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Thermotropic Properties and Conformational Studies on Poly(triethylene glycol *p,p'*-bibenzoate) and Poly(octamethylene *p,p'*-bibenzoate)

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ABSTRACT: The influence of oxygen atoms in the spacer on the thermotropic ability of poly(triethylene glycol *p,p'*-bibenzoate) (PTEB) has been studied by comparing the properties of this polymer with those of poly(octamethylene *p,p'*-bibenzoate) (P8MB), the analogue polyester with an all-methylene spacer. It has been found that the effect of the oxygen atoms is to lower the transition temperatures and to diminish the ability to develop a three-dimensional crystal. Moreover, a smectic S_c mesophase is formed in the case of PTEB. Both the integrated distributions of the angles between two successive rigid cores and the distribution of chain sequence extensions are calculated by the rotational isomeric state model for PTEB and P8MB, and it is found that these distributions are very sensitive to the presence of oxygen atoms in the spacer. The former polymer offers fewer conformers than the latter which are compatible in both orientation and extension with the requirements of the smectic layer determined from X-ray measurements. The internal energy of the highly extended conformer compatible with the layer thickness in PTEB is higher than the average energy of all the conformers, whereas the opposite occurs in P8MB.

Introduction

Several papers have been published concerning the thermotropic liquid crystal character of polyesters derived from bibenzoic acid and alkane diols.[1-3] These polymers are structurally symmetrical and show not only capability of forming mesophases but also can give structures with a three-dimensional order that influences the range of stability of the mesophases. The thermal properties of poly(heptamethylene *p,p'*-bibenzoate) (P7MB) and poly[oxybis(trimethylene) *p,p'*-bibenzoate] (PDTMB) have been recently studied[4,5] in order to compare the differences in stability of their respective mesophases caused by the change of the central methylene of P7MB by an oxygen atom in PDTMB. Both polyesters have in common that they are structurally symmetrical and semiflexible, and consequently do not present geometrical restrictions that hinder the formation of three dimensionally ordered structures when they are cooled from the melt. Moreover, the presence of a rigid unit like biphenyl, although small in size, leads to the occurrence of mesophases whose stabilities differ in both polymers. Thus, the structural difference between these polyesters is enough to suppress the crystalline phase, or at least to decrease its rate of formation in PDTMB, in such a way that only the mesophase is observed on the time scale of crystallization inside the calorimeter (even though at longer times and at the appropriate temperature a crystalline phase starts to develop). On the other hand, the mesophase of P7MB is rapidly transformed into a crystalline phase when cooled from the melt.[3,4]

Current theories provide little guidance concerning the effect of the spacer's structure on the type of mesophase formed or on the temperature range of stability of the liquid crystalline phase. Concerning thermotropic polymers, systematic experimental work might provide some insight into the effect of the structure of the repeating unit on the stability of the mesophase. Pursuing this objective, we have focused our attention in this study on poly(triethylene glycol *p,p'*-bibenzoate) (PTEB). Some properties of this polymer have been recently reported.[6] The purpose of this work is to investigate the influence of the presence of oxygen atoms in the spacer on the mesomorphic properties, and also to predict the ability to develop stable mesogenic structures in polyesters with flexible spacers. The thermotropic properties of PTEB are compared with those of poly(octamethylene *p,p'*-bibenzoate) (P8MB), the analogue polyester with an all-methylene spacer.

In this work both the angular correlation between two successive rigid cores and the distribution of chain sequences extension are also calculated for PTEB and P8MB using the rotational isomeric state (RIS) model, with the aim of interpreting the influence of the structure of the spacer on the formation and stability of liquid crystalline order in these systems.

Experimental Part

Poly(octamethylene *p,p'*-bibenzoate) and poly(triethylene glycol *p,p'*-bibenzoate) were synthesized by transesterification of diethyl *p,p'*-bibenzoate and the corresponding diol using isopropyl titanate as catalyst. The polyesters were purified by precipitating into methanol solutions of P8MB in tetrachloroethane and PTEB in chloroform. The values of the intrinsic viscosity, measured at 25 °C in tetrachloroethane, are 1.30 and 1.15 dL g^{-1}, for P8MB and PTEB, respectively.

^{13}C NMR measurements were carried out in a Varian XL-300 spectrometer. The corresponding spectra are shown in Figures 1 and 2, and the assignment of the different carbons and their experimental and calculated chemical shifts are presented in Table I.

The thermal transitions were determined with a Mettler TA3000 calorimeter. Wide-angle X-ray diffraction (WAXD) photographs were taken in a flat camera with a sample–film distance of 60 mm. X-ray diffraction patterns of unoriented samples were also obtained by using a Geiger counter X-ray diffractometer. In all the cases, nickel-filtered Cu Kα radiation was used. Polymer films for X-ray measurements were prepared in a Collin press fitted with smooth-polished plates. The polymer samples were hot pressed at the melting temperature for 5 min and then cooled at constant pressure by quenching the polymer between two water-cooled plates. Oriented films were treated by uniaxially stretching to a draw ratio about 10:1.

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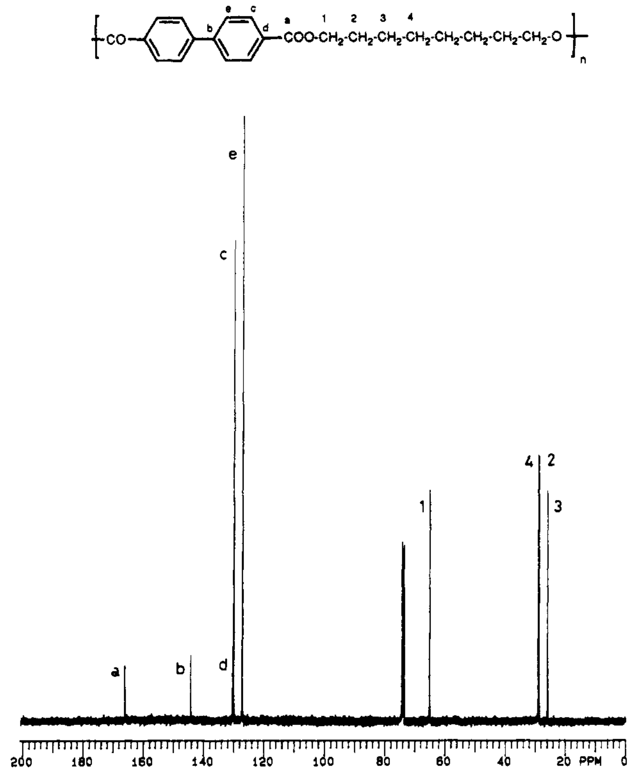

Figure 1. ^{13}C NMR spectrum of P8MB in deuterated tetrachloroethane at 90 °C.

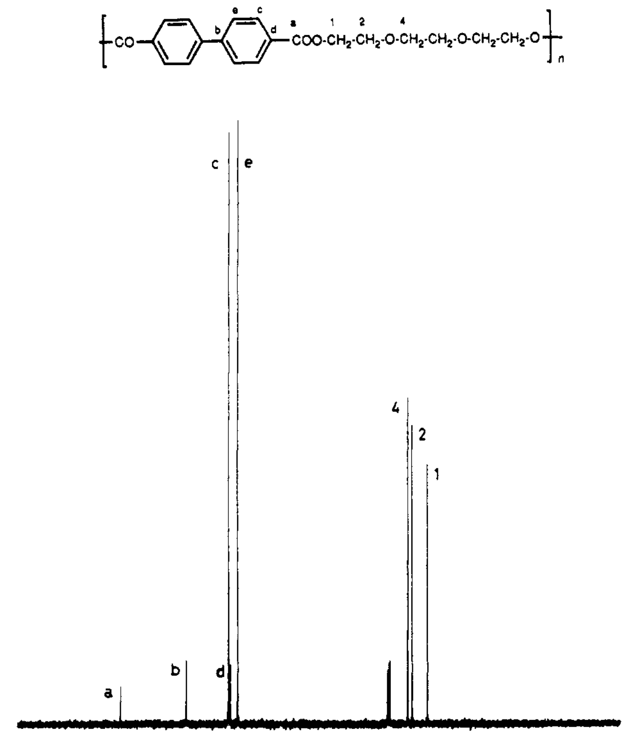

Figure 2. ^{13}C NMR spectrum of PTEB in deuterated chloroform at room temperature.

Results

Thermal Properties. A typical DSC thermogram for PTEB is given in Figure 3. Starting from the melt state at 150 °C and cooling the sample at a rate of 10 °C/min, an exothermic peak can be observed at 85 °C, followed by a second-order glass transition at 2 °C. The subsequent heating of the sample gives again the glass transition, now at 20 °C, and an endotherm at 114 °C, the nature of which corresponds, according to X-ray measurements (see below), to a smectic–isotropic transition with an associate enthalpy of 0.90 kcal mol^{-1} and an entropy of 2.32 cal mol^{-1} K^{-1}. An important characteristic of this smectic mesophase is that it is stable at room temperature for several days without detecting any transformation. However, when the temperature is raised and the sample is held at 55 °C for several days, a more ordered structure starts to develop, giving a thermogram that, besides the endotherm previously described, shows a complex melting peak centered around 90 °C. A more detailed analysis of the annealing of PTEB at other temperatures is in progress.

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

carbon atom	P8MB exp^a	P8MB calcd^b	PTEB exp^c	PTEB calcd^b
a	166.2	166.8	166.2	166.8
b	144.3	149.5	144.3	149.5
c	130.1	130.2	130.3	130.2
d	130.4	129.6	129.6	129.6
e	127.2	127.4	127.2	127.4
1	65.2	67.9	64.2	68.6
2	28.8	29.9	69.3	69.5
3	26.0	26.5		
4	29.1	30.0	70.7	70.6

^{a} Solvent was deuterated tetrachloroethane. ^{b} According to ref 7. ^{c} Solvent was deuterated chloroform.

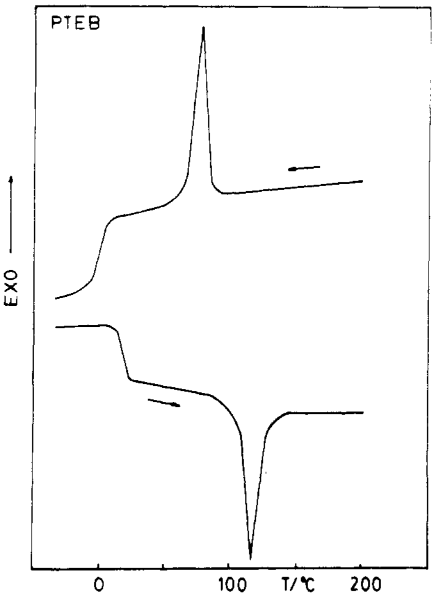

Figure 3. DSC curves of PTEB, corresponding to the crystallization from the melt (upper) and the subsequent melting (lower). Scanning rate was 10 °C/min.

It is of interest to compare the thermal behavior of PTEB with that of P8MB. The corresponding values are collected in Table II. The main thermal parameters for the latter polymer were previously reported by Watanabe and Hayashi.[3] The DSC results for our P8MB sample show substantial agreement with the thermal data reported by these authors with only minor differences in the transition temperatures. Mesophase formation is observed at 168 °C only on cooling. Following this, there is observed a transformation into a more ordered phase at a crystallization temperature of 142 °C. On heating from room temperature, a single melting endotherm appears at 202 °C. The enthalpy of this transition is 3.9 kcal mol^{-1} and the corresponding entropy is 8.2 cal mol^{-1} K^{-1}. Therefore, the mesophase of P8MB shows a monotropic appearance and

Table II
Thermodynamic Parameters of the Transition 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}					
polymer	c → i	s → i	i → s	s → c	c → i	s → i	s → c	c → i	s → i	s → c	d_{exp}, Å	l_{exp}, Å	l_{calc},[a] Å
PTEB		114	85			0.9			2.3		18.5	20.1	22.1
P8MB	202	196	168	142	3.9	2.3	1.6	8.2	4.9	3.8	20.6[b]	20.6[b]	22.0

[a] Assuming all-trans conformation. [b] Reference 3.

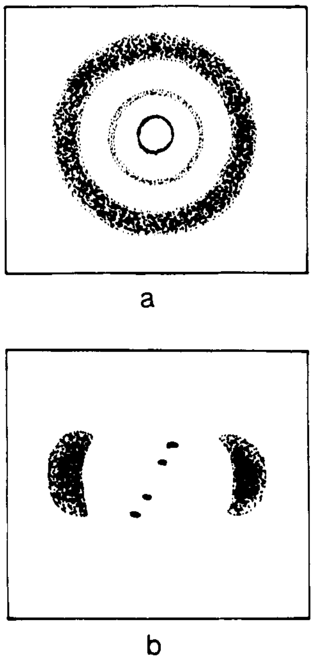

Figure 4. WAXD photographs of PTEB: (a) unoriented sample and (b) stretched specimen.

is only observed on cooling from the melt state, with a rapid transformation to a more ordered structure. This thermal behavior shows an important difference with respect to that exhibited by PTEB. However, it is comparable to that of P7MB,[4] and the mesophase can be isolated by cooling from the isotropic melt and holding the temperature in a region (around 185 °C for P8MB) where the transformation into a three-dimensional crystal is very slow. With this procedure, the temperature of the smectic–isotropic transition (on heating) for P8MB is found at 196 °C, with an enthalpy of 2.3 kcal mol^{-1}. The corresponding entropy is then 4.9 cal mol^{-1} K^{-1}. All the above thermal data are collected in Table II.

Mesophase Structure. As can be seen in Figure 4a, the flat-pattern X-ray diffractogram of an unoriented PTEB film, obtained after melting at 150 °C and quenching at room temperature, shows three diffractions. The presence of a sharp, small-angle maximum, (having a second-order reflection of low intensity) with a diffusional wide-angle scattering, indicates the formation of a smectic type structure in this polymer, with liquid internal layer packing. Texture observations by means of optical microscopy were not useful in confirming this point, as only very small birefringent spheres are observed. It seems that the presumably high molecular weight of the polymers precludes obtaining more revealing textures, as happens with other polybibenzoates.[3,6]

The scattering vector, $\mathbf{Q} = 4\pi \sin \theta/\lambda$, of the diffuse broad ring in Figure 4a is found to be 1.45 Å^{-1}, corresponding to a spacing of about 4.3 Å, and is approximately equal to the value commonly observed for low molar mesophases. It is assigned to the average distance between neighboring mesogenic groups. In stretching the sample, the outer reflection is transformed into two crescents centered on the equator (Figure 4b) and the intensity profile in this equatorial plane is not uniform, but has a liquidlike distribution, from the disordered net. Assuming that the broad reflection results mainly from the rigid mesogenic groups of bibenzoate units, these facts indicate that the mesogenic groups lie parallel to the fiber axis.[3]

The dominant feature of the scattering of unoriented samples at smaller angles is the presence of a sharp ring corresponding to a distance of 18.5 Å, which is considerably shorter than the calculated length of the extended repeating unit (22.1 Å). The inner-ring reflections are transformed into a very strong sharp reflection (two orders are observed) in the oriented sample, showing the existence of extensive layerlike correlations. Both spots form a finite angle with the chain molecular axis, and there are no layer reflections on the meridional line for this smectic phase. The displacements of the inner-layer reflections from the meridional line permit us to conclude that the smectic layers are inclined with their planes forming a finite angle with the fiber axis. This behavior, in which the chain is tilted with respect to the layers, corresponds to the accepted structure for the S_c mesophase. In contrast, P8MB and other even-numbered polybibenzoates have been reported to produce smectic S_A phases.[2,3]

The tilt angle of the chain molecule of PTEB with respect to the normal to the smectic layers can be directly measured from the photograph of Figure 4, finding for this quantity a value of 23°. By considering that the spacing d is related to the length l of the polymer repeating unit through the relation $d = l \cos \theta$ one finds the value of 20.1 Å for the length of the repeating unit in the layer. All the former results refer to the PTEB sample cooled from the isotropic melt. The corresponding studies on annealed samples are being performed.

Conformational Studies. Angular Correlations. Since in the polymeric smectic phase both the mesogenic group and the flexible spacer participate in each layer,[2,8,9] the molecular chains must adopt conformations that meet the dimensional requirements of a smectic layer. When a polymer is crystallized with three-dimensional order from the melt, the main chain usually adopts in the crystalline cell the most probable conformation in the melt state.[10] There are, however, deviations from this general behavior imposed by interactions peculiar to the crystal arrangement. In a similar way, it may be expected that more than a single conformation, compatible with the relatively low requirements of the mesophase order, could intervene in the formation of the smectic layers. Conformations which produce colinear alignment of two consecutive cores (X_i and X_{i+1} in Figure 5) will be easily accommodated in the mesophase. In this context, Abe[11] has pointed out that the orientational correlations of two successive rigid groups in polymers with polymethylene spacers $(CH_2)_n$ is strongly dependent on the even–odd character of the spacer.

Geometrical parameters required for the evaluation of the angular correlations in PTEB are given in Table III.

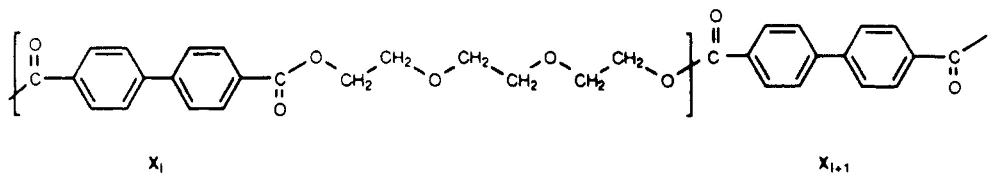

Figure 5. Repeating unit of PTEB in planar all-trans conformation, showing two successive rigid cores.

Table III
Geometrical Parameters

bond length, Å		skeletal bond angle, deg	
C*-Ph-Ph-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.

Rotational angles about O–CH_2 bonds of the ester and ether groups were considered to be located at[12] 0, ±104° and[13] 0, ±100°, respectively, whereas for CH_2–CH_2 bonds these angles were assumed to be[13] 0, ±120°; furthermore, O–C*O* bonds of the ester groups are restricted to a trans conformation.[14] As for the conformational energies associated with the rotational states, they are described in detail elsewhere.[13-18] Briefly, gauche states about O–CH_2 bonds of the ester and ether groups have energies of 0.4 and 0.9 kcal mol^{-1}, respectively, above those of the corresponding trans states,[13-17] whereas the energy of gauche states about CH_2–CH_2 bonds adjacent to the ester groups is 0.8 kcal mol^{-1} below that of the corresponding trans.[14,16] Gauche states about the central CH_2–CH_2 bonds of the repeating unit were assumed to be preferred by only 0.5 kcal mol^{-1} over the alternative trans states. Second-order interactions of C*O*···O, CH_2···O, and CH_2···CH_2 groups were considered to be 1.4, 0.6, and $\gg$ 2 kcal mol^{-1}, respectively.

Rotational angles about CH_2–CH_2 and CH_2–O bonds in P8MB were assumed to be 0, ±120° and 0, ±104°, respectively. Gauche states about CH_2–CH_2 bonds which give rise to first-order CH_2···O interactions have an energy 0.1 kcal mol^{-1} below that of the corresponding trans states,[13,18] whereas the value of this energy is 0.5 kcal mol^{-1} above that of the trans states when rotations about CH_2–CH_2 bonds cause first-order CH_2···CH_2 interactions.[14] Second order CH_2···CH_2 interactions resulting from rotations of different sign about two consecutive CH_2–CH_2 bonds have an energy[14] of 2 kcal mol^{-1}.

All the possible conformations for the repeating units of PTEB and P8MB were generated and both the statistical weight of each conformation at the respective transition temperatures (taken as 115 and 200 °C), and the angles θ, defined by two successive mesogenic groups, were evaluated. The integrated distribution curve, $P(\theta)$, was calculated for each polymer in the interval $0 \leq \theta \leq 180$, from the differential distribution curve, which in turn was obtained, in the form of a histogram, by summing for each integer value of θ, θ_m, the statistical weights of all the conformers with their respective angles of two successive rigid cores in the interval between $\theta_m - 0.5°$ and $\theta_m + 0.5°$ and normalizing it with respect to the total. Values of the integrated distribution curves for P8MB and PTEB are shown in Figure 6, where it can be seen that the curve corresponding to the former polymer is bimodal, exhibiting, as previously reported by Abe[11] for other similar polyesters, two wide plateaus. The successive rigid cores of nearly 28% of the conformations form angles that lie in the range 0–10°, whereas for nearly 72% of the conformers this range lies between 100 and 115°. Fulfilment of the requirements to adopt mesomorphic order in a polymer will require the transformation of the conformations of the second fraction to the linear arrangements (θ = 0–30°). On the other hand an inspection of the curve corresponding to PTEB reveals the presence of two diffuse plateaus for $\theta < 90°$; thus, for ca. 7% of the conformations the angles between two successive cores lie in the interval 0–15° and then the curve reaches a plateau with a height $P(\theta) \approx 0.24$ at $\theta_m \approx 40°$. For $\theta_m > 87°$, $P(\theta)$ steeply increases reaching the saturation $P(\theta) = 1$ for $\theta_m = 140°$. Therefore the integrated distribution curve of this polymer is more irregular than that corresponding to P8MB and exhibits a fraction of conformations in the melt with fair collinear alignment of core X_{i+1} with X_i significantly smaller than that calculated for P8MB.

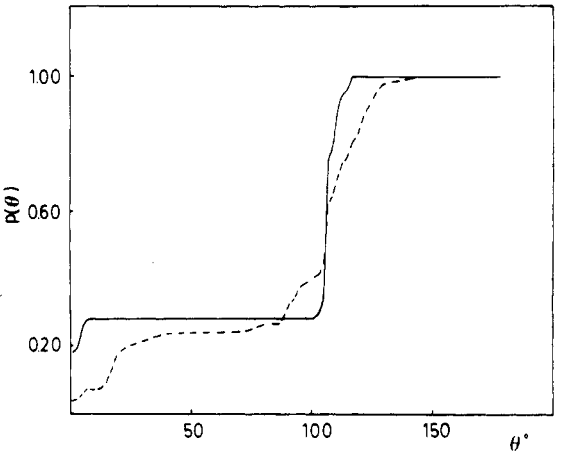

Figure 6. Integrated distribution curves for the angle θ defined by two successive mesogenic groups, calculated for PTEB (broken line) and P8MB (continuous line).

Average Energies and Chain Sequence Extension Distribution. Estimations of the transition entropy of thermotropic polyesters with polymethylene spacers, carried out by Abe[11] by selecting chain conformations on the basis of angular correlations, give values for the entropy which are much smaller than the experimental ones, suggesting that the orientational correlation of rigid cores is not a predominant factor for mesophase formation. In this regard, Yoon and Bruckner[12] have indicated that the probability of the chains to adopt highly extended conformations should be most critical in the development of liquid crystalline order.

The length of the repeating unit of PTEB in the all-trans conformation is 22.1 Å, 2 Å above the value determined from X-ray experiments for the actual length of the repeating unit in the smectic phase, suggesting that some bonds of the main chain in the layer may not be in trans conformation. The distribution of structural unit extensions was obtained by generating all the available conformations; then the extension l, the energy E, and the angle θ between two successive rigid cores were evaluated for each conformation. The distribution of l was determined in the form of a histogram for each integer value of l, l_m, by summing all the statistical weights for all the

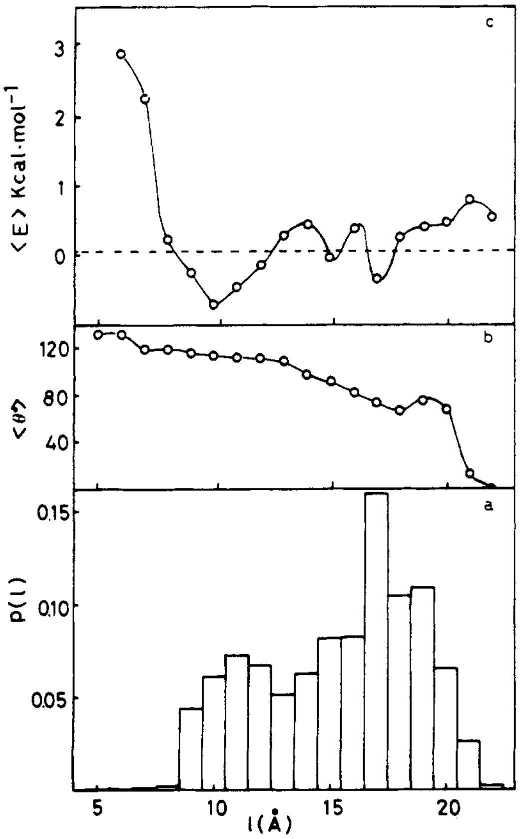

Figure 7. Distribution of chain extensions (a), average angles (b), and internal energy (c) as a function of the extension for PTEB (the broken line corresponds to the average energy of all the conformers).

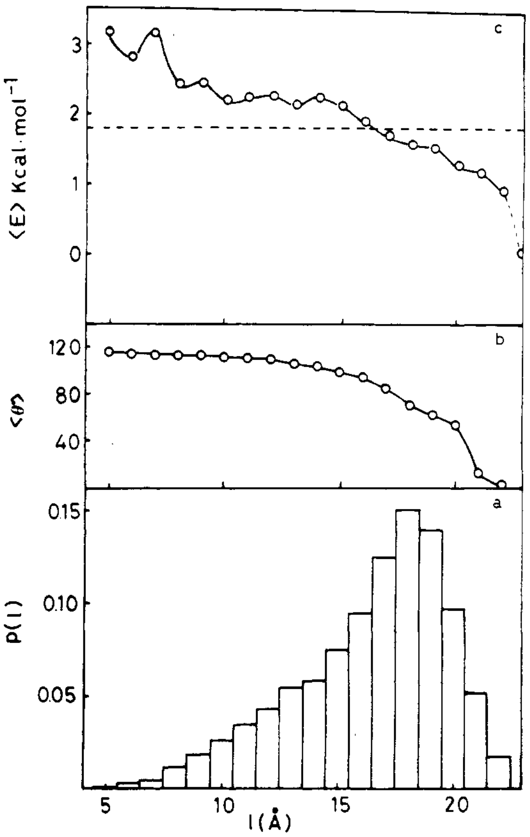

Figure 8. Distribution of chain extensions (a), average angles (b), and internal energy (c) as a function of the extension for P8MB (the broken line corresponds to the average energy of all the conformers).

conformations of the repeating unit whose spatial extensions lie in the interval between $l_m - 0.5$ and $l_m + 0.5$ and further normalization with respect to the total. In the same way, the average of both the conformational energy and the angle θ were also calculated for each interval of l_m.

The conformer fractions as a function of the repeating unit extension of PTEB and P8MB are shown in Figure 7a and 8a, respectively, where it can be seen that the former polymer presents a wide and irregular distribution with an ostensible maximum at l_m = 17 Å which comprises nearly 16% of the total conformers population. In contrast, the histogram corresponding to P8MB exhibits a smooth distribution extending from l_m = 5 to 22 Å, and presenting a maximum at l_m = 18 Å; here the conformers with repeating unit extensions $16.5 < l < 19.5$ comprise 41% of the total population.

The average angles between two successive cores for the conformers of each interval of l_m are shown in Figures 7b and 8b for PTEB and P8MB, respectively. In general the changes in θ with l_m follow the same trend in both polymers in the sense that $\langle\theta\rangle$ decreases as l_m increases. For the more coiled conformations $\langle\theta\rangle$ reaches values of 120° or larger, whereas for the highly extended conformations the average correlation angle sharply decreases as l_m increases.

The average energy $\langle E\rangle$ of the conformers corresponding to each interval l_m is plotted as a function of l_m in Figures 7c and 8c for PTEB and P8MB, respectively. The conformers of lowest extensions are generated by gauche rotations of different sign about OCH_2–CH_2–OCH_2 and CH_2CH_2–CH_2–CH_2CH_2 bonds in the former and latter polymer, respectively. There is a striking difference in the variation of $\langle E\rangle$ with l_m in the sense that whereas the average energy tends to decrease as l_m increases in P8MB, the variation of this quantity with l_m does not follow a definite trend in PTEB. It is worthwhile to point out that the distribution of conformers with $l_m > 18$ Å in PTEB have energies higher than the average energy of all conformers, this latter quantity being represented by dotted lines in Figure 7c, in opposition with what occurs in P8MB, where $\langle E\rangle$ lies below the average energy for the highly extended conformers. This behavior results from the fact that the fraction of high-energy gauche states in P8MB decreases as l_m increases, whereas the increase in l_m is mainly accompanied in PTEB by the decrease of low energy gauche states about CH_2–CH_2 bonds. From the histograms of Figures 7a and 8a one can see that the fractions of conformers compatible with the extensions of the repeating units determined in the mesophases, 20.1 Å for PTEB and 20.6 Å for P8MB,[3] are 0.062 and 0.074 for the former and latter polymers, respectively. Moreover, the value of Δh, this quantity being the difference between the average energy of all the conformers and the average energy of the conformers allowed in the smectic phase, amounts to ≈ –0.4 kcal mol^{-1} for PTEB (l_m = 20.1 Å), whereas this difference for l_m = 20.6 Å in P8MB is nearly 0.5 kcal mol^{-1}. The entropy change due to the restriction of the conformations in the smectic phase can be expressed by

$$\Delta S = -R \ln p(l_n) + \Delta h/T_s$$

where $p(l_n)$ is the fraction of the conformers in the melt allowed in the smectic phase (see Figures 7a and 8a) and T_s is the transition temperature. The values of ΔS obtained by means of the equation indicated above amount to 4.5 and 6.3 cal mol^{-1} K^{-1} for PTEB and P8MB, respectively. A close inspection of Figure 7b reveals that $\langle\theta\rangle$ = 70° in the interval l_m = 20.1 Å, suggesting that many conformers for PTEB in this interval exhibit poor alignment of the successive rigid cores, thus making mesophase formation difficult. The alignment is much better in P8MB where this angle is only ca. 30° if we take the average of the angles corresponding to l_m = 20 and 21 Å, as a consequence of the fact that the extension of the repeat unit is 20.6 Å in this polymer. Calculations were then performed for PTEB imposing the restriction that l_m = 20.1 Å and $\theta < 30°$ for two successive rigid cores. The results obtained indicate that the fraction of conformers that meets these requirements has a value of only 0.0233; moreover, the average energy of these conformers is 1.20 kcal mol^{-1} above the average of the energy of all conformers, and the average angle between two successive rigid cores is nearly 20°. By using these quantities one obtains ΔS = 4.4 cal mol^{-1} K^{-1}, in very good agreement with the value obtained before (ΔS = 4.5 cal mol^{-1} K^{-1}) without the restriction $\theta < 30°$. In other words, the entropy change due to smectic phase formation does not seem to be very sensitive to angular correlation.

Discussion

It has often been assumed that the molecular chains of polyesters with polymethylenic spacers adopt the all-trans conformation in the mesophase. However, there are experimental results that do not support this assumption. The results concerning the structure of the mesophase of P8MB are among them. Although several explanations have been given to account for the departure in the length of the repeat unit observed in the layer from that of the all trans conformation,[11,19] the most reasonable explanation might be that a variety of conformations of the repeating unit, with suitable extensions and favorable angular correlations of the successive rigid cores, will participate in the formation of liquid crystalline order.[12]

The layer thickness corresponding to the mesophase of P8MB is only slightly larger than that of PTEB. However, owing to the conformational differences between these polymers, the fraction of conformers suitable in both extension and angular correlations to comply with the thickness of the layers is, in PTEB, significantly smaller than in P8MB. Actually, the high preference for gauche/trans states exhibited by CH_2–CH_2/CH_2–O bonds in PTEB favors the formation of coiled conformations and, consequently, this polymer is rich/poor in conformers with relatively low/high spatial dimensions.[16] These conformational characteristics also suggest that the conformational entropy of PTEB is lower than that of P8MB and hence the value of the entropy change due to the restriction of chain conformations in the mesophase should be lower in the former polymer than in the latter, as the calculations reveal. A moderately high fraction of conformers with fairly well aligned cores in P8MB have spatial extensions that comply with the thickness of the smectic layers, their average energy being nearly 0.5 kcal mol^{-1} below that of all the conformers. By considering that the enthalpy of the transition is 2.3 kcal mol^{-1} in this polymer, the anisotropic interactions contribution to the enthalpy would be only 1.8 kcal mol^{-1}. In order to form the liquid crystalline order, these interactions should be somewhat larger in PTEB to overcome the unfavorable energetics (−1.2 kcal mol^{-1}) of the conformations whose spatial extensions and rigid core alignment comply with the structure of the smectic layers. In this case, the contribution of the anisotropic interactions amounts to 2.1 kcal mol^{-1}. The fact that the anisotropic interactions are somewhat larger in PTEB than in P8MB may be due to the higher polarity of the former polymer. Finally, comparison of the experimental and conformational entropies of change of phase gives for the entropy change due to steric exclusion the values of −2.2 and −1.2 cal mol^{-1} K^{-1} for PTEB and P8MB, respectively, the negative character of this contribution being a consequence of the more severe steric exclusion in the isotropic state.

Summing up, the conformational energy of the spacers has a moderate influence on smectic mesophase formation and a small distribution of conformations are consistent with the smectic layer. Anisotropic interactions of the spacer, and therefore the presence of oxygen in the spacer, appears to greatly favor smectic phase formation in thermotropic semiflexible polymers.

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