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Configurational Aspects of the Odd–Even Effect in Thermotropic Liquid Crystalline Polyesters

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ABSTRACT: Conformational analysis has been performed on semiflexible polyesters having repeat units such as $-[X-O-CO(CH_2)_nCO-O]-$ and $-[X-CO-O(CH_2)_nO-CO]-$. These polymers are known to exhibit thermotropic mesophases when (aromatic) rigid cores X are sufficiently anisotropic. Spatial orientations of a given core have been elucidated in a Cartesian coordinate system fixed to the preceding core. The angle θ defined by unit vectors attached to two successive rigid cores has been evaluated for each conformation of the intervening flexible segment. When the number of methylene units n in the flexible segment is even, the angle θ is found to be distributed in the range 0–30° (30–40%) and 85–130° (60–70%). For polymers with n = odd, the major portion of the calculated angle θ is located in the region 50–90°, and to a varying degree (0–20%), orientations are also permitted in the range $\theta > 160°$. Only the n = even polymers conform to the concept of an ordinary nematic ordering. Based on these results, an explanation has been offered for the observed odd–even oscillation in the entropy change ΔS_{ni} at the isotropization temperature. For the n = even polymers, the orientational and combinatorial contributions to the entropy change at the nematic–isotropic transition have been estimated from the calculated distribution curves within the framework of the modified Flory–Ronca theory. The results are compared with experimental data reported in the literature.

Introduction

The thermotropic liquid crystalline behavior of polymers comprising a rigid core segment and a flexible spacer group in a repeating unit have been actively investigated.[1] Roviello and Sirigu[2] discussed the role of flexible spacers in determining properties of the mesophase in relation to the well-known odd–even effect. They reported distinct examples for two series of polyesters having a repeating unit such as

$$-[X-O-CO(CH_2)_nCO-O]- \qquad (n = 6\text{–}12)$$

where

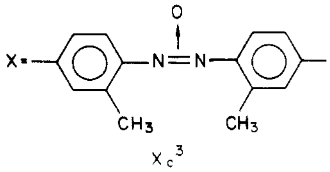
$$X = -C_6H_4C(CH_3){=}CHC_6H_4-$$
$$X_a$$

or

$$X = -C_6H_4C(CH_3){=}N-N{=}(CH_3)CC_6H_4-$$
$$X_b$$

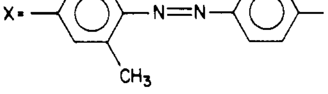
(For a later purpose, each rigid core segment (X) is distinguished by an alphabetical notation suffixed to X.) In both examples, the mesophase was found to be nematic by X-ray examination. Polymers with n = even showed higher isotropization temperatures T_{ni} than those of the immediate neighbors with n = odd. While T_{ni} decreases with increasing length of the flexible segment for a given homologous series, the odd–even oscillation in the isotropization entropy ΔS_{ni} ($=\Delta H_{ni}/T_{ni}$) was found to be remarkably stable. Higher values of ΔH_{ni} and ΔS_{ni} for the n = even series are unmistakable.

Recently, Blumstein and collaborators[3,4] reported other examples of the odd–even effect for polyesters having the same backbone structure as depicted above. The rigid cores are however replaced by



X_c[3]

or



X_d[4]

Values of ΔH_{ni} and ΔS_{ni} observed for X_c tend to increase gradually with n for the odd (n = 3–11) and for the even series (n = 6–14). The entropy change ΔS_{ni} has been usually found to be larger for polymers ($\Delta S_{ni}/R$ = 0.5–2.5 per mol of repeating units; R is the gas constant) than for conventional low molecular weight liquid crystalline compounds ($\Delta S_{ni}/R$ = 0.2–0.5).[5] Blumstein, Stickles, and Blumstein[6] carried out a detailed analysis on the molecular weight dependence of T_{ni}, ΔH_{ni}, and ΔS_{ni} for poly(2,2′-methyl-4,4′-oxyazoxybenzene dodecanedioyl) (polymer X_c with n = 10). The isotropization entropy, expressed in terms of moles of backbone atoms, increases very rapidly with the degree of polymerization. After the maximum is reached at about $M_n \simeq 5 \times 10^3$ (DP $\simeq$ 11), this entropy tends to decrease slowly toward higher molecular weight.

Polyesters derived from aromatic diacids and α,ω-alkanediols have also been studied. Ober, Jin, and Lenz[7] reported properties of the polymers having a repeating unit such as

$$-[X-CO-O(CH_2)_nO-CO]- \qquad (n = 2\text{–}12)$$

where

$$X = -C_6H_4O-CO-C_6H_4-CO-OC_6H_4-$$
$$X_e$$

From microscopic examination, they suggested that these polymers form nematic liquid crystals up to n = 8. The T_{ni} vs. n curve exhibits a regular odd–even effect with higher values for n = even over the range n = 2–7. At n = 8, the curve reaches a minimum. The corresponding values of ΔH_{ni} and ΔS_{ni} (reported for $n \geq 5$) also exhibit an odd–even oscillation, but in the order opposite to that reported for the aforementioned polymers: i.e., the odd members show higher values in polymers X_e.

Krigbaum, Watanabe, and Ishikawa[8] studied a homologous series of polyesters based on 4, 4′-dihydroxybiphenyl and α,ω-alkanedioic acids and found that the polymers having an odd number of methylene units exhibit a nematic phase, while those having an even number show a smectic mesophase. Krigbaum et al.[9] also investigated

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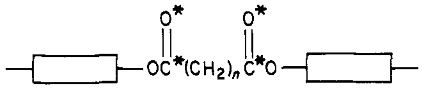
polyesters in the reverse combination: i.e., 4,4′-bibenzoic acid with α,ω-alkanediols. They concluded that none of the polymers from this series forms a nematic mesophase.

Besides the polyesters mentioned above, other types of polymers such as polycarbonates[2,10] or polyethers[11] were found to show similar odd–even effects. These phenomena are not necessarily limited to polymeric liquid crystalline systems. A series of low molecular weight dicarboxylic acid esters carrying the p-methoxyazobenzene groups on both terminals (i.e., a dimer model) have long been known to exhibit an odd–even oscillation in their clearing points when plotted against the number of backbone methylene units.[12] Recently, Jin et al.[13] observed a very distinct odd–even oscillation in ΔH_{ni} and ΔS_{ni} for a series of dimers having a similar structure.

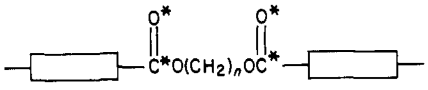
In this study, we have attempted to examine the angular correlation between two successive rigid cores interconnected by a flexible segment. Polyesters were chosen as typical examples which exhibit an odd–even effect in various thermodynamic quantities at the nematic–isotropic transition. Conformational analyses have been carried out for both types of ester linkages. They are represented by



$$-\square-OC^*(=O^*)(CH_2)_nC^*(=O^*)O-\square-$$

I

and



$$-\square-C^*(=O^*)O(CH_2)_nOC^*(=O^*)-\square-$$

II

with n varying from 1 to 8 for polyester I and from 2 to 10 for polyester II. The rectangles situated on both sides indicate rigid core segments (typically, phenylene rods) with which the diester residues are connected. The carbonyl carbons and oxygens are distinguished by an asterisk.

Unless angular correlation between two successive cores is negligibly small, a straightforward application of the Flory–Ronca theory[14] cannot be justified. According to the theory, the molar free energy A for the liquid includes three major contributions:

$$A = A_{\text{comb}} + A_{\text{orient}} + E_{\text{orient}} \tag{1}$$

The combinatorial (A_{comb}) and energy terms (E_{orient}) may be readily evaluated as prescribed by the theory.[14] The difficulty rests in the estimation of the orientational term

$$\begin{aligned} A_{\text{orient}}/RT &= S_{\text{orient}}/R \\ &= -\sum_y (n_{xy}/n_x) \ln (\omega_{xy} n_x / n_{xy}) \end{aligned} \tag{2}$$

where S_{orient} represents the entropy regarding the orientational distribution of ridid cores, each having an axial ratio x. As usual, n_x is the total number of rigid cores, n_{xy}/n_x is the fraction of rigid cores with the disorientation index y, and ω_{xy} denotes the solid angle associated with y. The index y is in turn defined by

$$y = (4/\pi)x \sin \psi \tag{3}$$

where ψ represent the angle of inclination of the rigid core to the preferred direction of the domain. In practice, eq 2 has been modified so that we can estimate the orientational part of the entropy for a polymeric system in which intramolecular orientational correlation between neighboring rigid core segments persists successively along the chain. By using the modified expression, the entropy difference ΔS_{ni} between the isotropic and nematic phases has been evaluated for polymers with an even number of methylene units (n = even). According to the results of the conformational analysis, polymers with n = odd may form a mesophase, but it does not seem to conform to the ordinary one-dimensional nematic ordering. Therefore, a similar treatment of ΔS_{ni} for the latter polymer systems has not been attempted.

Table I
Geometrical Parameters Used for Polyesters I and II

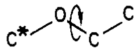
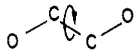
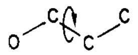
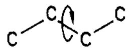
bond	length, Å	bond angle	angle, deg
	Polyesters I		
O–C*	1.35	∠C^{ph}OC*	116.7
C*–C	1.53	∠OC*C	111.4
C–C	1.53	∠C*CC	112.0
		∠CCC	112.0
	Polyesters II		
C*–O	1.37	∠C^{ph}C*O	110.9
O–C	1.44	∠C*OC	118.3
C–C	1.53	∠OCC	110.0
		∠CCC	112.0

Geometrical Data and Elucidation of Conformations of the Flexible Spacer

For simplicity, let us assume that the rigid core is a straight rod that extends between two ester oxygens (polyester I) or between two carbonyl carbons (polyester II). Thus, C^{ph}–O or C^{ph}–C* bonds, i.e., the first neighboring bonds extending from the rods, are taken to be collinear with the rigid core axis. Lengths of these core segments will become important at a later stage.

Parameters required for the description of polyester I were taken from a recent paper[15] which dealt with the dipole moments of dialkyl esters of dicarboxylic acids. Bond lengths and bond angles adopted for the skeletal portion of the flexible segment are listed in Table I. Since the ester groups are all assumed to be in the trans configuration, short-range interactions between consecutive rigid cores are unimportant. As for the rotation around the OC*–CC bond (for n = 1, OC*–CC*), the six-state scheme (termed model I in the previous paper[15]) was employed throughout the present treatment: the rotational isomeric states occur in this model at 0°, 57.3°, 122.7°, 180.0°, 237.3°, and 302.7°, the trans state (0°) being taken to be the reference. The statistical weight parameter α representing the relative importance of the *reversed* ester conformations (O–C* eclipsing C–C and two C–H's at 180.0°, 57.3°, and 302.7°, respectively) with respect to the normal ones (0°, 122.7°, and 237.3°) was set equal to unity.[15] The three-state scheme (termed model II) proposed alternatively in the previous paper[15] was examined for chains with n = 5 and 6 for comparison. In this model, the C*O*/CC eclipsed form is assumed to be intrinsically more stable than the C*O*/CH form: a stabilization energy (E_β) of 1.2 kcal mol^{-1} was adopted. When the number n of the intervening methylene groups is less than three in polyester I, the two adjoining ester groups may interact with each other in close proximity; e.g., for the glutaric acid residue (n = 3), short-range interactions between the two terminal ester groups occur when the two internal C–C bonds are in the g$^+$g$^-$ or g$^-$g$^+$ conformation. The interaction energies are very much dependent on the rotation around the neighboring C*–C and C–C* bonds as well. For $n \leq 3$, therefore, statistical weights were deduced for the individual conformations of the residue from the calculated total energies.[15] In these cases, contributions from each of the constituent bonds were not estimated separately. For polyester I with $n \geq 4$, the conventional matrix mul-

Table II
Rotational Angles and Statistical Weights[a] Adopted for Polyesters II

first-order interactions			second-order interactions	
bond[b]	rot angles for gauche states, deg	statistical weight	bond pair[b]	statistical weight
	±104	0.7		0.1
	±120	1.7		0.0
	±120	1.0		0.4
	±112.5	0.6		0.6
				0.13

[a] A weight of unity is assigned to the trans state. [b] The carbonyl carbons are indicated by an asterisk.

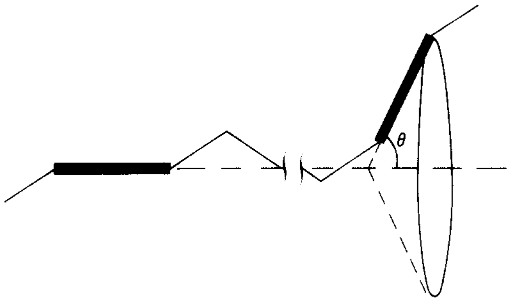


Figure 1. Schematic diagram of a semiflexible polymer chain comprising rigid cores interconnected with flexible segments. The angle θ may be defined by the unit vectors fixed to two successive cores.

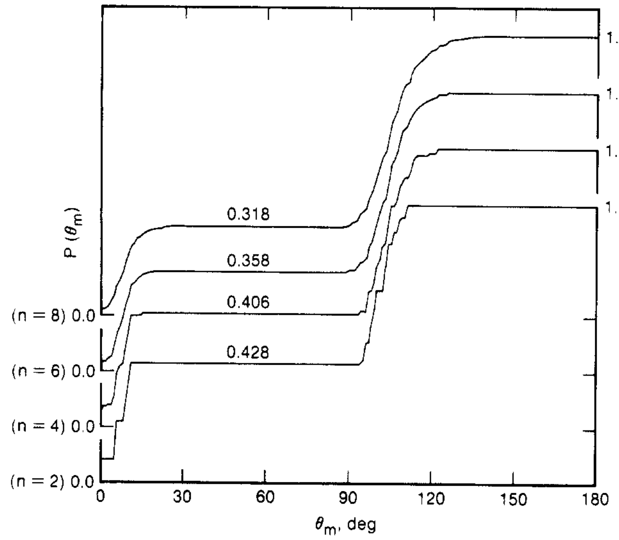


Figure 2. Integrated distribution curves for the angle θ defined by two successive rigid cores. Calculated for polyesters I with $n = 2, 4, 6$, and 8 (even series). The origin of the figure is indicated for each curve on the left-hand ordinate. The value $P(\theta_m)$ indicates the fraction of the rigid core inclined in the range $0 \leq \theta \leq \theta_m$. Given for each curve is the value of $P(\theta_m)$ in the plateau region.

tiplication method[16] was employed. Locations and relative energies of the rotational isomeric states were estimated as described in the previous paper.[15] Considering that the isotropization temperatues of these polymers are relatively high, statistical weight parameters were calculated for the temperature 500 K.

Geometrical parameters employed for polyesters II are also included in Table I. Bond lengths and bond angles associated with the ester group are those used in the analysis of aromatic polyesters by Erman, Flory, and Hummel.[17] The bond length for C*–O (1.37 Å) is slightly longer than that (1.35 Å) adopted for polyester I. The ester group is taken to be in the trans form. Statistical weight parameters were estimated for the temperature 500 K from the conformational energies given in the literature[16,18] and are summarized in Table II. Statistical weight matrices may be formulated for any given residue by the usual procedure.[16] Rotation angles adopted for the gauche states are also listed in the table. A value of ±104° was assigned to the C*O–CC bond from the energy calculation. The other rotation angles were taken from the literature.[16,18]

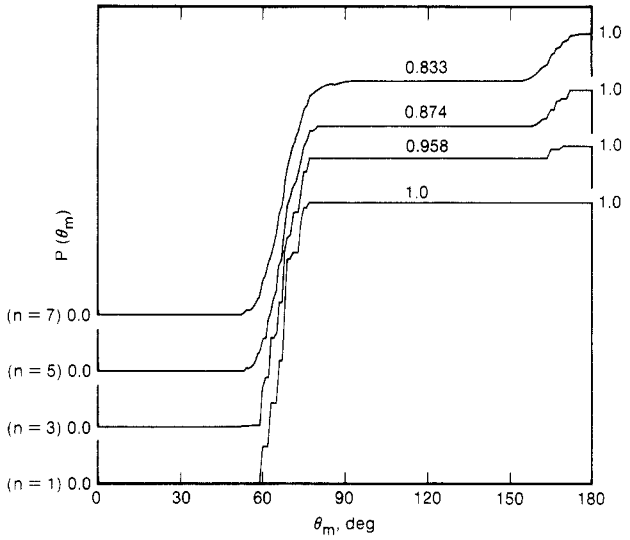


Figure 3. Integrated distribution curves for the angle θ, calculated for polyesters I with $n = 1, 3, 5$, and 7 (odd series). See legend to Figure 2.

Results and Discussion

Angular Correlation between Two Successive Rigid Cores. We consider an isolated polymer chain in the free state. The angle θ defined by two successive rigid cores, X_i and X_{i+1}, is depicted in Figure 1. (Or, to be more exact, the angle θ should be defined by the unit vectors affixed to cores X_i and X_{i+1}.) All possible conformations and orientations of core X_{i+1} were enumerated in the Cartesian coordinate system fixed to the preceding core X_i.[16] For each conformation, the statistical weight was evaluated. The fractions $P(\theta_m)$ of cores X_{i+1} inclined in the range $0 \leq \theta \leq \theta_m$ were calculated therefrom for given values of θ_m.

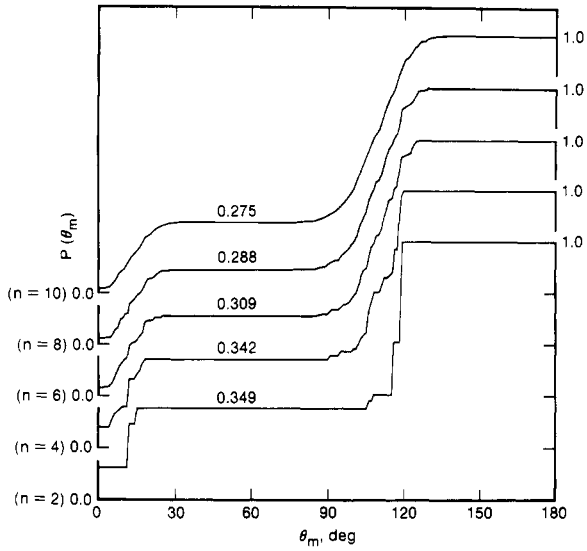


Figure 4. Integrated distribution curves for the angle θ, calculated for polyesters II with n = 2, 4, 6, 8, and 10 (even series). See legend to Figure 2.

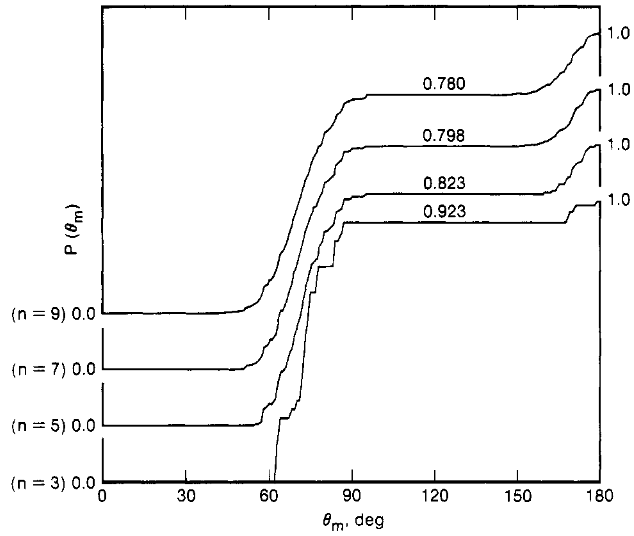


Figure 5. Integrated distribution curves for the angle θ, calculated for polyesters II with n = 3, 5, 7, and 9 (odd series). See legend to Figure 2.

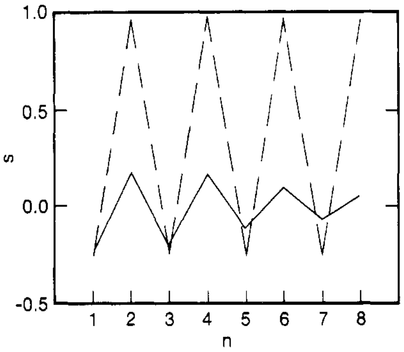


Figure 6. Variation of the order parameter s (eq 4) with the number of methylene units n, calculated for polyesters I. The solid lines were drawn for values averaged over an entire distribution of the angle θ. The broken lines were derived for the postulated nematic mesophases (see text).

The reference angle θ_m was varied from 0 to 180° with 1° intervals. Calculations were carried out for polyester I from $n = 1$ to $n = 8$, and for polyester II from $n = 2$ to $n = 10$. Integrated distribution curves, $P(\theta_m)$ vs. θ_m, thus obtained are shown in Figures 2–5. Numerical values given to the individual curves indicate the fraction $P(\theta_m)$ for the plateau region. The results were found to be quite sensitive to the parity, even or odd, of the number of methylene units involved in the flexible segment of the chain. General features of the curves are amazingly similar within the same parity. As is evident from the procedure described above, the analysis is not specifically addressed to a polymer system. The results shown should be applicable to a dimer as well as to polymers.

Figures 2 and 3 indicate the results for polyester I with n = even and odd, respectively. Calculations were performed by assuming the six-state scheme around the C*–C bond of the ester group. An alternative modification, i.e., the three-state scheme (see the preceding section), was also examined for polymers with n = 5 and 6. The resulting $P(\theta_m)$ vs. θ_m curves were found to be very similar to those shown for the six-state scheme in Figures 2 and 3. The characteristics of the curves derived by using the three-state scheme may be summarized as follows. For $n = 5$, a sharp rise occurs at $\theta_m = 55°$, and the curve reaches the plateau with a height $P(\theta_m) = 0.879$ at $\theta_m = 75°$. The curve tends to go up again around $\theta_m = 153°$. For $n = 6$, the plateau region appears in the range θ_m = 20–90° with a height $P(\theta_m) = 0.361$, and the curve reaches saturation, i.e., $P(\theta_m) = 1.0$, at $\theta_m = 130°$. As is evident by comparison with the corresponding curves in Figures 2 and 3, whether the rotational isomeric states around the C*–C bond are expressed in the six-state or the three-state scheme is quite insignificant in these polymer systems (polyester I). Shown in Figures 4 and 5 are the curves derived for polyester II with n = even and odd, respectively.

A preliminary examination of Figures 2–5 leads to the following remarks:

1. General features of the curves are little affected by the inversion of the ester group from –CO–O– to –O–CO–. Except in the case of polyester I with $n = 1$, distribution of the angle θ tends to be bimodal as manifested by the abrupt transitions in the integrated distribution curves. Locations of such transitions, however, differ very much between the even and odd series. Characteristic features are summarized below for each series.

2. For chains with n = even (cf. Figures 2 and 4), a sizable amount (30–40%) of core X_{i+1} is found in a rather confined range of θ (<30°). Occurrences exactly at 0° arise from the artificiality of the rotational isomeric state model. A large fraction (60–70%) of core X_{i+1} is disposed at an inclination of $85° < \theta < 130°$ relative to core X_i.

3. When n = odd (cf. Figures 3 and 5), the major portion of the calculated angle θ is distributed over a range 50–90°. To a varying degree (0–20%), orientations are also permitted in the range $\theta > 160°$; i.e., core X_{i+1} is folded back nearly antiparallel to core X_i.

The orientation of core X_{i+1} at angles other than those implied in Figures 2–5 require disposition of rotation angles about the intervening bonds that leads to excessive energies; hence, they may be ignored. The characteristics of the distribution curves described above were found to be little affected by small displacements (of the order of ±10°) in the gauche states of the internal C–C bonds.

In consequence of the disparity in the angular distribution curves between the even and odd series, the order parameter s calculated for a free chain according to

$$s = 1 - (3/2)\langle \sin^2 \theta \rangle \qquad (4)$$

exhibits an oscillation when plotted against n. The solid lines in Figures 6 and 7 indicate the results for polyesters I and II, respectively. Since the order parameter does not distinguish whether the neighboring cores are in the parallel or antiparallel orientation, the odd–even effects re-

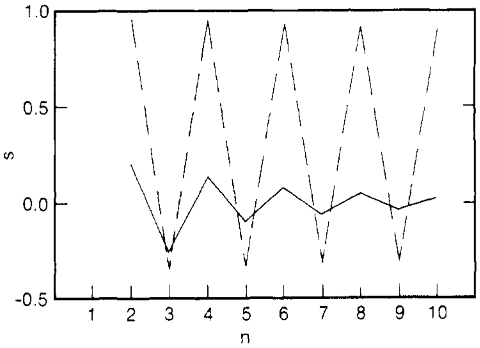


Figure 7. Variation of the order parameter s with n, calculated for polyesters II. See legend to Figure 6.

vealed in these figures are moderate. Let us now assume that these polymer chains are brought into a nematic mesophase. If the collinear alignment of core X_{i+1} with X_i is the one of lowest energy in the free state, it should be easy for the polymer to adopt *nematic* order[19] in the mesophase. This may be the case for polymers with n = even; i.e., the requirement can be fulfilled by transformation of the conformation affiliated with the nonlinear fraction ($\theta = 85$–$130°$) to the linear arrangements ($\theta = 0$–$30°$). For polymer chains with n = odd, however, no such favorable orientations are permitted (cf. Figures 3 and 5). A large accumulation of the antiparallel conformation ($\theta > 160°$) does not conform to the requirements of a nematic arrangement.[19] Due to configurational restrictions imposed by the intramolecular correlation, alignment of rigid cores along one preferred domain axis is improbable. These considerations strongly suggest that a mesophase derived from polymers with n = odd should deviate markedly from regular nematic ordering. On going from the isotropic liquid to the mesophase, some of the conformations in the range 50–90° (cf. Figures 3 and 5) may be preferred over others, but the entropy change will be smaller than for n = even. Neglecting this selection of states, calculations on basis of the 50–90° range gave the order parameters s as shown in Figures 6 and 7 (lower points on the dotted lines). Also indicated in these figures are the values of s obtained for the n = even series in the range 0–30° (upper points on the dotted lines). These values were derived solely from consideration on the intramolecular requirements imposed by the conformation of the flexible part of the chain. A large oscillation in the order parameter may be indicative of the difference in the structure of mesophase between the even and odd series.

In this connection, studies on copolymers by Iannelli, Roviello, and Sirigu[20] should be worth noting. They examined isotropization temperatures and associated entropy changes for copolymers containing an equimolar amount of $-OOC(CH_2)_{n'}COO-$ and $-OOC(CH_2)_{n''}COO-$ within a single chain. When n', n'', and their average $n''' = (n' + n'')/2$ are all even or odd, the mesophasic behavior is very similar to that shown by the corresponding homopolymer with n'''. The pseudoeven (n', n'' = odd; n''' = even) and pseudoodd polymers (n', n'' = even; n''' = odd) showed a significant deviation from this rule. The latter polymers exhibited intermediate properties between the two homopolymers with n' and n''. These observations are understandable if the liquid crystalline structures are dissimilar between the n = even and n = odd polymers.

Estimation of ΔS_{orient} for Polymers with n = Even. As shown in Figures 2 and 4, the distribution curves for n = even possess two characteristic modes. We designate these two regions as 1 for $\theta = 0$–$30°$ and 2 for $\theta = 85$–$130°$, starting from the one in the lower angle. In the nematic state, the rigid cores are correlated with the preferred axis of the domain. This correlation restricts conformation of the flexible segment joining two successive rigid curves. The restriction depends on the angle ψ of inclination of the preceding core with the domain axis. Detailed account of this dependence is difficult. In the interest of simplicity, we consider that the average of sin θ, weighted according to the solid angle, is equal to $\langle \sin \psi \rangle$. That is, we identify

$$\langle \sin \psi \rangle \equiv \langle \sin \theta \rangle_1 \tag{5}$$

where the suffix 1 refers to the region over which averages are taken. This condition should be asymptotically approached as the degree of polymerization increases. We further assume free rotation for a rigid core inclined in the range $0 < \theta < \theta^*$, with values $\theta > \theta^*$ excluded and with θ^* such that

$$\langle \sin \psi \rangle = \int_0^{\theta^*} \sin^2 \theta \, d\theta \Big/ \int_0^{\theta^*} \sin \theta \, d\theta \tag{6}$$

or

$$\langle \sin \psi \rangle = (\theta^* - \sin \theta^* \cos \theta^*)/2(1 - \cos \theta^*) \tag{7}$$

The associated solid angle is given by

$$\Omega_1 = 2\pi \int_0^{\theta^*} \sin \theta \, d\theta = 2\pi(1 - \cos \theta^*) \tag{8}$$

Then by introducing the relations such as $\omega_{xy} = \sin \theta_y$ and $n_{xy}/n_x = \sin \theta_y / \int_0^{\theta^*} \sin \theta \, d\theta$ (defined in a unit range of θ), the reduced entropy is expressed as

$$\begin{aligned} S_n/R &= \sum_{\text{aniso}} (n_{xy}/n_x) \ln (\omega_{xy} n_x / n_{xy}) \\ &= \ln \left[\int_0^{\theta^*} \sin \theta \, d\theta \right] \\ &= \ln (1 - \cos \theta^*) \end{aligned} \tag{9}$$

were y specifies inclination of the rigid core.

For the isotropic state, in which the rigid cores are all oriented at random, the sum must be taken over all regions.[21] Again assuming free rotation for the core in region 2 ($85° < \theta < 130°$), we have

$$\begin{aligned} S_i/R &= \sum_{\text{iso}} (n_{xy}/n_x) \ln (\omega_{xy} n_x / n_{xy}) \\ &= p_1 \ln [(1 - \cos \theta^*)/p_1] + \\ &\qquad p_2 \ln [(\cos \theta_a^* - \cos \theta_b^*)/p_2] \end{aligned} \tag{10}$$

where p_1 and p_2 denote fractions of the rigid core oriented in regions 1 and 2, respectively, and θ_a^* and θ_b^* are chosen so that

$$\langle \sin \theta \rangle_2 = \int_{\theta_a^*}^{\theta_b^*} \sin^2 \theta \, d\theta \Big/ \int_{\theta_a^*}^{\theta_b^*} \sin \theta \, d\theta \tag{11}$$

The quantity on the left-hand side may be evaluated by integration over region 2 of the distribution in Figure 2 or 4. The range $\theta_b^* - \theta_a^*$ was so adjusted as to optimize agreement with the corresponding distribution curve. The reduced entropy difference between the two states is given by

$$\Delta S_{\text{orient}}/R = (S_i - S_n)/R \tag{12}$$

Values of $\Delta S_{\text{orient}}/R$ estimated in this manner are summarized in Tables III and IV, together with other quantities used in the calculation. The entropy changes ΔS_{orient} are roughly figured in the range 4.6–5.5 cal mol^{-1} deg^{-1} (19–23 J mol^{-1} deg^{-1}) for polyester I and 4.5–5.3 cal mol^{-1} deg^{-1} (19–22 J mol^{-1} deg^{-1}) for polyester II. Apart from the magnitude of ΔS_{orient}, it should be noted here that the entropy change due to orientation–disorientation of rigid

Table III
Values of $\Delta S_{\mathrm{orient}}/R$ Estimated according to Eq 9, 10, and 12, Parameters Required Being Evaluated from the Distribution Curves Shown in Figure 2 (for Polyesters I)

	region 1			region 2				
n	p_1	$\langle \sin \theta \rangle_1$	θ^*, deg	p_2 $(=1 - p_1)$	$\langle \sin \theta \rangle_2$	θ_a^*, deg	θ_b^*, deg	$\Delta S_{\mathrm{orient}}/R$
2	0.428	0.112	9.4	0.572	0.577	95.0	108.4	2.30
4	0.406	0.113	9.4	0.594	0.964	94.0	114.4	2.60
6[a]	0.358	0.131	11.4	0.642	0.961	90.0	117.9	2.68
	(0.361)	(0.126)	(10.9)	(0.639)	(0.966)	(90.0)	(116.2)	(2.70)
8	0.318	0.145	11.9	0.682	0.953	90.0	120.9	2.79

[a] Values in parentheses are those derived by using the three-state scheme for rotation around the C*–C bond.

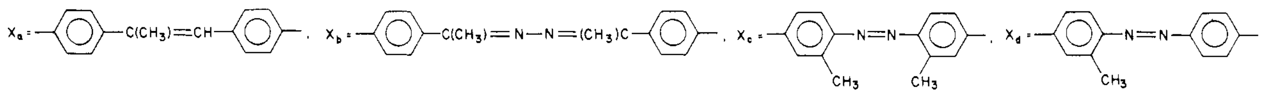
Table IV
Values of $\Delta S_{\mathrm{orient}}/R$ Estimated according to Eq 9, 10, and 12, Parameters Required Being Evaluated from the Distribution Curves Shown in Figure 4 (for Polyesters II)

	region 1			region 2				
n	p_1	$\langle \sin \theta \rangle_1$	θ^*, deg	p_2 $(=1 - p_1)$	$\langle \sin \theta \rangle_2$	θ_a^*, deg	θ_b^*, deg	$\Delta S_{\mathrm{orient}}/R$
2	0.349	0.140	11.9	0.651	0.894	108.0	124.4	2.26
4	0.342	0.149	12.4	0.658	0.925	95.0	126.9	2.67
6	0.309	0.185	15.9	0.691	0.930	90.0	128.4	2.54
8	0.288	0.207	17.4	0.712	0.931	90.0	127.9	2.45
10	0.275	0.224	18.9	0.725	0.931	87.0	129.9	2.44

Table V
Values of $\Delta S_{\mathrm{comb}}/R$ for Polyesters I[a] Estimated according to Eq 13

				polymer[b]					
				X_a		X_b		X_c and X_d	
n	$\bar{y}/x = (4/\pi) \times \langle \sin \theta \rangle_1$	$(\bar{y}/x) - 1 - (\bar{y}/x) \times \ln (\bar{y}/x)$	Δl, Å	x	$\Delta S_{\mathrm{comb}}/R$	x	$\Delta S_{\mathrm{comb}}/R$	x	$\Delta S_{\mathrm{comb}}/R$
2	0.142	−0.581	4.9	3.94	−2.29	3.52	−2.04	3.44	−2.00
4	0.144	−0.578	6.0	4.17	−2.41	3.76	−2.17	3.68	−2.12
6	0.166	−0.535	7.1	4.41	−2.36	4.00	−2.14	3.92	−2.10
8	0.184	−0.504	8.2	4.62	−2.33	4.21	−2.12	4.13	−2.08

[a] $-[X-O-C^*O^*-(CH_2)_n-C^*O^*-O]-$. [b] Polymers illustrated differ from one another in the chemical structure of rigid cores (X):



cores is remarkably invariant with n provided that n is even.

Values in parentheses given in the fourth row of Table III (for polyesters I with $n = 6$) were obtained by assuming the three-state scheme for the rotation around the C*–C bond. As stated earlier, use of the three-state scheme yielded the core distribution curve, $P(\theta_m)$ vs. θ_m, very similar to those for the six-state scheme. Parameters derived from distributions of similar characteristics are also alike. The reduced entropy changes $\Delta S_{\mathrm{orient}}/R$ calculated from these parameters are therefore nearly identical with each other (cf. the last column of Table III). These results support the previous conclusion that choice of the three-state or six-state scheme is quite inconsequential in the present analysis.

Estimation of ΔS_{comb} for Polymers with n = Even. According to the Flory–Ronca theory,[14] the contribution to the entropy change from the combinatorial term is given by

$$\Delta A_{\mathrm{comb}}/RT = \Delta S_{\mathrm{comb}}/R = x[\bar{y}/x - 1 - (\bar{y}/x) \ln (\bar{y}/x)] \quad (13)$$

where $\bar{y}/x = (4/\pi)\langle \sin \psi \rangle$ (cf. eq 3). Adopting the identity $\langle \sin \psi \rangle \equiv \langle \sin \theta \rangle_1$, set forth in eq 5, the quantity in brackets can be evaluated without resort to x, and the results are given in the third column of Tables V and VI for polyesters I and II, respectively. In estimating effective values of the axial ratio x, we assume that x comprises a rigid core plus a contribution from half of each of the two flanking flexible segments. Averages of the projection of these flexible segments on the axis along the rigid core were taken into account. The increments (Δl) in the length of rigid core segments thus estimated are given in the fourth column of the tables. Shown in the following columns are the axial ratios x and the calculated values of $\Delta S_{\mathrm{comb}}/R$ for the polymer systems mentioned in the introductory section. In these calculations, lengths of the rigid cores were obtained for the individual polymer systems from the relevant X-ray data:[22] 14.0 (X_a), 12.0 (X_b), 11.7 (X_c and X_d), and 17.6 (X_e), units being Å. The diameter of the rigid core segment was taken[14] to be 4.8 Å in each case.

Table VI
Values of $\Delta S_{\mathrm{comb}}/R$ for Polyesters II[a] Estimated according to Eq 13

				polymer X_e[b]	
n	$\bar{y}/x = (4/\pi) \times \langle \sin \theta \rangle_1$	$(\bar{y}/x) - 1 - (\bar{y}/x) \times \ln (\bar{y}/x)$	Δl, Å	x	$\Delta S_{\mathrm{comb}}/R$
2	0.179	−0.514	4.3	4.56	−2.34
4	0.190	−0.494	5.1	4.73	−2.34
6	0.236	−0.424	5.8	4.88	−2.07
8	0.263	−0.386	6.4	5.01	−1.93
10	0.285	−0.358	6.9	5.10	−1.82

[a] $-[X-C^*O^*-O(CH_2)_nO-C^*O^*]-$. [b] The rigid core (X) of the polymer is given by $X_e = -C_6H_4-O-CO-C_6H_4-CO-O-C_6H_4-$.

Entropy Change ΔS_{ni} at the Nematic–Isotropic Transition. Values of ΔS_{comb} calculated for several polymer systems (Tables V and VI) are in the range 3.6–4.8

Table VII
Reduced Entropy Difference $\Delta S_{ni}/R$ between Isotropic and Anisotropic Phases Estimated for Polymers with n = Even[a]

	polyesters I[b]						polyesters II[b]	
	X_a		X_b		X_c, X_d		X_e	
n	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl
2	0.01		0.26		0.30		−0.08	
4	0.19		0.43		0.48		0.33	
6[c]	0.32 (0.34)	2.0[d]	0.54 (0.56)	2.4[d]	0.58 (0.60)	1.4,[e] 0.9[f]	0.47	0.6[g]
8	0.46	2.0[d]	0.67	2.2[d]	0.71	1.5,[e] 1.4[f]	0.52	1.2[g]
10							0.62	

[a] Calculated for a repeating unit. [b] For chemical structures of rigid cores (X), see footnotes to Tables V and VI. [c] Values in parentheses are those derived by using the three-state scheme for rotation around the C*–C bond. [d] Reference 2. [e] Polymers with X_c: ref 3. [f] Polymers with X_d: ref 4. [g] Reference 7a; polymers with $n \geqslant 9$ were reported to form smectic mesophases.[7b]

cal mol^{-1} deg^{-1} (15–20 J mol^{-1} deg^{-1}), being somewhat smaller in magnitude than ΔS_{orient} (Tables III and IV) and opposite in sign. The reduced entropy difference $\Delta S_{ni}/R$ derived directly from the values of $\Delta S_{orient}/R$ and $\Delta S_{comb}/R$ calculated in the preceding sections are summarized in Table VII. Experimental values are also included in instances where the data are available. In most cases, the calculated values are much below those observed. In order to reproduce experimental observations, we must assume either a smaller magnitude for ΔS_{comb} or an enhanced value of ΔS_{orient}.

In the aforementioned treatment, the average inclination of rigid cores defined by $\langle \sin \psi \rangle = (\pi/4)(\bar{y}/x)$ was identified with $\langle \sin \theta \rangle_1$, a quantity calculated on the basis of the intramolecular correlation depicted in Figures 2 and 4. The order parameters s computed for region 1 are in the range 0.90–0.98 as shown in Figures 6 and 7. The value of $\langle \sin \psi \rangle$ in the real system may be higher owing to intermolecular effects. Experimental values of the order parameter determined by NMR measurements are reported to be 0.6–0.7 for polymers in the mesophase.[23,24] The microscopic order within a well-defined mesophasic domain may be even higher: recently, Mueller et al.[25] reported a micro-order parameter of 0.81 for a polyether with decamethylene spacers by using a spin probe technique. Adoption of this value for s leads to $\langle \sin^2 \psi \rangle^{1/2} = 0.36$ in comparison with $\langle \sin^2 \theta \rangle_1{}^{1/2} = 0.12$–$0.26$. In recognition of these differences, use of a slightly higher value of $\langle \sin \psi \rangle$ for ΔS_{comb} (but not for ΔS_{orient}) may be justified. A tentative calculation with $\langle \sin \psi \rangle = 0.3$ in eq 13 gave a considerable decrease (ca. 50%) in ΔS_{comb} and thus, when combined with ΔS_{orient} listed in Tables III and IV, yielded values of ΔS_{ni} in agreement with those observed.

On the other hand, values of ΔS_{orient} given in the preceding section may also be subject to some sizable alteration. In the nematic state, some of the conformations assigned to region 1 (cf. Figures 2 and 4) may suffer restrictions from intermolecular correlations, either entropic or enthalpic in nature. If such restrictions exist in the mesophase, ΔS_{orient} must be enhanced. For a speculation, let us assume that phenylene rings embedded in a rigid core are coplanar and that cores tend to orient parallel with each other when the molecules are kept in the nematic state. With these postulations, we calculated fractions of such orientations that the ester groups situated on both sides of the flexible spacer are coplanar within a deviation of ±10°. With this requirement, the fraction p_1 for conformations in region 1 becomes significantly small: e.g., for polyester I with $n = 6$, $p_1 = 0.154$ (cf. $p_1 = 0.358$ in Table III); for polyester II with $n = 6$, $p_1 = 0.094$ (cf. $p_1 = 0.309$ in Table IV). A considerable enhancement in the ΔS_{orient} terms may be anticipated in this example. Detailed analysis beyond this level needs more information regarding the nature of nematic polymer liquids.

Alternatively, values of ΔS_{orient} could be doubled if the spacer joining two successive rigid cores is taken to be ideally flexible in the isotropic state. By this idealization, orientational correlations among rigid cores vanish entirely: i.e., $\theta_a{}^* = \theta^*$ and $\theta_b{}^* = \pi$ in eq 10. Most of the experimental values of ΔS_{ni} may be reproduced by such calculations. However, this model apparently deviates too far from actuality as indicated by the present analysis (cf. Figures 2 and 4). As we have shown in our previous treatment of the odd–even effect in the dipole moments of α,ω-dihalo-n-alkanes,[26] directional correlations between the terminal bond vectors are far from random even for n values of 10 or higher.

Comment on the Enthalpy Change at the Nematic–Isotropic Transition. As shown by Blumstein et al.,[6] values of ΔH_{ni} observed for polymers exceed greatly those for simple low molecular weight nematogens. Especially for polymers with n = even (ΔH_{ni} = 1–2 kcal mol^{-1}),[2-4,7] the difference amounts to 5–10 times. According to the theory,[14] the orientation-dependent energy is given by

$$E_{orient} \simeq -\Delta H_{ni} = -(R/2)xs^2T^* \qquad (14)$$

where T^* is the characteristic temperature which measures interaction between rigid core segments. The order parameters of polymers are reported[23-25] to be 0.6–0.8, being nearly twice those observed for low molecular weight liquid crystals (~0.4).[19] As we have shown, the contribution from the flexible segment to the axial ratio x is also significant (20–40% in x: cf. Tables V and VI). These changes in s and x should raise the value of E_{orient} several-fold. In some cases, the increment may still be insufficient to match the observed enhancement in ΔH_{ni} for polymers. Variation in the magnitude of T^* remains as a possible source of enhancement in ΔH_{ni}. In a highly ordered nematic state, as discussed previously, mesogenic groups composed of phenylene rods may be so arranged as to promote pairwise (intermolecular) interaction between the neighbors. If such attractive interactions are operative, the magnitude of T^*, and hence that of E_{orient}, should increase.

The large enhancement observed in both ΔH_{ni} and ΔS_{ni} for the n = even polymers may be thereby explicable on the same basis. Somewhat lower values of ΔH_{ni} were generally reported for the n = odd polymers.[2-4] The observed odd–even oscillation in ΔH_{ni} probably originates from the difference in the order parameters in the mesophases.

Concluding Remarks

Assuming a nematic ordering for polymers with n = even, the entropy changes ΔS_{orient} due to orientation–disorientation of rigid core segments were estimated. The calculated values of $\Delta S_{\mathrm{orient}}$ generally exceed in magnitude the corresponding contributions from the ΔS_{comb} term (note that these two ΔS's are opposite in sign). The sum $\Delta S_{\mathrm{orient}} + \Delta S_{\mathrm{comb}}$ generally leads to an underestimate of the observed entropy change at the nematic–isotropic transition. Some possible amendments in the theoretical calculations are suggested.

Experimental values of ΔS_{ni} vary little[2] or tend to increase gradually[3,4] with n, of comparison is made within the same parity of n. These observations are supported by the present calculations; i.e., both $\Delta S_{\mathrm{orient}}$ and ΔS_{comb} remain nearly invariant with the number of methylene units for a homologous series of polymers with n = even. Calculated values of ΔS_{ni} tend to increase somewhat.

The observed values of ΔS_{ni} cited in this paper are those determined under constant pressure. Since information required to correct for the volume change at the transition is not available for these polymers, the effect arising from this source has been entirely neglected in the present treatment.

For polymers with n = odd, as pointed out above, a simple nematic ordering is inconsistent with the requirement imposed by conformations of flexible segments. The angle θ defined by two successive rigid cores should remain mostly in the range $50° < \theta < 90°$ even in the mesophase. Accordingly, the entropies liberated at the nematic-to-isotropic transition are generally lower than those for the n = even polymers. Ober et al.[7] reported DSC studies on polyester II having bis(p-carboxyphenyl) terephthalate (X_e). The ΔS_{ni} vs. n plot exhibits an odd–even oscillation over the range n = 5–9, with higher values for the odd members. These results are at variance with our expectation dictated by the distribution curves shown in Figures 4 and 5. More detailed experimental information is required regarding the nature of the mesophase of this series of polymers.

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