and P7MB, respectively. According to the results of Figures 9c and 10c, the conformations that can form part of the mesophases have correlation angles between two successive mesogenic groups of 70°. It should be stressed that this value is in good agreement with the tilt angle between the mesogenic groups and the fiber axis deduced from the X-ray analysis.

Finally, the polyesters are highly polar chains in which each ester group has a dipole of 1.89 D, its direction forming an angle of 123° with the C^{ph}–C*O* bond. In addition the dipole of the CH_2OCH_2 group in PDTMB amounts to 1.07 D. Calculations were performed to investigate the mean-square dipole moment $\langle\mu^2\rangle$ of the conformers lying in the range $l_m \pm 0.5$ Å. The results shown in Figures 9b and 10b indicate that the dependence of $\langle\mu^2\rangle$ on l_m is different for both polyesters. A common feature, however, is that the polarity of the conformations compatible with the mesophase seems to be somewhat lower than that of the overall conformations in the isotropic state.

Discussion

The effect of the ether group in the spacer of PDTMB on inhibiting the crystal formation is parallel to that reported[6] for PTEB. On the contrary, PDTMB presents very similar isotropization parameters in relation to its analogue P7MB (see Table II) while a great decrease in both the enthalpy and the temperature of isotropization and a different kind of smectic phase were found for PTEB[6] compared to P8MB. It has to be considered, though, that the spacer of PTEB includes two oxygen atoms, while there is only one in PDTMB.

Therefore, an important feature of the thermotropic properties of PDTMB and P7MB is the similarity of their respective isotropization enthalpies. These enthalpies involve the difference of intramolecular and of intermolecular energy of the conformers between the mesophase and the isotropic state. As far as the first contribution is concerned, the results of Figures 9d and 10d show that the difference between the average energy of the conformers compatible with the thickness of the layers and the average energy of all the conformers in the isotropic state amounts to −0.3 and −0.2 kcal mol^{-1}, respectively, for P7MB and PDTMB. The closeness between the intramolecular contributions and the fact that the transition enthalpy is nearly the same also suggest that the values of the difference of intermolecular interactions in the mesophase and in the melt are similar for both polymers. It seems that the difference in polarity of PDTMB and P7MB chains does not affect in a significant way the intermolecular contributions to the transition enthalpy.

The influence of the even–odd character of spacers with all methylene groups on the correlation angles between successive mesogenic moieties was first indicated by Abe.[15] In bibenzoate polyesters with an even number of methylene groups in the spacer, a significant fraction of conformers in the isotropic state have correlation angles lying in the range 0–30°. However, if the number of methylene groups is odd, a large fraction of conformers have correlation angles lying in the range 60–70°. In fact, conformers with correlation angles below 30° are not found. Similar behavior is observed when some methylene groups are substituted by oxygen atoms. Thus poly(triethylene glycol *p,p'*-bibenzoate) (PTEB) and poly(octamethylene *p,p'*-bibenzoate) (P8MB) exhibit similar behavior as far as the correlation angles between mesogenic groups is concerned.[6] Although, strictly speaking, the distribution of correlation angles is somewhat more irregular in PTEB than in P8MB, the consecutive mesogenic groups of a high fraction of conformers show a fair alignment in the former polymer. This is not the case for polymers with an odd character of the spacers like P7MB and PDTMB. In these polyesters the major portion of conformers have correlation angles between successive mesogenic groups located in the region 50–70°. Moreover, the all-trans conformation of the spacer is not compatible with the layer thickness, as it is substantially larger. It may be expected, however, that the mesogenic groups are tilted toward each other by about 60° (see Figure 5) as has been pointed out[10] before and confirmed by the X-ray and conformational analysis in the present work.

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