one first solves eq VIII.35 to zero order (i.e., for a rod). Regular perturbation theory gives the first-order term expressing deviations from the rigid rod configuration (one must also retain terms of order contour length squared). Next we get the distribution $f(\theta)$ from eq VIII.28 and the expression $\sigma k_B T = \mathcal{F} - \langle U_{ex} \rangle$ is rewritten in terms of this $f$ by the use of the identity $\langle \Delta U_{ex} \rangle = {}^1/_2 N_P \langle (\nabla U_{ex})^2 \rangle$ obtained by integrating by parts. It is interesting to note that this scheme is regular even though all quantities are singular; one would usually resort to a WKB approximation.

(94) The free energy difference per rod $(\Delta F_i - \Delta F_a)/N$ is much smaller than $k_B T$ so in this sense the first-order transition can be considered weak. However, from this viewpoint the order parameter and difference in densities are then anomalously large. Compare with the discussions in ref 14 and 23.

(95) The mechanism of the electrostatic twisting force is exhaustively reviewed and analyzed in ref 22. A scaling argument may help in understanding the form of eq VI.1. Consider two line charges skewed at an angle $\gamma$ and separated by more than a screening distance $\kappa^{-1}$ so that the outer double layers can be treated in the Debye–Hückel approximation. The cross section of the two overlapping double layers can be seen to be of order

$\kappa^{-2} \sin^{-1} \gamma$. If the effective linear charge density is $\nu$ charges per unit length, we have

$$w(x \simeq \kappa^{-1}) \sim \nu^2/(\kappa \sin \gamma)$$

This must be multiplied by a screening factor in order to arrive at eq V.1.

(96) Some numerical work has also been published recently by: Lee, S. D.; Meyer, R. B. *J. Chem. Phys.* **1986**, *84*, 3443. For comments, see ref 22.

(97) McMullen, W. E.; Gelbart, W. M.; Ben-Shaul, A. *J. Chem. Phys.* **1985**, *82*, 5616. These authors use a Legendre expansion to only second order which gives qualitative results (see ref 20). In this review we discuss expansions appropriate to highly ordered nematics.

(98) Some of these (qualitative) conclusions were first reached by Frost and Flory (Frost, R. S.; Flory, P. J. *Macromolecules* **1978**, *11*, 1134) within the Flory approximation.

(99) The approaches outlined in this review are applied to calculations of the elastic moduli in Odijk (Odijk, T. *Liq. Cryst.*, in press) and to micellar solutions in Odijk (Odijk, T. *J. Phys. (Les Ulis, Fr.)*, in press).

# Articles

## A Statistical Thermodynamic Theory of Thermotropic Linear Main-Chain Polymeric Liquid Crystals

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**ABSTRACT:** A statistical thermodynamic theory of thermotropic, main-chain polymeric liquid crystalline melts is developed by application and extension of a previously formulated statistical mechanical theory of rigid rod fluids (Boehm, R. E.; Martire, D. E. *Mol. Phys.* **1978**, *36*, 1). Each polymer molecule consists of $M$ monomeric units bonded contiguously along a chain, and each monomeric unit in the isotropic melt consists of a rigid mesogenic core of $r + 1$ consecutive segments followed by $t$ contiguous flexible segments. A free energy density is formulated that includes both short-range packing contributions and long-range anisotropic and isotropic dispersion energy contributions. Ordering of the mesogenic cores in the nematic melt is assumed to generate an environmentally induced tension that acts along the backbone of each chain and increases the average end-to-end chain length along the preferred direction, and an extension or enhanced ordering of the spacer groups in each monomer results. The enhanced ordering of the spacer groups leads to predictions of somewhat larger order parameters, transition entropies, and transition enthalpies than those typically observed for low molecular weight nematogens. Also under certain conditions an additional highly anisotropic mesophase is predicted to appear, in agreement with the results of Vasilenko et al. (Vasilenko, S. V.; Khokhlov, A. R.; Shibaev, V. P. *Macromolecules* **1984**, *17*, 2270). The thermodynamic properties of (hypothetical) homologous series of linear mesogenic polymers formed by increasing $t$ for fixed $r$ and $M$ are also calculated and predict the experimentally observed trends of decreasing transition temperature and increasing transition entropy and enthalpy with increasing $t$. A possible mechanism for inclusion of odd–even variations in the thermodynamic properties is also discussed. The dependence of the statistical thermodynamic properties on $M$ is also determined, and the results appear to be consistent for the most part with the experimental trends.

## I. Introduction

Liquid crystalline polymers which have their mesogenic elements separated by flexible or semiflexible spacer groups such as $-(CH_2)_n-$, $-[Si(CH_3)_2O]_n-$, or $-(CH_2CH_2O)_n-$ often exhibit thermotropic mesophases with moderate anisotropic–isotropic phase transition temperatures considerably below that required for thermal degradation of the macromolecule. Several different linear nematic, smectic, and cholesteric polymers with moderate transition temperatures have been synthesized by condensation of mesogenic diols, diphenols, or diacid chlorides with flexible diols, silanols, or diacid chlorides.[1] The

thermodynamic and structural properties have also been measured for a variety of linear polymeric liquid crystals. For example, Blumstein and Thomas (BT)[2] have measured the thermodynamic transition properties of a homologous series of mesogenic, thermotropic polyesters derived from 4,4'-dihydroxy-2,2'-dimethylazoxybenzene and alkanedioic acids having from $n = 2$ to $n = 14$ methylene groups which exhibit isotropic–nematic transitions for $n > 2$ at moderate temperatures (255 to 120 °C). Krigbaum, Watanabe, and Ishikawa[3] (KWI) have investigated the thermodynamic and structural properties of the mesophases of thermotropic polyesters synthesized from 4,4'-dihydroxybiphenyl

and aliphatic dibasic acids. Both homologous series of polyesters exhibit odd–even variations in their transition temperatures, transition enthalpies, and transition entropies. Furthermore, the liquid crystalling polyesters investigated by KWI and formed from acids having an odd (even) number of methylene units exhibit a nematic (smectic) mesophase formed by cooling from the isotropic phase. The entropy changes measured for the nematic- or smectic–isotropic transitions by BT and KWI are considerably larger than the transition entropies typically observed for low molecular weight mesogens. These results suggest that the flexible $-(CH_2)_n-$ spacers possess a somewhat more extended distribution of conformations in the ordered meosphase.[2]

NMR measurements of the order parameter, $S_{NI}$, at the nematic–isotropic transition temperature, $T_{NI}$, of low-melting, linear-chain nematic polymers formed by condensation of 2,2'-dimethyl-4,4'-azoxybenzene with the diacid chloride of dodecanedioic or 3-methyladipic acid are somewhat larger $(S_{NI} \sim 0.69)^1$ than that observed for *p*-azoxyanisole (PAA) $(S_{NI} \sim 0.4)$, which is nearly congruent structurally to the mesogenic moiety incorporated along the backbone of these polymeric liquid crystals. Magnetic susceptibility measurements yield $S_{NI} \sim 0.6$ for the mesogenic polyester $(C_{10}H_{20}OC_6H_4COOC_6H_4OC_{10}H_{20}OC_6H_4OOCC_6H_4O)_x$ compared to $S_{NI} \sim 0.4$ and $S_{NI} \sim 0.5$ for the corresponding monomer and dimer, respectively.[4] The transition entropy and transition enthalpy of the polyester are also considerably larger than those of the monomer and dimer and are comparable to those observed by BT and KWI for their homologous series of polyesters.

A completely successful theoretical description of the mesomorphic behavior of polymeric liquid crystals must ultimately predict the rather large transition enthalpies and entropies, odd–even variations of the transition properties, including the structural mesomorphism of the ordered phase for homologous series of polymeric liquid crystals, the somewhat larger order parameters and their temperature variation observed in the ordered polymeric phase, and the dependence of the thermodynamic properties on the degree of polymerization. Presumably the individual constituent molecules of polymeric melts which exhibit thermotropic mesomorphism must adopt molecular orientations and configurations and a packing arrangement compatible with the symmetry of the corresponding mesophase, and this must involve both intra- and intermolecular coupling between the polymeric and mesogenic attributes and also interactions between monomer pairs. Several theoretical analyses have been developed and have provided considerable insight into various aspects of the statistical thermodynamics of thermotropic liquid crystalline polymers. For example, Flory[5] has investigated the thermodynamic properties of polymer molecules which consist of a sequence of rigid rod moieties connected by freely flexible joints using a lattice model and assuming the athermal limit. The analysis indicated that these polymers exhibited a nematic–isotropic phase equilibrium very similar to that displayed by disconnected rodlike molecules with the same axial ratio; and it was also concluded that the axial ratio of the rigid rod sequences coupled with their combined volume fraction should be the primary determinant of the thermodynamic properties. Subsequently Matheson and Flory[6] extended the analysis to solutions of semirigid macromolecules which consist of alternating rigid, rodlike sequences with mutually independent orientations interspersed with completely flexible sequences of random coil segments.

Ronca and Yoon[7] have developed a statistical mechanical theory of semiflexible, nematic polymers by modifying the Kratky–Porod model of a wormlike chain to include finite chain extensibility. The predicted order parameters are between 0.4 and 0.7, which is consistent with observation.[1,4] However, the predicted transition entropies are rather small and comparable to those typically observed for low molecular weight nematogens rather than the large entropic changes measured by BT and KWI for linear mesogenic polyesters. Recently, ten Bosch, Maissa, and Sixou[8] have formulated a mean field theory of semiflexible nematic polymers based on a Landau–de Gennes free energy expansion for an elastic semiflexible chain with orientationally dependent dispersion interactions included. The theory appears to coincide with the observed behavior of the transition temperature with molecular weight for certain polymeric liquid crystals.

Recently, Vasilenko, Khokhlov, and Shibaev (VKS)[9] have extended the Matheson–Flory lattice model treatment to include the induced ordering of the flexible spacer segments in the anisotropic melt. The VKS analysis applies in the athermal limit, utilizes a freely rotating junction segment to connect successive monomers, assumes unit packing fraction of polymer segments in the melt, and yields theoretical predictions which are independent of the degree of polymerization. For completely flexible spacer segments, VKS theory predicts the existence of two distinctly different anisotropic mesophases termed "highly anisotropic" and "weakly anisotropic". The highly anisotropic phase is characterized by significant ordering of the flexible segment bond orientations along the preferred direction of alignment of the rigid mesogenic groups. The highly (weakly) anisotropic phase is favored when the fraction of flexible segments to the total number of segments per monomer is small (large) and the length-to-breadth ratio of the rigid group is large (small).

Here we extend a previously developed statistical mechanical theory of a rigid rod fluid[10] which is derived from the van Kampen analysis of condensation[11] to melts of thermotropic, linear main-chain polymeric liquid crystalline molecules. The analysis is applied to polymers composed of monomers which consist of a rigid mesogenic group connected to a sequence of completely flexible spacer segments. Successive monomers are assumed to be connected by a completely flexible junction segment as in the VKS analysis.

In section II we formulate an expression for the free energy of a linear main-chain polymeric liquid crystalline melt which includes both short-range packing contributions and longer range dispersion interactions. The short-range contributions include the free energy for a hypothetical reference system where all rigid units in every polymer molecule are fully aligned along a specified direction and a short-range configurational free energy difference between the actual less ordered state and the reference state. The calculation of the latter configurational free energy is simplified by restricting the orientations of the rigid moieties to three mutually orthogonal orientations and it is implemented through application of Flory–DiMarzio lattice statistics[12,13] on a cubic lattice. The long-range energetic contributions include an anisotropic dispersion interaction which tends to promote alignment of the mesogenic groups and an isotropic interaction energy involving rigid–rigid, flexible–flexible, and rigid–flexible segment–segment interactions.

Environmentally induced ordering of the rigid rodlike moieties in the anisotropic phase is assumed to generate an internal tension along the backbones of the individual

polymer chains and this has important consequences. In particular, as in the VKS analysis both highly and weakly anisotropic mesophases are predicted. The internal tension is responsible for an increase (decrease) in the number of rigid (flexible) segments (or segmental bonds) in each monomer in the ordered mesophases. The highly ordered anisotropic phase is characterized by an essentially complete conversion of flexible to rigid segments in each monomer and an order parameter of $\sim 1$. The weakly anisotropic phase manifests a considerably smaller incremental increase in the number of rigid bond segments per monomer and smaller core order parameters. The tension is derived from a length–tension relationship of entropic origin which utilizes an estimate of the change in the projected end-to-end separation vector along the preferred direction of individual chains in the melt which is based on the wormlike chain model. The internal tension possesses a dependence on the degree of polymerization $M$, which vanishes as $M \rightarrow \infty$, and imparts a corresponding $M$ dependence upon the predicted statistical thermodynamic properties characterizing the order–disorder transition.

In section III, we derive expressions for the changes in order parameter, entropy, enthalpy, and volume fraction of polymer which accompany the anisotropic–isotropic transitions. We also determine the temperature dependence of the order parameter at constant volume fraction to be an implicit universal function of the monomer composition, $M$, and the reduced temperature, $T/T_{\mathrm{NI}}$, where $T_{\mathrm{NI}}$ is the transition temperature.

In section IV, we present theoretical predictions of the order parameters, transition entropies, and chain extensions for both types of order–disorder transitions and investigate the conditions required for the appearance of a highly anisotropic mesophase. The enhanced ordering of the flexible spacer units in both the weakly and highly anisotropic mesophases generates somewhat larger transition entropies than those typically observed for low molecular weight nematogens. The corresponding entropies for transition to a weakly (highly) anisotropic phase tend to be less than or comparable to (somewhat larger than) the experimentally observed results. Futher comparisons of the predictions of the present analysis with experiment are provided. We also suggest a mechanism for inclusion of odd–even effects although the analysis is not sufficiently sophisticated to simulate the self-consistent mean field approach developed by Marčelja.[14] Finally we briefly compare this analysis with the VKS results and with other theoretical investigations and suggest possible modifications and extensions.

## II. Derivation of the Free Energy of a Thermotropic, Main-Chain Polymeric Liquid Crystalline Melt

We consider a melt of $N$ monodisperse thermotropic liquid crystalline polymer molecules confined to a volume $V$. Each molecule consists of a periodically repeating sequence of $M$ monomeric units bonded contiguously, without branching, along a linear chain. Every monomer possesses a rigid group of $r + 1$ consecutive segments connected to $t$ successive, completely flexible segments. The molecular volumes of a rigid and a flexible segment are assumed to be comparble, and the total number of segments per polymer chain is

$$L = M(r + t + 1) \tag{1}$$

Successive monomers are assumed to be always connected by a completely flexible junction segment as in the VKS analysis. In the subsequent analysis we allow redistribu-

tion in the numbers of rigid and flexible segments in each monomeric unit as the melt undergoes an isotropic–anisotropic transition. If $r_{\mathrm{N}} + 1$ and $t_{\mathrm{N}}$ denote the number of rigid and flexible segments in each monomeric unit when the melt is an ordered mesophase, then $r_{\mathrm{N}} + 1 + t_{\mathrm{N}} = r + 1 + t$. The flexible segments are in general chemically different from the rigid core segments.

In general, at sufficiently high temperatures or low volume fractions $\phi = LN/V$ of polymer segments, an infinite number of equally probable orientations are possible for the rigid groups in each monomeric unit and the melt is isotropic. However, at lower temperatures and/or higher $\phi$, alignment of the mesogenic units along a preferred direction (or set of nearly equivalent directions) may represent a thermodynamically more stable configuration, and a transition to an ordered nematic melt occurs. For simplicity in the subsequent derivation of the free energy, we restrict the allowed orientations of the rodlike groups to three mutually orthogonal directions (1, 2, 3). This restriction permits direct application of Flory–DiMarzio lattice statistics[12,13] to construct an approximate short-range configurational free energy and it also simplifies the form of the attractive dispersion interaction between pairs of mesogenic groups.[10]

Let $N_k$ ($k = 1, 2, 3$) represent the total number of rodlike groups oriented along direction $k$ and $n_k = N_k/V$ represent their corresponding number densities. We express the reduced Helmholtz free energy density as

$$f \equiv f(\phi, n_1, n_2, n_3, r, t, M) \equiv \beta V^{-1} F(V, N_1, N_2, N_3, r, t, M) = f_{\mathrm{c}} + f_{\|} + f_{\mathrm{d}} \tag{2}$$

where $F$ is the total Helmholtz free energy, $\beta \equiv (k_{\mathrm{B}}T)^{-1}$, $f_{\mathrm{c}}$ represents the change in the short-range contribution to the configurational free energy density when the rodlike groups undergo a transition from a hypothetical perfectly aligned reference state ($\phi, n_1=0, n_2=0, n_3=MN/V$) to the state ($\phi, n_1, n_2, n_3$), $f_{\|} = f_{\|}(\phi, n_1=0, n_2=0, n_3=MN/V, r, t, M)$ denotes a hypothetical reference free energy density corresponding to complete alignment of all rodlike moieties along direction 3, and $f_{\mathrm{d}}$ represents the free energy density contribution derived from all segment–segment pair dispersion interactions.

The contribution $f_{\mathrm{c}}$ is estimated from Flory–DiMarzio lattice statistics[12,13] applied on a cubic lattice to polymeric liquid crystals. We assume

$$f_{\mathrm{c}} = V^{-1} \ln \left[ Q_{\mathrm{c}}(V, N_1, N_2, N_3, r, t, M) / Q_{\mathrm{c}}(V, 0, 0, MN, r_1, t_1, M) \right] \tag{3}$$

where $Q_{\mathrm{c}} = Q_{\mathrm{c}}(V, N_1, N_2, N_3, r, t, M)$ is the configurational partition function which enumerates the number of distinguishable ways $N$ polymer molecules each consisting of $L = M(r + t + 1)$ segments can be introduced on a lattice of $V$ sites such that only single-segment occupancy per site is allowed, $Q_{\mathrm{c}}(V, 0, 0, MN, r_1, t_1, M)$ is the corresponding partition function when all rodlike moieties are aligned along direction 3, and $r_1 + 1$ and $t_1$ are the number of rigid and flexible segments with $r_1 + t_1 = r + t$. If $v_{j+1}$ represents the number of ways the $(j + 1)$th molecule can be successfully placed on the lattice given that $j$ polymer molecules have already been introduced, then

$$Q_{\mathrm{c}}(V, N_1, N_2, N_3, r, t, M) = (N!)^{-1} \sum_{\{N_i(1)\}} \sum_{\{N_i(2)\}} \cdots \sum_{\{N_i(N)\}} \prod_{j=0}^{N-1} v_{j+1}(N_i(j + 1)) \tag{4}$$

where $\sum_{\{N_i(j)\}}$ actually denotes the triple sum $\sum_{N_i(1)} \sum_{N_i(2)} \sum_{N_i(3)}$ and each term in the multiple sum must satisfy the constraints $\sum_{j=0}^{N-1} N_i(j + 1) = N_i$ ($i = 1, 2, 3$). Also $\sum_{i=1}^{3} N_i(j) = M$ ($j = 1, 2, ..., N$). We propose that

$$v_{j+1} = (c/2(c - 1))(V - Lj)[(1 - Lj/V) \times$$
$$(c - 1)]^{M(t+1)-1} \prod_{i=1}^{3} [(V - Lj)/(V - r\sum_{k=1}^{j} N_i(k))]^{rN_i(j+1)} \quad (5)$$

where $N_i(j + 1)$ represents the number of rigid rodlike groups of $r + 1$ segments along the backbone of molecule $j + 1$ orientated along direction $i$ ($i = 1, 2, 3$) and $c$ is the coordination number of the lattice ($c = 6$ for a simple cubic lattice). The factor $V - Lj$ is the number of vacant lattice sites available to the first segment of molecule $j + 1$. The factor $(1 - Lj/V)(c - 1)$ is the number of vacant adjacent sites which can be occupied by either a completely flexible segment or the initial segment of a rigid rod sequence of $r + 1$ segments which are in contiguous alignment along an allowed direction. The initial segment of the $r + 1$ rigid rod segments can be regarded as the completely flexible segment which connects adjacent monomers. The factor $(V - Lj)/(V - r\sum_{k=1}^{j} N_i(k))$ denotes the probability of a given vacant site to be adjoined by another in orientation $i$ if $\sum_{i=1}^{3} \sum_{k=1}^{j} N_i(k) = Mj$ rigid rod sequences have already been inserted on the lattice. The factor $c/2(c - 1)$ corrects for the fact that the second segment can be placed on any of $c$ rather than $c - 1$ adjacent sites and that either end of the $(j + 1)$th chain can be considered as the initial segment for lattice placement.

In order to simplify evaluation of the multiple summations in eq 4, we shall assume that the $N_1(k)$, $N_2(k)$, and $N_3(k)$ rodlike groups with orientations 1, 2, and 3, respectively, are randomly distributed along polymer chain $k$ and that for all the chains in the melt, the set $\{N_i(k)\}$ is given in terms of the average order parameter, $S$, ($-1/2 \leq S \leq 1$) by

$$N_1(k) = N_2(k) = (1 - S)M/3$$
$$N_3(k) = (1 + 2S)M/3 \qquad (k = 1, 2, ..., N) \quad (6)$$

where clearly $\sum_{i=1}^{3} N_i(k) = M$ and $\sum_{k=1}^{N} \sum_{i=1}^{3} N_i(k) = MN$. Utilization of the random distribution approximation yields

$$Q_c = (N!)^{-1}(c/2(c - 1))^N (c - 1)^{(M(t+1)-1)N} [M!/(((1 - S)M/3)!)^2((1 + 2S)M/3)!]^N ((V - rNM(1 - S)/3)!)^2(V - rNM(1 + 2S)/3)![(V - LN)! V^{(M(t+1)-1)N}(V!)^2]^{-1} \quad (7)$$

where we have employed

$$\prod_{j=0}^{N-1} (V - Lj)^L \simeq V!/(V - LN)!$$

$$\prod_{j=0}^{N-1} (V - rjN_i)^{rN_i} = V!/(V - rN_i)! \qquad (i = 1, 2, 3)$$

and the random distribution approximation for $\{N_i(j)\}$ to evaluate the multiple summation in eq 4. Application of Stirling's approximation to eq 7 gives

$$\ln Q_c = N \ln (c/2(c - 1)) +$$
$$N(M(t + 1) - 1)[\ln [(c - 1)/V] - 1] - N \ln N +$$
$$(NM/3)[3 \ln 3 - 2(1 - S) \ln (1 - S) - (1 + 2S) \ln (1 + 2S)] + 2(V - rNM(1 - S)/3) \ln (V - rNM(1 - S)/3) +$$
$$(V - rNM(1 + 2S)/3) \ln (V - rNM(1 + 2S)/3) -$$
$$(V - LN) \ln (V - LN) - 2V \ln V \quad (8)$$

When $r = 0$, $S = 0$, eq 8 reduces to

$$\ln Q_c = N \ln (c/2(c - 1)) + N(M(t + 1) - 1) \times$$
$$[\ln [(c - 1)/V] - 1] - N \ln N + NM \ln 3 + V \ln V -$$
$$(V - (t + 1)MN) \ln (V - (t + 1)MN)$$

or

$$Q_c \simeq (N!)^{-1}(c/2(c - 1))^N (3^{NM}) V![(V - (t + 1)MN)!]^{-1}[(c - 1)/V]^{(M(t+1)-1)N}$$

which is essentially the Flory-Huggins configurational partition function[15,16] (except for the orientational degeneracy factors $3^{NM}$ and $2^{-N}$) for $N$ completely flexible polymer molecules each with $M(t + 1)$ identical segments distributed on a cubic lattice of $V$ sites. When $t = 0$ and $M = 1$, eq 8 reduces to

$$\ln Q_c = N \ln (c/2(c - 1)) - N \ln N +$$
$$(N/3)[3 \ln 3 - 2(1 - S) \ln (1 - S) - (1 + 2S) \ln (1 + 2S)] + 2(V - rN(1 - S)/3) \ln (V - rN(1 - S)/3) +$$
$$(V - rN(1 + 2S)/3) \ln (V - rN(1 + 2S)/3) -$$
$$(V - (r + 1)N) \ln (V - (r + 1) N) - 2V \ln V$$

or

$$Q_c \simeq [(V - rN(1 - S)/3)!]^2(V - rN(1 + 2S)/3)![((N(1 - S)/3)!)^2(N(1 + 2S)/3)!]^{-1}[(V - (r + 1)N)!(V!)^2]^{-1}$$

which represents the DiMarzio configurational partition function[12] for $N$ rigid rods with length-to-breadth ratio $r + 1$ distributed on a cubic lattice of $V$ sites and restricted to three mutually orthogonal orientations.

When $S = 1$ complete alignment of the rigid rodlike moieties along the preferred direction is attained, and

$$\ln Q_c(V,0,0,MN,r_1,t_1,M) = N \ln (c/2(c - 1)) +$$
$$N[M(t_1 + 1) - 1][\ln ((c - 1)/V) - 1] + (V - r_1MN) \ln (V - r_1MN) - (V - LN) \ln (V - LN) - N \ln N \quad (9)$$

Substitution of eq 8 and 9 into eq 3 gives with $r \to r_N$, $t \to t_N$, and $r_N + t_N = r + t = r_1 + t_1$

$$f_c = f_c(\phi_N, S, r_N, t_N) =$$
$$-3\lambda_N r_N^{-1}[\ln (2(c - 1)/c) + (t_N - t_1)(\ln (c - 1) - 1) + \ln 3] + \lambda_N r_N^{-1}[2(1 - S) \ln (1 - S) + (1 + 2S) \ln (1 + 2S)] - 2(1 - \lambda_N(1 - S)) \ln (1 + \lambda_N S(1 - \lambda_N)^{-1}) - (1 - \lambda_N(1 + 2S)) \ln (1 - 2\lambda_N S(1 - \lambda_N)^{-1}) - 3(1 - \lambda_N) \ln (1 - \lambda_N) + (1 - 3r_1\lambda_N/r_N) \ln (1 - 3r_1\lambda_N/r_N)$$
$$(10)$$

where $\lambda_N \equiv \phi_N r_N/3(r_N + t_N + 1)$ and $\phi_N = M(r_N + t_N + 1)\rho_N$ where $\phi_N$ and $\rho_N$ are the volume fraction and number density of polymer molecules in the anisotropic phase. Similarly, for the isotropic phase $S = 0$ and

$$f_c(\phi_I, 0, r, t) =$$
$$-3\lambda_I r^{-1}[\ln (2(c - 1)/c) + (t - t_1)(\ln (c - 1) - 1) + \ln 3] - 3(1 - \lambda_I) \ln (1 - \lambda_I) + (1 - 3r_1\lambda_I/r) \ln (1 - 3r_1\lambda_I/r)$$
$$(11)$$

where $\lambda_I \equiv \phi_I r/3(r + t + 1)$ and $\phi_I = M(r + t + 1)\rho_I$ where $\phi_I$ and $\rho_I$ are the volume fraction and number density of polymer molecules in the isotropic melt. In formulating eq 10 and 11 we have assumed that the difference in the number of rigid segments (or internal bonds) per monomer unit $r_N - r = t - t_N$ in the ordered and isotropic melts always involves conversion of those flexible segments immediately adjacent to the original $r$ mesogenic core segments.

Ordering of the rigid mesogenic moieties along the backbones of the individual polymer molecules in the anisotropic melt alters their configurations relative to the random coil configurations anticipated in the isotropic melt.[17] Such configurational alterations are conspicuously evident for the isotropic–smectic transitions observed by KWI[3] for the even-membered homologues of the polyesters synthesized from 4,4'-dihydroxybiphenyl and aliphatic dibasic acids. An anticipated manifestation of such configurational changes is an increase in the mean end-to-end length, $l$, along the preferred direction 3 of the polymer molecules in the anisotropic phase relative to that preva-

lent in the isotropic phase. This increase in $l$ per chain can be regarded as imparted by an internal, environmentally induced tension, $\tau$, which acts along the backbone of the chain and is generated by the nonrandom orientational alignment of the mesogenic groups. Here we present an approximate formulation of a relationship between $\tau$ and the order parameter $S$ from a length–tension relationship, and from this we develop an expression which connects the relative change in the rigidity of each monomer unit, $\Delta \equiv (r_N + 1/r + 1) - 1$, to $S$ at the transition.

We assume that the tension and the reduced length $d = l/Mb$, where $b$ is the end-to-end length of a monomer unit, are connected through a length–tension relationship:[18]

$$d = l/Mb = (\langle \mathbf{R} \cdot \mathbf{e}_3 \rangle_{AN} - \langle \mathbf{R} \cdot \mathbf{e}_3 \rangle_I)/Mb = \mathcal{L}(\beta \tau b) \quad (12)$$

where $\mathcal{L}(y) = \coth y - y^{-1}$ is the Langevin function and $\mathbf{e}_3$ denotes a unit vector along direction 3. The averages $\langle \mathbf{R} \cdot \mathbf{e}_3 \rangle_{AN}$ and $\langle \mathbf{R} \cdot \mathbf{e}_3 \rangle_I$ respectively represent the configurationally averaged projection of the end-to-end length vector of a polymer chain along direction 3 in the anisotropic and isotropic melts. We propose that the $\langle \mathbf{R} \cdot \mathbf{e}_3 \rangle$ can be estimated from the end-to-end vector distance projected onto a unit vector along 3 and located at one end of an equivalent wormlike (i.e., Kratky–Porod) chain.[19] Hence $\langle \mathbf{R} \cdot \mathbf{e}_3 \rangle = (1 - \exp(-2\gamma Mb))/2\gamma$, where $1/2\gamma = b/(1 + (-\cos \theta))$ is the persistence length of the chain and $(-\cos \theta) = -\langle \cos^2 \theta \rangle^{1/2}$ is taken to be the negative of the square root of the mean-square supplement of the bond angle between the rigid core moieties of consecutive monomer units.[19] We then introduce the formal definition of the order parameter for the rigid cores $S = \langle (3 \cos^2 \theta - 1) \rangle/2$ and equate $-\cos \theta = -\langle \cos^2 \theta \rangle^{1/2} = -((2S + 1)/3)^{1/2}$. Thus in terms of $S$

$$\langle \mathbf{R} \cdot \mathbf{e}_3 \rangle_{AN} = bg(S)[1 - \exp[-M(1 - S)/g(S)]]/(1 - S) \quad (13)$$

where $g(S) = (3/2)[1 + ((1 + 2S)/3)^{1/2}]$ is a slowly varying function of $S$ in the relevant range $0 \le S \le 1$. In the subsequent analysis, we shall employ $g(S = 1) = 3$ for simplicity and adopt the length–tension relationship

$$d = d(M,S) = 3M^{-1}[(1 - \exp[-M(1 - S)/3]) \times (1 - S)^{-1} - 1 + \exp[-M/3]] = \mathcal{L}(\beta \tau b) \quad (14)$$

where $\langle \mathbf{R} \cdot \mathbf{e}_3 \rangle_I = 3b(1 - \exp[-M/3])$ has been utilized. This result is the postulated relationship between $\tau$ and $S$. Since $S$ depends on the statistical thermodynamic properties of a bulk anisotropic polymeric melt, the induced internal tension is coupled in a self-consistent manner to environmentally promoted intermolecular ordering and is *not* an intrinsic chain stiffness.

For the isotropic melt $S = 0$ and eq 14 reduces to $d = \mathcal{L}(\beta \tau b) = 0$ and $\tau = 0$. In the anisotropic melt $d$ and $\tau$ increase monotonically with $S$ and $d \to 1$ and $\tau \to \infty$ as $S \to 1$ for sufficiently large $M$.

A relationship between the increment, $\Delta = (r_N + 1)(r + 1)^{-1} - 1$, in the number of rigid segments per monomer unit and $\tau$ is deduced from the following considerations. Each polymer molecule in the melt possesses $Mt$ internal bonds which connect the centers of adjacent flexible segments and these bonds are allowed three mutually orthogonal orientations in the present model. Let $u$ represent the fraction of flexible bonds which connect adjacent flexible segments and/or adjacent rigid–flexible segments which are *not* in the orientation of the preceding rigid core associated with the same monomer. The fraction of flexible bonds in the direction of the rigid moiety in the associated monomer is then $1 - 2u$. The total number of flexible bonds which are along the preferred direction 3 for any given polymer chain is $Mt_\parallel = (1 + 2S)(1 - 2u)Mt/3$

$+ (1 - S)(2uMt)/3 = Mt[1 + 2S(1 - 3u)]/3$. The increment $\Delta(r + 1)$ in the number of rigid bond segments per monomer unit in the anisotropic melt is assumed to be given by the difference in the number of flexible bond segments aligned along the preferred direction which occurs in response to the ordering of the rigid cores:

$$\Delta(r + 1) = r_N - r = t - t_N =$$
$$t[(1 + 2S)(1 - 2u) + 2u(1 - S) - 1]/3 = 2tS(1 - 3u)/3 \quad (15)$$

where $t/3$ is the number of flexible bonds along direction 3 per monomer in the isotropic phase. We assume that

$$u = \exp[-\beta \tau(r + 1)a]/[1 + 2 \exp[-\beta \tau(r + 1)a]) \quad (16)$$

and thus

$$\Delta = (2xS(1 - \exp[-\beta \tau(r + 1)a])/3) \times$$
$$(1 + 2 \exp[-\beta \tau(r + 1)a])^{-1} \quad (17)$$

where $x \equiv t/(r + 1)$, $(r + 1)a$ is the length of the rigid moiety in each monomer, and $\tau$ depends on $S$ and $M$ through eq 14. The derivative $\partial \Delta/\partial S$, which is also required in the subsequent analysis, is given by

$$\partial \Delta/\partial S = \Delta S^{-1} + 2xS(r + 1)(a/b)[1 - d^2 - 2d/\beta \tau b]^{-1} \times$$
$$\exp[-\beta \tau(r + 1)a](1 + 2 \exp[-\beta \tau(r + 1)a])^{-2}(\partial d/\partial S) \quad (18)$$

where $\partial d/\partial S = 3M^{-1}(1 - S)^{-2}[1 - (1 + M(1 - S)/3) \exp[-M(1 - S)/3]]$. In the isotropic melt, $S = 0$, $\gamma = 0$, and both $\Delta$ and $\partial \Delta/\partial S$ vanish. In the subsequent analysis, we shall employ $b/a = (r + 1 + t) = (r + 1)(1 + x)$. In a more sophisticated description of the flexible spacer groups such as that based on the rotational isomeric model of Flory,[20] $\Delta > 0$ would correspond to an increase in the trans conformer population in the ordered mesophase.

The free energy density $f_\parallel \equiv f_\parallel(\phi, n_1 = 0, n_2 = 0, n_3 = MN/V, r_1, t_1, M)$ pertains to a hypothetical reference state where all rigid, rodlike groups are completely aligned along direction 3 and from eq 15 with $S = 1$ and $u = 0$, $r_1 \equiv r + 2t/3$ and $t_1 \equiv t/3$. Theoretical calculations of the thermodynamic properties for this system are not available. Perhaps an appropriate modification of the scaled-particle theory of Cotter and Martire for perfectly aligned spherocylinders could be applied.[21] A lattice model provides an equation of state which is too compressible compared to that obtained for a dense fluid of hard spheres or rods and is not considered as a viable means for estimating $f_\parallel$. Fortunately, a detailed specification of $f_\parallel$ is not required unless the density change accompanying the nematic–isotropic transition is considered.

The dispersion interaction contribution to the free energy density may be expressed as

$$f_d = -(\beta/2V)\left[ \sum_{i=1}^{3} \sum_{j=1}^{3} \int \int d^3\mathbf{R} \, d^3\mathbf{R'} \, n_i(\mathbf{R})w_{ij;rr}(\mathbf{R} - \mathbf{R'};\Omega_i,\Omega_j)n_j(\mathbf{R'}) + \sum_{i=1}^{3} \int \int d^3\mathbf{R} \, d^3\mathbf{R'} \, [n_i(\mathbf{R})w_{rt}(\mathbf{R} - \mathbf{R'})n_t(\mathbf{R'}) + n_t(\mathbf{R})w_{tr}(\mathbf{R} - \mathbf{R'})n_i(\mathbf{R'})] + \int \int d^3\mathbf{R} \, d^3\mathbf{R'} \, n_t(\mathbf{R})w_{tt}(\mathbf{R} - \mathbf{R'})n_t(\mathbf{R'})\right] \quad (19)$$

where $n_k(\mathbf{R})$ ($k = 1, 2, 3$) and $n_t(\mathbf{R})$ respectively denote the average number density of rodlike groups in orientation $k$ and flexible segments in a region of the melt localized about $\mathbf{R}$; also $w_{ij;rr}(\mathbf{R},\Omega_i,\Omega_j)$, $w_{rt}(\mathbf{R}) = w_{tr}(\mathbf{R})$, and $w_{tt}(\mathbf{R})$ respectively represent pair interaction energies between two rigid rod groups in orientations $i$ and $j$, a rigid group, and a flexible segment and two flexible segments where each pair of moieties are separated by a distance $\mathbf{R}$ be-

tween their centers. We assume that

$$w_{ij;rr}(\mathbf{R},\Omega_i,\Omega_j) = w_{\|}(\mathbf{R})\delta_{ij} + w_{\perp}(\mathbf{R})(1 - \delta_{ij}) \quad (20)$$

where $w_{\|}(\mathbf{R})$ and $w_{\perp}(\mathbf{R})$ respectively represent the attractive interaction energy between two rigid, rodlike groups averaged over all possible mutually parallel or perpendicular rod orientations consistent with a center of mass separation $\mathbf{R}$ betweeen the pair. An explicit determination of $w_{\|}(\mathbf{R})$ and $w_{\perp}(\mathbf{R})$ is not required in the subsequent analysis.

If we assume that the number densities $n_k(\mathbf{R})$ ($k = 1$, 2, 3) and $n_t(\mathbf{R})$ are spatially uniform throughout the melt and we set $n_1 = n_2 = (1 - S)MN/3V$, $n_3 = (1 + 2S)MN/3V$, where $\sum_{k=1}^{3}n_k = MN/V$ as required, and $n_t = t_N MN/V$ and then substitute into eq 19 using eq 20, we obtain

$$f_d(\phi,S,r,t,M) = -\beta(MN/V)^2[(\bar{w}_{\|} - \bar{w}_{\perp})S^2/3 + (\bar{w}_{\|} +$$
$$2\bar{w}_{\perp})/6 + t_N(r + 1)\bar{w}_{rt} + t_N^2\bar{w}_{tt}/2 + t_N\Delta(r + 1)\bar{w}_{tt}] \quad (21)$$

where $\bar{w}_{\|} \equiv \int_{\|}d^3\mathbf{R}\,w_{\|}(\mathbf{R})$, $\bar{w}_{\perp} \equiv \int_{\perp}d^3\mathbf{R}\,w_{\perp}(\mathbf{R})$, $(r + 1)\bar{w}_{rt} \equiv \int d^3\mathbf{R}\,w_{rt}(\mathbf{R})$, and $\bar{w}_{tt} \equiv \int d^3\mathbf{R}\,w_{tt}(\mathbf{R})$. The notation $\int_{\|}$ ($\int_{\perp}$) denotes that the integration extends over all allowed nonoverlapping configurations of two interacting rigid groups with parallel (perpendicular) axes of symmetry which are always aligned along either 1, 2, or 3. (The assumption of spatially uniform densities employed to obtain eq 21 is only viable for uniform nematic, isotropic, and perhaps cholesteric phases. For a smectic phase spatially uniform densities are untenable.) The first two terms on the right-hand side of eq 21 correspond respectively to the total anisotropic and isotropic pair dispersion interactions between the $r_N \equiv r + \Delta(r + 1)$ rigid segments of two different monomeric groups in the ordered phase. The third, fourth, and fifth terms on the right-hand side of eq 21 respectively correspond to the total pairwise interactions between the original $r + 1$ rigid segments in one monomer and the remaining $t_N \equiv t - \Delta(r + 1)$ flexible segments of another monomer group; the total interaction energy between the remaining flexible segments of all pairs of monomers and the total interaction energy between the $t_N \equiv t - \Delta(r + 1)$ remaining flexible segments on any monomer with the $\Delta(r + 1)$ converted flexible to rigid segments in another monomer. The flexible segments in the isotropic phase which are converted to rigid segments in the ordered phase in each monomeric unit are assumed to remain chemically identical.

It is convenient to rewrite $\bar{w}_{\|} - \bar{w}_{\perp}$ and $\bar{w}_{\|} + 2\bar{w}_{\perp}$ in eq 21 as

$$\bar{w}_{\|} - \bar{w}_{\perp} =$$
$$(r + 1)^2[(\bar{w}_{\|} - \bar{w}_{\perp})_{rr} + 2\Delta(\bar{w}_{\|} - \bar{w}_{\perp})_{rt} + \Delta^2(\bar{w}_{\|} - \bar{w}_{\perp})_{tt}] \quad (22a)$$

and

$$(\bar{w}_{\|} + 2\bar{w}_{\perp})/3 = (r + 1)^2[\bar{w}_{rr} + 2\Delta\bar{w}_{rt} + \Delta^2\bar{w}_{tt}] \quad (22b)$$

where $\bar{w}_{ab} = (\bar{w}_{\|} + 2\bar{w}_{\perp})_{ab}/3$ ($a = r,t$; $b = r,t$). Substitution of eq 22a,b, $t_N = (r + 1)[x - \Delta]$, and $\phi_N = (r + t + 1)MN/V$ into eq 21 gives

$$f_d = f_d(\phi_N,S,r,t) = -\beta\phi_N^2 D_N S^2 - \beta\phi_N^2 E \quad (23a)$$

where

$$D_N \equiv D_N(\Delta) = ((r + 1)/(r + t + 1))^2[(\bar{w}_{\|} - \bar{w}_{\perp})_{rr} +$$
$$2\Delta(\bar{w}_{\|} - \bar{w}_{\perp})_{rt} + \Delta^2(\bar{w}_{\|} - \bar{w}_{\perp})_{tt}]/3 \quad (24a)$$

and

$$E = ((r + 1)/(r + t + 1))^2[\bar{w}_{rr} + 2x\bar{w}_{rt} + x^2\bar{w}_{tt}]/3 \quad (24b)$$

For the isotropic phase $S = 0$, $\Delta = 0$, and $\phi = \phi_I$

$$f_d(\phi_I,0,r,t) = -\beta\phi_I^2 E \quad (23b)$$

The reduced dispersion energy in the ordered phase consists of an anisotropic contribution, $-\beta\phi_N^2 D_N S^2$, and an isotropic component, $-\beta\phi_N^2 E$ while in the isotropic phase only the isotropic component, $-\beta\phi_I^2 E$, persists. The change in the dispersion energy accompanying the nematic–isotropic transition also depends upon the attendant relative change, $\Delta\phi/\phi \equiv (\phi_N - \phi_I)/((\phi_N + \phi_I)/2)$ in the volume fraction at the transition. If $\Delta\phi/\phi$ is small, as is the case for low molecular weight nematogens, the resultant lowest order contribution to the isotropic dispersion energy, $-2\beta\phi^2(\Delta\phi/\phi)E$, does not significantly stabilize the ordered mesophase by comparison with $-\beta\phi^2 D_N S^2$ although the latter probably constitutes only a fraction (normally 10–25%) of the total attractive interaction energy.[10,22,23]

For most applications of the present analysis, we shall assume $(\bar{w}_{\|} - \bar{w}_{\perp})_{rt} = (\bar{w}_{\|} - \bar{w}_{\perp})_{tt} = 0$. However, if the anisotropic dispersion interaction contributions proportional to $2\Delta(\bar{w}_{\|} - \bar{w}_{\perp})_{rt}$ and $\Delta^2(\bar{w}_{\|} - \bar{w}_{\perp})_{tt}$ do not vanish, they will either tend to reinforce or disrupt intermolecular ordering between the converted flexible segments depending upon whether they are positive or negative. Odd–even variations in the order parameters, transition entropies, and transition enthalpies between different members of a homologous series of polymeric liquid crystals can in principle be incorporated into the present formulation by permitting alternating odd–even variations in the values of $2\Delta(\bar{w}_{\|} - \bar{w}_{\perp})_{rt} + \Delta^2(\bar{w}_{\|} - \bar{w}_{\perp})_{tt}$ depending upon whether $t$ is odd or even. Odd–even variations in the transition properties of low molecular weight nematogens have been generated in the self-consistent analysis of terminal-chain ordering developed by Marčelja.[14] Marčelja regards the anisotropic dispersion interaction between a given terminal chain in the mean field produced by all other molecules as the source of the odd–even phenomenon, and the present formulation is consistent with this viewpoint.

## III. Determination of the Thermodynamic Properties of Polymeric Liquid Crystals at the Nematic–Isotropic Transition

The total free energy densities in units of $kT$ from eq 2, 10, 11, and 23 for the nematic and isotropic phases, respectively, are

$$f_N(\phi_N,S,r,t) =$$
$$f_c(\phi_N,S,r,t) + f_{\|}(\phi_N,r_1,t_1) - \beta\phi_N^2 D_N S^2 - \beta\phi_N^2 E \quad (25a)$$

and

$$f_I(\phi_I,0,r,t) = f_c(\phi_I,S=0,r,t) + f_{\|}(\phi_I,r_1,t_1) - \beta\phi_I^2 E \quad (25b)$$

These free energy densities represent the point of departure for the statistical thermodynamic theory of polymeric liquid crystals to be developed here.

The order parameter, $S$, which minimizes the free energy density (eq 25a) satisfies

$$\partial f_N/\partial S = 0 =$$
$$\partial f_c/\partial S - 2\beta\phi_N^2 D_N S - \beta\phi_N^2 S^2(\partial D_N/\partial\Delta)(\partial\Delta/\partial S)$$

where $\Delta$, $\partial\Delta/\partial S$, and $D_N$ are given by eq 17, 18, and 24a, respectively, and explicitly using eq 10

$$\partial f_N/\partial S = 0 =$$
$$\ln\,[(1 + 2S)(1 - S)^{-1}[(1 - \lambda_N(1 + 2S))/(1 - \lambda_N(1 - S))]^{r_N}] - 3(r + t + 1)\beta\phi_N D_N S + (\partial\Delta(r + 1)/\partial S)[h(S,\phi)$$
$$- 3(r + 1)S^2(\lambda_N/r_N)\beta[(\bar{w}_{\|} - \bar{w}_{\perp})_{rt} + \Delta(\bar{w}_{\|} - \bar{w}_{\perp})_{tt}]] \quad (26)$$

where $h(S,\phi) \equiv [3\ln\,(c - 1) + 2(1 - S)\ln\,(1 - \lambda_N(1 - S)) + (1 + 2S)\ln\,(1 - \lambda_N(1 - 2S))]/2$. Since $\partial\Delta/\partial S = 0$ when

$S = 0$, $S = 0$ is always a solution and corresponds to the isotropic state where all orientations of the mesogenic groups are equally probable. When $r = 0$, $\lambda_N = 0$, $D_N = (t + 1)^{-2}\Delta^2(\bar{w}_\parallel - \bar{w}_\perp)_{tt}/3$, and $S = \Delta = \tau = 0$ is the only solution to eq 26. However, for $r > 0$, $S \neq 0$ solutions in the range $0 < S \leq 1$ are possible although only those which minimize $f_N$ and hence render $\partial^2 f_N/\partial S^2 > 0$ are physically acceptable.

The chemical potentials, $\mu_I$ and $\mu_N$, and the pressures, $P_I$ and $P_N$, of the isotropic and anisotropic polymer melts are evaluated respectively from $\beta\mu_k = L\partial f_k/\partial\phi_k$ and $\beta P_k = \beta\mu_k\phi_k/L - f_k = (\phi_k\partial/\partial\phi_k - 1)f_k$ ($k \equiv I, N$). If an isotropic–nematic transition occurs at $T_{NI} \equiv (\beta_{NI}k_B)^{-1}$, then the chemical potentials and pressures of the coexisting phases must be equal and

$$\beta_{NI}\mu_I/L = \partial f_I/\partial\phi_I = \partial f_N/\partial\phi_N = \beta_{NI}\mu_N/L \quad (27)$$

and

$$\beta_{NI}P_I = (\phi_I\partial/\partial\phi_I - 1)f_I = (\phi_N\partial/\partial\phi_N - 1)f_N = \beta_{NI}P_N \quad (28)$$

At constant pressure the transition is characterized by $\phi_I$, $\phi_N$, $S$, and $T_{NI}$ and their values depend on $M$, $r$, $t$, $D_N$, and $E$. In general, simultaneous solutions of eq 26–28 for a fixed pressure and preassigned values of $D_N$ and $E$ will suffice to determine $\phi_I$, $\phi_N$, $S$, and $T_{NI}$.[10]

The analysis of the transition can be simplified by introducing $\phi_N = \phi + \Delta\phi$, $\phi_I = \phi - \Delta\phi$, $\phi \equiv (\phi_N + \phi_I)/2$, and $\phi_N - \phi_I = 2\Delta\phi$ and then assuming $\Delta\phi/\phi \ll 1$. Insertion into eq 27 and 28 and expansion in powers of $\Delta\phi/\phi$ gives

$$\partial f_N/\partial\phi - \partial f_I/\partial\phi + (\Delta\phi/\phi)[\phi(\partial^2(f_N + f_I)/\partial\phi^2)] +$$
$$(\Delta\phi/\phi)^2\left[(\phi^2/2)\frac{\partial^3}{\partial\phi^3}(f_c(S) - f_c(0))\right] + \mathcal{O}(\Delta\phi/\phi)^3 = 0 \quad (29)$$

and

$$\phi^{-1}(f_N - f_I) + (\Delta\phi/\phi)^2[(\phi/2)(\partial^2 f_I/\partial\phi^2 - \partial^2 f_N/\partial\phi^2)] +$$
$$\mathcal{O}(\Delta\phi/\phi)^3 = 0 \quad (30)$$

The derivatives appearing in eq 29 and 30 are evaluated at $\phi = (\phi_N + \phi_I)/2$ and either at $S = 0$ or that value of $S > 0$ which satisfies eq 26 for the average volume fraction $\phi$ and the various dispersion interactions. Through first-order terms in $\Delta\phi/\phi$ at $T = T_{NI}$, eq 30 reduces to

$$\beta_{NI}\phi D_N S^2 = \phi^{-1}[f_c(\phi,S,r,t) - f_c(\phi,0,r,t)] \quad (31)$$

which is a result that is strictly valid when $\Delta\phi/\phi = 0$. Equation 31 describes the balance between the dispersion energy changes and the entropic changes which accompany nematic ordering of the mesogenic groups and the distortion of the chain configurations in the anisotropic melt.

Employing eq 31 to eliminate $3\beta_{NI}\phi D_N(r + t + 1)S$ in eq 26 when $\beta = \beta_{NI}$ and $\phi_N = \phi$ and then utilizing eq 11 and 12 to explicitly express $\phi^{-1}[f_c(\phi,S,r,t) - f_c(\phi,0,r,t)]$ give after some manipulation

$$(1 + S)\ln(1 + 2S) + (2 - S)\ln(1 - S) +$$
$$3r\lambda_I^{-1}(1 - \lambda_I)\ln(1 - \lambda_I) + 3\Delta(r + 1)[\ln(c - 1) - 1] -$$
$$r\lambda_I^{-1}(2 - 2\lambda_N + \lambda_N S)\ln(1 - \lambda_N(1 - S)) -$$
$$r\lambda_I^{-1}(1 - \lambda_N(1 + S))\ln(1 - \lambda_N(1 + 2S)) +$$
$$(\partial\Delta(r + 1)/\partial S)[3(r + 1)r^{-1}\lambda_I S^3\beta_{NI}[(\bar{w}_\parallel - \bar{w}_\perp)_{rt} + \Delta(\bar{w}_\parallel - \bar{w}_\perp)_{tt}] - Sh(S,\phi)] = 0 = -\partial f/\partial S \quad (32)$$

When $t = 0$, $\Delta(r + 1) = 0$, and $\lambda_N = \lambda_I$, eq 32 reduces to the theory formulated for rigid rod fluids (see eq 24 of ref 10). When $\phi$, $M$, $r$, $t$, $\beta_{NI}(\bar{w}_\parallel - \bar{w}_\perp)_{rt}$, and $\beta_{NI}(\bar{w}_\parallel - \bar{w}_\perp)_{tt}$ are specified, the order parameter at the nematic–isotropic transition is obtained from eq 32, and possible solutions

are discussed in detail in section IV.

The temperature dependence of $S$ for $T < T_{NI}$ at constant $\phi$ can be obtained from eq 26 after application of eq 32 to determine $S \equiv S_{NI}$ at $T_{NI}$: $T/T_{NI} = G(\phi,S_{NI},\Delta_{NI})/G(\phi,S,\Delta)$, where

$$G(\phi,S,\Delta) \equiv (3(r + t + 1)\phi D_N S)^{-1}[\ln[(1 + 2S) \times$$
$$(1 - S)^{-1}((1 - \lambda_N(1 + 2S))/(1 - \lambda_N(1 - S)))^{r_N}] +$$
$$h(S,\phi)(\partial\Delta(r + 1)/\partial S)]/(1 + Y(S)(\partial\Delta(r + 1)/\partial S)) \quad (33)$$

with $Y(S) \equiv (r + 1)S[(\bar{w}_\parallel - \bar{w}_\perp)_{rt} + \Delta(\bar{w}_\parallel - \bar{w}_\perp)_{tt}]/(3(r + t + 1)^2 D_N)$ and where $\Delta$ is related to $S$ through eq 17. This result indicates that $S$ is an implicit universal function of $T/T_{NI}$, $\phi$, $r$, $t$, and $M$. When $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$, eq 33 simplifies to $T/T_{NI} = G^*(\phi,S_{NI},\Delta_{NI})/G^*(\phi,S,\Delta)$, where $G^*(\phi,S,\Delta) \equiv S^{-1}[\ln[(1 + 2S)(1 - S)^{-1}((1 - \lambda_N(1 + 2S))/(1 - \lambda_N(1 - S)))^{r_N}] + h\partial\Delta(r + 1)/\partial S]$.

The Helmholtz free energy, entropy, and enthalpy (neglecting $P$–$V$ expansion) changes at the nematic–isotropic transition are respectively

$$\beta_{NI}\Delta F_{NI}/MN = (r + t + 1)\phi^{-1}[f_I(\phi) - f_N(\phi)] -$$
$$(\Delta\phi/\phi)(r + t + 1)(\partial/\partial\phi)[f_c(\phi,S=0) + f_c(\phi,S) +$$
$$2f_\parallel(\phi) + \beta_{NI}D_N\phi^2 S^2] + \mathcal{O}(\Delta\phi/\phi)^2 \quad (34)$$

$$\Delta S_{NI}/MNk_B = -\partial(\Delta F_{NI}/MNk_B)/\partial T_{NI} =$$
$$(r + t + 1)\phi^{-1}[f_c(\phi,S) - f_c(\phi,0)] + (\Delta\phi/\phi)(r + t + 1)[\partial(f_c(\phi,0) + f_c(\phi,S) + 2f_\parallel(\phi))/\partial\phi] + \mathcal{O}(\Delta\phi/\phi)^2 \quad (35)$$

and since at $T = T_{NI}$, $\Delta F_{NI} = 0$ and $\beta_{NI}\Delta H_{NI}/MN = \Delta S_{NI}/MNk_B$

$$\beta_{NI}\Delta H_{NI}/MN = (r + t + 1)\beta_{NI}\phi D_N S^2 -$$
$$(\Delta\phi/\phi)(2\beta_{NI}\phi D_N S^2(r + t + 1)) + \mathcal{O}(\Delta\phi/\phi)^2 \quad (36)$$

The transition entropy can be explicitly expressed by eq 10, 11, and 32 to lowest order in $\Delta\phi/\phi$ as

$$\Delta S_{NI}/MNk_B = (S/3)\ln[(1 + 2S)(1 - S)^{-1}((1 - \lambda_N(1 + 2S))/(1 - \lambda_N(1 - S)))^{r_N}] + ((r + 1)\partial\Delta/\partial S)[Sh(S,\phi)/3 - \beta_{NI}\lambda_I r^{-1}S^3(r + 1)((\bar{w}_\parallel - \bar{w}_\perp)_{rt} + \Delta(\bar{w}_\parallel - \bar{w}_\perp)_{tt})] \quad (37)$$

where $\Delta$ and $\partial\Delta/\partial S$ are given by eq 17 and 18, respectively. Clearly, $\Delta S_{NI}/MNk_B$ depends on $r$, $t$, $M$, $\phi$, and the order parameter $S$ which satisfies eq 32 for $T = T_{NI}$. The temperature dependence of $S$ does not contribute to $\Delta S_{NI}$ since that involves a contribution proportional to $(\partial f_N/\partial S)(\partial S/\partial T)$, which vanishes for the order parameter $S = S_{NI}$ which renders $f_N$ a minimum. The dependence of $\Delta S_{NI}/MNk_B$ on $M$ appears through the length–tension relationship given by eq 14 and the assumed functional dependence of $\Delta$ on $\tau$ (see eq 17).

The ratio of the nematic–isotropic transition temperatures, $T_{NI}(2)/T_{NI}(1)$, for two different polymeric liquid crystals can be determined from eq 31:

$$T_{NI}(2)/T_{NI}(1) = \phi_2(r_2 + t_2 + 1)D_{N_2}S_2^2\Delta S_{NI}(1)/\phi_1(r_1 + t_1 + 1)D_{N_1}S_1^2\Delta S_{NI}(2) \quad (38)$$

If $r_1 = r_2$, $\rho_1 M_1 \equiv \phi_1(r_1 + t_1 + 1)^{-1} \simeq \phi_2(r_2 + t_2 + 1)^{-1} \equiv \rho_2 M_2$, $S_1 \sim S_2$, $t_2 > t_1$, $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$, and $\Delta S_{NI}(2) > \Delta S_{NI}(1)$, eq 38 predicts that $T_{NI}(2) < T_{NI}(1)$, which is consistent with the experimental results obtained by BT and KWI for homologous series of linear, main-chain mesogenic polymers.

The fractional change in the volume fraction occurring at the transition may be estimated from eq 29:

$$\Delta\phi/\phi = (\partial(f_I - f_N)/\partial\phi)[\phi\partial^2(f_I + f_N)/\partial\phi^2]^{-1} \quad (39)$$

provided $\Delta\phi/\phi \ll 1$. The derivatives are evaluated at $\phi = (\phi_I + \phi_N)/2$, and the value of $S$ is determined from eq 32 employing the same value of $\phi$. The hypothetical ref-

**Table I**
**Minimum Integral Value of $M$, $M_c$, Required for the Appearance of a Highly Anisotropic Phase as a Function of $t$ for the Values of $(r, 0)$ Specified and $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0^a$**

| $t$ | (3, 1) | (3, 0.8) | (3, 0.6) | (4, 0.8) |
|-----|--------|----------|----------|----------|
| 1   |        |          |          |          |
| 2   | 28     | 59       |          | 42       |
| 3   | 32     | 48       | 59       | 39       |
| 4   | 38     | 52       | 60       | 42       |
| 5   | 45     | 58       | 65       | 47       |
| 6   | 52     | 65       | 72       | 52       |
| 8   | 66     | 80       | 87       | 64       |
| 10  | 82     | 96       | 104      | 77       |
| 12  | 98     | 113      | 121      | 90       |
| 16  | 131    | 149      | 158      | 117      |

$^a$ The blank entries indicate nonexistence of a highly anisotropic mesophase.

erence state free energy $f_\parallel(\phi)$ is required to evaluate $\Delta\phi/\phi$ from eq 39.

The dependences of $S$, $\Delta S_{NI}/MNk_B$, and $d$ on $M$ are investigated in the following section.

## IV. Results and Discussion

Here we employ eq 32 to determine the average core order parameter $S$ of polymeric liquid crystalline melts as a function of $r$, $t$ (i.e., monomeric structure), $M$, $\phi$, and the anisotropic dispersion interaction energies $(\bar{w}_\parallel - \bar{w}_\perp)_{rt}$ and $(\bar{w}_\parallel - \bar{w}_\perp)_{tt}$. In order to simplify the calculations, we have replaced the Langevin function, $\mathcal{L}(\beta\tau b)$, in the length–tension relationship (eq 14) by its asymptotic approximation $1 - (\beta\tau b)^{-1}$, which requires that $\beta\tau b > 1$. Equation 14 then simplifies to $\beta\tau b = (1 - d(S,M))^{-1}$ in this approximation. Under certain conditions two different anisotropic solutions ($S \neq 0$, $S > 0$) satisfy eq 32 and correspond to free energy minima. When two anisotropic solutions are possible there actually exists a third solution with an intermediate value of $S$, which is discarded since it corresponds to a free energy maximum. Following VKS we designate the anisotropic mesophases with the smaller and larger values of $S$ as weakly and highly anisotropic, respectively.

The appearance of a highly anisotropic phase for a fixed monomeric composition (i.e., $r$ and $t$) and $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$ depends on $\phi$ and $M$. This constitutes an important departure between the present analysis and the VKS analysis, which assumes $\phi = 1$ and does not generate $M$-dependent statistical thermodynamics for the anisotropic mesophases. The highly anisotropic mesophase predicted in both analyses is characterized by $S \approx 1$ and nearly complete conversion of the originally flexible spacer segments in each monomer unit in the isotropic phase to rigid bond segments aligned along the preferred direction. There exists a minimum (integral) value of $M$, $M_c$, which depends on $r$, $t$, $\phi$, and the anisotropic dispersion energies below which the highly anisotropic mesophase disappears. Some examples of $M_c$ values are listed in Table I for various selections of $r$, $t$, and $\phi$ with $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$. For any given $r$ and $t$, the lowest possible of $M_c$ occurs when $\phi = 1$.

The present analysis predicts important differences in the configurational behavior of the individual polymer molecules in the weakly and highly anisotropic mesophases. For instance, the relative increase in converted flexible to rigid bond segments per monomer as measured by $\Delta(r + 1)/(2t/3)$ ranges approximately between 0.1 and 0.5 when $t \leq 10$ for the weakly anisotropic phase and approaches unity for the highly anisotropic phase. Furthermore, since $S \simeq 1$ in the highly anisotropic mesophase,

this implies almost complete alignment and extension of the polymer molecules along the preferred direction. The relative average chain extension, $d = l/Mb$, is determined from eq 14, and it varies between 0.05 and 0.45 for the weakly anisotropic mesophase while $d = 1 - 3M^{-1}$ for sufficiently large $M$ in the highly anisotropic mesophase, which essentially corresponds to full extension.

Core order parameters with the corresponding values for $d$ and $\Delta(r + 1)$ obtained from utilizing eq 14 and 17, respectively, in eq 32 for various selections of $r$, $t$, $\phi$, and $M$ with $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$ appear in Tables II and III. Also included are the transition entropies per mole of monomer repeat units calculated from eq 35. The segment volume fraction averaged order parameter defined by $S^* = [S(r + 1)(1 + \Delta) + St/3]/(r + t + 1)$ is also recorded for the weakly anisotropic entries. This order parameter is probably more meaningful for comparison with experimentally determined order parameters.[1,4,24,25]

Table II exhibits the dependence of $S$, $\Delta(r + 1)$, $S^*$, $d$, $\Delta S_{NI}$, and the ratio of transition temperatures, $T_{NI}(M)/T_{NI}(2) = (S(M)/S(2))^2[\Delta S_{NI}(2)/\Delta S_{NI}(M)]$, determined from eq 38 for constant $r$, $t$, $\phi$, and $D_N$ on $M$ for the following sets $(r, t, \phi)$: (4, 4, 0.8), (4, 5, 0.8), and (6, 3, 0.6). Both $S$ and $\Delta S_{NI}$ show shallow minima for $M \simeq 15$ and $M \simeq 40$ ($M \simeq 100$) respectively for the polymers composed of $r = 4$ ($r = 6$) monomers. As $M$ increases, both $S$ and $\Delta S_{NI}$ monotonically increase for both anisotropic phases. The predicted order parameters and transition entropies are considerably larger than those customarily observed for low molecular weight nematogens where typically $S \simeq 0.4$ and $\Delta S_{NI} \sim 1$–3 J K$^{-1}$ mol$^{-1}$, and this is consistent with the experimental observations.[2-4] For $2 \leq M \leq 5$, the predicted values of $S$ and $\Delta S_{NI}$ are also significantly larger than those observed for monomeric liquid crystals at the nematic–isotropic transition, and this is consistent with the observations of Sigaud, Yoon, and Griffin[4] on dimers of the mesogenic monomer $C_5H_{11}OC_6H_4COOC_6H_4OC_5H_{11}$. The present analysis is not applicable for $M = 1$ unless $\tau = 0$ since the tension–length relationship (eq 14) correlates the projected lengths of successive monomers along the preferred direction as one proceeds along a chain of connected monomers.

When $r = 4$ and $\phi = 0.8$ ($r = 6$ and $\phi = 0.6$), the ratio $T_{NI}(M)/T_{NI}(2)$ passes through a minimum at $M = 10$ and then monotonically increases with $M$, and eventually at $M \simeq 100$ ($M \simeq 150$) $T_{NI}(M)/T_{NI}(2) \geq 1$. Hence for $M \geq 10$ the transition temperature is predicted to increase with $M$, which is in agreement with the observations of Blumstein et al.[26] However, for the dimer and the corresponding mesogenic polymer studied by Sigaud et al.,[4] $T_{NI}(2)$ is smaller than $T_{NI}(M)$, contrary to our prediction unless $M \geq 100$. This disagreement may reflect the failure of the assumption of constant $\phi$ at the transitions of both the dimer and polymer. For example, if $\phi = 0.6$ when $r = 4$, $t = 5$, and $M = 2$, then $S = 0.967$, $\Delta S_{NI} = 13.9$ J/(K mru) and $T_{NI}(10) = 1.1T_{NI}(2)$, $T_{NI}(25) = 1.2T_{NI}(2)$, and $T_{NI}(100) = 1.5T_{NI}(2)$ if the same results for the $M$-mers given in Table II are employed.

Table III lists results for $S$, $S^*$, $d$, and $\Delta S_{NI}$ calculated for the weakly anisotropic transition of mesogenic polymers with variable $r$ and fixed $t$ ($t = 5$), $M = 100$, $\phi = 0.8$, and $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$. The order parameters $S$ and $S^*$ increase monotonically with $r$ while the transition entropies decrease monotonically for $r \geq 3$ and become negative (thus passing through zero) when $10 \leq r \leq 11$. These results illustrate that application of eq 31 can become suspect when $r$ becomes too large for a given $t$ and $\phi$ and that the change in density accompanying the tran-

**Table II**
**Calculated Values of $S$, $\Delta(r + 1)$, $S^*$, $d$, $\Delta S_{NI}$, and $T_{NI}(M)/T_{NI}(2)$ as a Function of $M$ When $(\bar{w}_{\parallel} - \bar{w}_{\perp})_{rt} = (\bar{w}_{\parallel} - \bar{w}_{\perp})_{tt} = 0$ for the Specified Values of $(r, t, \phi)^a$**

$(r = 4, t = 4, \phi = 0.8)$

| $M$ | $S$ | $\Delta(r + 1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $T_{NI}(M)/T_{NI}(2)$ |
|---|---|---|---|---|---|---|
| 2 | 0.972 | 0.704 | 0.760 | 0.261 | 10.48 | 1.00 |
| 3 | 0.965 | 0.800 | 0.765 | 0.351 | 11.27 | 0.92 |
| 4 | 0.948 | 0.871 | 0.759 | 0.414 | 11.73 | 0.85 |
| 5 | 0.912 | 0.884 | 0.732 | 0.444 | 11.64 | 0.79 |
| 6 | 0.866 | 0.842 | 0.690 | 0.445 | 11.03 | 0.76 |
| 8 | 0.797 | 0.745 | 0.627 | 0.423 | 9.84 | 0.72 |
| 10 | 0.761 | 0.684 | 0.593 | 0.400 | 9.12 | 0.71 |
| 25 | 0.744 | 0.565 | 0.570 | 0.293 | 7.83 | 0.79 |
| 42 | 0.777 | 0.543 | 0.594 | 0.235 | 7.72 | 0.87 |
| 42 | 0.999 | 2.662 | 0.999 | 0.926 | 25.62 | 0.43 |
| 50 | 0.790 | 0.539 | 0.603 | 0.217 | 7.73 | 0.90 |
| 50 | 1.000 | 2.666 | 1.000 | 0.940 | 25.65 | 0.43 |
| 100 | 0.839 | 0.530 | 0.640 | 0.156 | 7.85 | 1.00 |
| 100 | 1.000 | 2.666 | 1.000 | 0.970 | 25.66 | 0.43 |
| 500 | 0.915 | 0.520 | 0.697 | 0.065 | 8.22 | 1.13 |
| 500 | 1.000 | 2.666 | 1.000 | 0.993 | 25.66 | 0.43 |

$(r = 4, t = 5, \phi = 0.8)$

| $M$ | $S$ | $\Delta(r + 1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $T_{NI}(M)/T_{NI}(2)$ |
|---|---|---|---|---|---|---|
| 2 | 0.975 | 0.793 | 0.727 | 0.262 | 12.23 | 1.00 |
| 3 | 0.966 | 0.899 | 0.731 | 0.351 | 13.13 | 0.92 |
| 5 | 0.901 | 0.966 | 0.688 | 0.435 | 13.23 | 0.79 |
| 10 | 0.751 | 0.744 | 0.557 | 0.390 | 10.27 | 0.71 |
| 25 | 0.739 | 0.623 | 0.538 | 0.287 | 8.92 | 0.79 |
| 47 | 0.781 | 0.599 | 0.568 | 0.219 | 8.85 | 0.89 |
| 47 | 1.000 | 3.328 | 0.999 | 0.935 | 32.53 | 0.39 |
| 75 | 0.817 | 0.593 | 0.593 | 0.176 | 8.96 | 0.96 |
| 75 | 1.000 | 3.333 | 1.000 | 0.960 | 32.58 | 0.39 |
| 100 | 0.837 | 0.590 | 0.608 | 0.153 | 9.05 | 1.00 |
| 100 | 1.000 | 3.333 | 1.000 | 0.970 | 32.52 | 0.40 |

$(r = 6, t = 3, \phi = 0.6)$

| $M$ | $S$ | $\Delta(r + 1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $T_{NI}(M)/T_{NI}(2)$ |
|---|---|---|---|---|---|---|
| 2 | 0.969 | 0.667 | 0.839 | 0.260 | 7.84 | 1.00 |
| 3 | 0.961 | 0.753 | 0.841 | 0.349 | 8.59 | 0.90 |
| 4 | 0.934 | 0.815 | 0.832 | 0.411 | 9.10 | 0.82 |
| 5 | 0.910 | 0.828 | 0.803 | 0.442 | 9.15 | 0.76 |
| 6 | 0.868 | 0.796 | 0.763 | 0.446 | 8.82 | 0.71 |
| 8 | 0.802 | 0.712 | 0.698 | 0.428 | 8.00 | 0.67 |
| 10 | 0.766 | 0.655 | 0.663 | 0.405 | 7.44 | 0.66 |
| 15 | 0.737 | 0.585 | 0.633 | 0.358 | 6.73 | 0.68 |
| 25 | 0.746 | 0.539 | 0.637 | 0.295 | 6.23 | 0.75 |
| 38 | 0.770 | 0.521 | 0.656 | 0.246 | 6.03 | 0.82 |
| 38 | 0.999 | 1.996 | 0.999 | 0.915 | 19.57 | 0.43 |
| 50 | 0.790 | 0.514 | 0.673 | 0.217 | 5.96 | 0.88 |
| 50 | 1.000 | 1.999 | 1.000 | 0.938 | 19.61 | 0.43 |
| 100 | 0.839 | 0.505 | 0.714 | 0.155 | 5.89 | 1.00 |
| 100 | 1.000 | 2.000 | 1.000 | 0.966 | 19.61 | 0.43 |
| 500 | 0.914 | 0.495 | 0.777 | 0.064 | 5.94 | 1.18 |

$^a$ When $M \geq M_c$ calculated results appear for both the weakly and highly anisotropic mesophases. $M_c = 42$, 47, and 38 for (4, 4, 0.8), (4, 5, 0.8) and (6, 3, 0.6), respectively. The $\Delta S_{NI}$ values are given in joule kelvins$^{-1}$ per mole of repeat units (J/(K mru)).

**Table III**
**Dependence of $S$, $\Delta(r + 1)$, $S^*$, $d$, and $\Delta S_{NI}$ (J/(K mru)) as a Function of $r$ for ($t = 5$, $\phi = 0.8$, $M = 100$) and as a Function of $\phi$ for ($r = 10$, $t = 1$, $M = 100$) When $(\bar{w}_{\parallel} - \bar{w}_{\perp})_{rt} = (\bar{w}_{\parallel} - \bar{w}_{\perp})_{tt} = 0^a$**

$(t = 5, \phi = 0.8, M = 100)$

| $r$ | $S$ | $\Delta(r + 1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ |
|---|---|---|---|---|---|
| 2 | 0.821 | 0.420 | 0.522 | 0.137 | 9.53 |
| 3 | 0.830 | 0.512 | 0.570 | 0.146 | 9.54 |
| 4 | 0.837 | 0.590 | 0.608 | 0.153 | 9.05 |
| 5 | 0.844 | 0.658 | 0.638 | 0.161 | 8.18 |
| 6 | 0.850 | 0.717 | 0.664 | 0.168 | 7.01 |
| 8 | 0.860 | 0.817 | 0.706 | 0.183 | 3.98 |
| 10 | 0.870 | 0.902 | 0.738 | 0.197 | 0.25 |
| 11 | 0.874 | 0.940 | 0.751 | 0.205 | −1.83 |
| 12 | 0.878 | 0.976 | 0.763 | 0.212 | −4.02 |
| 25 | 0.919 | 1.36 | 0.860 | 0.315 | −39.5 |
| 50 | 0.967 | 2.32 | 0.950 | 0.578 | −127. |

$(r = 10, t = 1, M = 100)$

| $\phi$ | $S$ | $\Delta(r + 1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ |
|---|---|---|---|---|---|
| 0.1 | 0.793 | 0.199 | 0.763 | 0.115 | 6.06 |
| 0.2 | 0.799 | 0.202 | 0.768 | 0.119 | 4.38 |
| 0.3 | 0.807 | 0.205 | 0.776 | 0.125 | 2.52 |
| 0.4 | 0.818 | 0.210 | 0.787 | 0.135 | 0.40 |
| 0.5 | 0.834 | 0.218 | 0.802 | 0.150 | −2.07 |
| 0.8 | 0.854 | 0.230 | 0.823 | 0.174 | −5.10 |

$^a$ For $10 < r < 11$ and $\phi = 0.8$ and $0.4 < \phi < 0.5$ for $r = 10$, $\Delta S_{NI}$ passes through 0 and eq 31 is no longer a viable approximation.

Hence the assumption that $\Delta\phi/\phi = 0$ and the application of eq 31 should be completely acceptable for these systems.

Table IV lists the variation of $S$, $d$, and $\Delta S_{NI}$ as a function of $t$ for mesogenic polymers with $r$, $M$, and either $\phi$ or $\lambda_I$ fixed when $(\bar{w}_{\parallel} - \bar{w}_{\perp})_{rt} \geq 0$ and $(\bar{w}_{\parallel} - \bar{w}_{\perp})_{tt} = 0$. These calculated results represent an endeavor for a theoretical description and simulation of the statistical thermodynamics of homologous series of main-chain mesogenic polymers. For the case where $r = 3$, $M = 100$, $\phi = 0.6$, and $(\bar{w}_{\parallel} - \bar{w}_{\perp})_{rt} = (\bar{w}_{\parallel} - \bar{w}_{\perp})_{tt} = 0$, $S$ remains nearly constant as $t$ varies while $\Delta S_{NI}$ increases monotonically with $t$. For both weakly and highly anisotropic mesophases the predicted results for $S$ and $\Delta S_{NI}$ are considerably larger than that observed for low molecular weight nematogens, which is consistent with experiment.[2,3]

The ratio of the transition temperatures of two different members of a homologous series is obtained from eq 38. When $\phi$ is the same and $(\bar{w}_{\parallel} - \bar{w}_{\perp})_{rt} = (\bar{w}_{\parallel} - \bar{w}_{\perp})_{tt} = 0$ for the pair

$$T_{NI}(2)/T_{NI}(1) = (1 + x_1)S_2^2 \Delta S_{NI}(1)/(1 + x_2)S_1^2 \Delta S_{NI}(2)$$

Also the ratio of the enthalpies of transition is $\Delta H_{NI}(2)/\Delta H_{NI}(1) = (1 + x_1)S_2^2/(1 + x_2)S_1^2$. When $t_2 > t_1$, $x_2 > x_1$, and $\Delta S_{NI}(2) > \Delta S_{NI}(1)$, $T_{NI}(2)/T_{NI}(1) < 1$, and the corresponding calculated values are given in Table IV. The trend of decreasing $T_{NI}$ for the higher homologues when compared with $T_{NI}(1)$, the transition temperature for the $t = 1$ homologue, is consistent with the experimental results of BT and KWI.

Additional calculations of $S$, $d$, and $\Delta S_{NI}$ appear in Table IV for the weakly anisotropic mesophases of hypothetical homologous series of mesogenic homopolymers whose members have identical $r$, $M$, and $\lambda_I \equiv \phi r/3(r + t + 1)$ rather than $\phi$ values. For these series $\phi$, $S$, and $\Delta S_{NI}$ increase monotonically with $t$ and $(\bar{w}_{\parallel} - \bar{w}_{\perp})_{rt}$ and/or $(\bar{w}_{\parallel} - \bar{w}_{\perp})_{tt}$ (for a given value of $t$). The monotonic increase of $\Delta S_{NI}$ with $t$ is consistent with the monotonic increase observed for the odd- and even-membered homologues respectively of the mesogenic polyesters investigated by BT and KWI.

sition must be considered. Indeed when $\Delta S_{NI} < 0$ and $(\bar{w}_{\parallel} - \bar{w}_{\perp})_{rr} > 0$ (the physically reasonable choice), eq 31 implies that $T_{NI} < 0$, which is physically untenable. Also included in Table III are calculated values of $S$ and $\Delta S_{NI}$ for $r = 10$, $t = 1$, $M = 100$, and $(\bar{w}_{\parallel} - \bar{w}_{\perp})_{rt} = (\bar{w}_{\parallel} - \bar{w}_{\perp})_{tt} = 0$ as a function of $\phi$ which reveal a monotonic increase in $S$ and decrease in $\Delta S_{NI}$ as $\phi$ increases. When $0.4 < \phi < 0.5$, $\Delta S_{NI}$ proceeds from positive to negative values, again indicating that eq 31 must be supplemented to include the density change at the transition. For the mesogenic polymers of primary interest here, $r \leq 6$, $1 \leq t \leq 10$, and $\Delta S_{NI} > 0$ for typical polymer melt (i.e., liquid) densities where $\phi > 0.5$.

## Table IV
**Calculated Values of $S$, $\Delta(r+1)$, $S^*$, $d$, $\Delta S_{NI}$ (J/(K mru)), and $T_{NI}(t)/T_{NI}(1)$ for the Weakly Anisotropic Mesophase Unless Otherwise Indicated as a Function of $t$ for the Hypothetical Homologous Series with the Indicated Values of $r$, $\phi$ or $\lambda_I$, and $(\bar{w}_\| - \bar{w}_\perp)_{rt}$ and with $M = 100$ and $(\bar{w}_\| - \bar{w}_\perp)_{tt} = 0^a$**

$(r = 3, \phi = 0.6, M = 100)$ $(\bar{w}_\| - \bar{w}_\perp)_{rt} = (\bar{w}_\| - \bar{w}_\perp)_{tt} = 0$

| $t$ | $S$ | $\Delta(r+1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $T_{NI}(t)/T_{NI}(1)$ | $t$ | $S$ | $\Delta(r+1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $T_{NI}(t)/T_{NI}(1)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Weakly Anisotropic Mesophase | | | | | | | Highly Anisotropic Mesophase[b] | | | | |
| 1 | 0.808 | 0.179 | 0.729 | 0.126 | 4.78 | 1.00 | 3 | 0.999 | 1.999 | 0.999 | 0.965 | 26.43 | 1.00 |
| 2 | 0.820 | 0.306 | 0.680 | 0.137 | 6.83 | 0.60 | 4 | 1.000 | 2.666 | 1.000 | 0.969 | 33.93 | 0.68 |
| 3 | 0.823 | 0.393 | 0.634 | 0.139 | 8.26 | 0.43 | 5 | 1.000 | 3.333 | 1.000 | 0.970 | 41.44 | 0.50 |
| 4 | 0.823 | 0.457 | 0.596 | 0.139 | 9.34 | 0.33 | 6 | 1.000 | 4.000 | 1.000 | 0.970 | 49.00 | 0.38 |
| 5 | 0.823 | 0.505 | 0.565 | 0.139 | 10.17 | 0.27 | 7 | 1.000 | 4.666 | 1.000 | 0.970 | 56.25 | 0.30 |
| 6 | 0.823 | 0.542 | 0.539 | 0.139 | 10.84 | 0.23 | 8 | 1.000 | 5.333 | 1.000 | 0.970 | 64.95 | 0.24 |
| 8 | 0.823 | 0.598 | 0.498 | 0.139 | 11.83 | 0.18 | 9 | 1.000 | 5.999 | 1.000 | 0.970 | 71.91 | 0.20 |
| 10 | 0.823 | 0.635 | 0.468 | 0.139 | 12.54 | 0.14 | | | | | | | |
| 12 | 0.822 | 0.664 | 0.445 | 0.139 | 13.07 | 0.12 | | | | | | | |
| 20 | 0.822 | 0.727 | 0.390 | 0.138 | 14.30 | 0.07 | | | | | | | |

$(r = 3, \lambda_I = 0.1, M = 100)$ $(\bar{w}_\| - \bar{w}_\perp)_{rt} = (\bar{w}_\| - \bar{w}_\perp)_{tt} = 0$

| $t$ | $\phi$ | $S$ | $\Delta(r+1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $T_{NI}(t)/T_{NI}(1)$ | $t$ | $\phi$ | $S$ | $\Delta(r+1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $T_{NI}(t)/T_{NI}(1)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.5 | 0.801 | 0.177 | 0.723 | 0.121 | 5.24 | 1.00 | 4 | 0.8 | 0.831 | 0.465 | 0.602 | 0.147 | 8.63 | 0.65 |
| 2 | 0.6 | 0.820 | 0.306 | 0.680 | 0.137 | 6.83 | 0.81 | 5 | 0.9 | 0.833 | 0.517 | 0.573 | 0.149 | 9.20 | 0.62 |
| 3 | 0.7 | 0.827 | 0.397 | 0.638 | 0.143 | 7.87 | 0.71 | 6 | 1.0 | 0.835 | 0.558 | 0.548 | 0.151 | 9.65 | 0.59 |

$(r = 3, \lambda_I = 0.1, M = 100)$ $(\bar{w}_\| - \bar{w}_\perp)_{rt} = 2.24RT_{NI}(1)$; $(\bar{w}_\| - \bar{w}_\perp)_{tt} = 0$

| $t$ | $\phi$ | $S$ | $\Delta(r+1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $(\bar{w}_\| - \bar{w}_\perp)/RT_{NI}(t)$ | $t$ | $\phi$ | $S$ | $\Delta(r+1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $(\bar{w}_\| - \bar{w}_\perp)/RT_{NI}(t)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.5 | 0.844 | 0.196 | 0.765 | 0.162 | 5.98 | 2.24 | 4 | 0.8 | 0.912 | 0.620 | 0.679 | 0.292 | 11.90 | 3.43 |
| 2 | 0.6 | 0.879 | 0.361 | 0.737 | 0.214 | 8.32 | 2.78 | 5 | 0.9 | 0.924 | 0.741 | 0.658 | 0.334 | 13.61 | 3.64 |
| 3 | 0.7 | 0.898 | 0.498 | 0.705 | 0.254 | 10.20 | 3.16 | 6 | 1.0 | 0.938 | 0.887 | 0.646 | 0.391 | 15.71 | 3.80 |

Simulated Odd–Even Variations in $S^*$ and $S$ When $(\bar{w}_\| - \bar{w}_\perp)_{rt} = 0$ for $t = 1, 3,$ and 5 and $(\bar{w}_\| - \bar{w}_\perp)_{rt} = 2.24RT_{NI}(1)$ for $t = 2, 4,$ and 6 with the Transition Temperature Ratios $T_{NI}(t)/T_{NI}(1)$ for Even $t$ Assumed To Be Equal to Those Calculated for $(\bar{w}_\| - \bar{w}_\perp)_{rt} = (\bar{w}_\| - \bar{w}_\perp)_{tt} = 0$

| $t$ | $S^*$ | $\Delta S_{NI}$ | $d$ | $t$ | $S^*$ | $\Delta S_{NI}$ | $d$ |
|---|---|---|---|---|---|---|---|
| 1 | 0.723 | 5.24 | 0.121 | 4 | 0.679 | 11.90 | 0.292 |
| 2 | 0.737 | 8.32 | 0.214 | 5 | 0.572 | 9.20 | 0.149 |
| 3 | 0.638 | 7.87 | 0.143 | 6 | 0.646 | 15.71 | 0.391 |

$(r = 3, \lambda_I = 0.083, M = 100)$ $(\bar{w}_\| - \bar{w}_\perp)_{rt} = (\bar{w}_\| - \bar{w}_\perp)_{tt} = 0$

| $t$ | $\phi$ | $S$ | $\Delta(r+1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $T_{NI}(t)/T_{NI}(1)$ | $t$ | $\phi$ | $S$ | $\Delta(r+1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $T_{NI}(t)/T_{NI}(1)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.417 | 0.797 | 0.175 | 0.718 | 0.117 | 5.60 | 1.00 | 5 | 0.750 | 0.828 | 0.510 | 0.568 | 0.144 | 9.70 | 0.62 |
| 2 | 0.500 | 0.816 | 0.303 | 0.676 | 0.132 | 7.24 | 0.81 | 6 | 0.833 | 0.829 | 0.551 | 0.543 | 0.146 | 10.17 | 0.60 |
| 3 | 0.583 | 0.822 | 0.393 | 0.634 | 0.138 | 8.33 | 0.72 | 7 | 0.917 | 0.831 | 0.583 | 0.522 | 0.147 | 10.54 | 0.58 |
| 4 | 0.667 | 0.826 | 0.459 | 0.598 | 0.142 | 9.11 | 0.66 | 8 | 1.000 | 0.832 | 0.610 | 0.504 | 0.148 | 10.85 | 0.56 |

$(r = 3, \lambda_I = 0.083, M = 100)$ $(\bar{w}_\| - \bar{w}_\perp) = 3.00RT_{NI}(1)$; $(\bar{w}_\| - \bar{w}_\perp)_{tt} = 0$

| $t$ | $\phi$ | $S$ | $\Delta(r+1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $(\bar{w}_\| - \bar{w}_\perp)_{rt}/RT_{NI}(t)$ | $t$ | $\phi$ | $S$ | $\Delta(r+1)$ | $S^*$ | $d$ | $\Delta S_{NI}$ | $(\bar{w}_\| - \bar{w}_\perp)_{rt}/RT_{NI}(t)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.417 | 0.844 | 0.196 | 0.765 | 0.162 | 6.46 | 3.00 | 5 | 0.75 | 0.925 | 0.747 | 0.659 | 0.339 | 14.76 | 4.81 |
| 2 | 0.500 | 0.880 | 0.362 | 0.737 | 0.215 | 8.97 | 3.70 | 6 | 0.833 | 0.939 | 0.896 | 0.647 | 0.396 | 17.08 | 5.03 |
| 3 | 0.583 | 0.898 | 0.499 | 0.706 | 0.255 | 11.00 | 4.19 | 7 | 0.917 | | | | | | 5.19 |
| 4 | 0.667 | 0.913 | 0.623 | 0.680 | 0.295 | 12.86 | 4.55 | 8 | 1.000 | | | | | | 5.34 |

Simulated Odd–Even Variations in $S^*$, $S$, and $d$ When $(\bar{w}_\| - \bar{w}_\perp)_{rt} = 0$ for $t = 1, 3, 5,$ and 7 and $(\bar{w}_\| - \bar{w}_\perp)_{rt} = 3.00RT_{NI}(1)$ for $t = 2, 4, 6,$ and 8 with the Transition Temperature Ratios $T_{NI}(t)/T_{NI}(1)$ for Even $t$ Assumed To Be Equal to Those Calculated for $(\bar{w}_\| - \bar{w}_\perp)_{rt} = (\bar{w}_\| - \bar{w}_\perp)_{tt} = 0$

| $t$ | $S^*$ | $\Delta S_{NI}$ | $d$ | $t$ | $S^*$ | $\Delta S_{NI}$ | $d$ | $t$ | $S^*$ | $\Delta S_{NI}$ | $d$ | $t$ | $S^*$ | $\Delta S_{NI}$ | $d$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.718 | 5.60 | 0.117 | 5 | 0.568 | 9.70 | 0.144 | 3 | 0.634 | 8.33 | 0.138 | 7 | 0.522 | 10.54 | 0.147 |
| 2 | 0.737 | 8.97 | 0.215 | 6 | 0.647 | 17.08 | 0.396 | 4 | 0.680 | 12.86 | 0.295 | 8 | | | |

$^a$ When $r = 3$, $\lambda_I = 0.083$, and $(\bar{w}_\| - \bar{w}_\perp)_{rt} = 3.00RT_{NI}(1)$, the weakly anisotropic mesophase vanishes when $t = 7$ and 8 as indicated by the blank entries. Such mesophase disappearance occurs whenever $t$, $\phi$, and $(\bar{w}_\| - \bar{w}_\perp)_{rt}/T_{NI}(t)$ become too large. $^b$ The highly anisotropic mesophase appears for (integral) values of $t$ between 3 and 9 only.

The ratio of the transition temperatures of two different members of a series with $r$ and $\lambda_I$ fixed becomes from eq 38

$T_{NI}(2)/T_{NI}(1) =$
$(1 + x_2)^2 D_{N_2} S_2^2 \Delta S_{NI}(1)/(1 + x_1)^2 D_{N_1} S_1^2 \Delta S_{NI}(2)$

and when $(\bar{w}_\| - \bar{w}_\perp)_{rt} = (\bar{w}_\| - \bar{w}_\perp)_{tt} = 0$, $T_{NI}(2)/T_{NI}(1) = S_2^2 \Delta S_{NI}(1)/S_1^2 \Delta S_{NI}(2)$ and also $\Delta H_{NI}(2)/\Delta H_{NI}(1) = S_2^2/S_1^2$. Again if $t_2 > t_1$, $\Delta S_{NI}(2) > \Delta S_{NI}(1)$, $S_2^2/S_1^2 \simeq 1$, and $T_{NI}(2)/T_{NI}(1) < 1$, which is consistent with the observations of BT and KWI. The calculated ratios $T_{NI}(t)/T_{NI}(1)$ are recorded for those series where $(\bar{w}_\| - \bar{w}_\perp)_{rt} = (\bar{w}_\| - \bar{w}_\perp)_{tt}$

= 0. The relative variation between successive homologues depends on $r$ and $\lambda_I$ and is somewhat larger than the transition temperature ratios obtained experimentally for the lower members of the series but the variation attenuates somewhat for the higher members and this is consistent with experiment.[2,3] The variation in $T_{NI}$ is somewhat larger for the homologous series with $\phi$ rather than $\lambda_I$ held constant ($r = 3$, $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$). This suggests that experimental measurements of the densities of the isotropic and nematic melts at the transition should prove important for comparison between theory and experiment. Such measurements would alleviate uncertainty about transition densities and their variation through a homologous series and would test the assumption that $\Delta\phi/\phi$ is small at the transition.

An estimate of the magnitude of $(\bar{w}_\parallel - \bar{w}_\perp)_{rr}$, the anisotropic dispersion energy due to core–core interactions, can be deduced from eq 31 and 35 and when $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$

$$(\bar{w}_\parallel - \bar{w}_\perp)_{rr} = 3(r + t + 1)(r + 1)^{-2}\phi^{-1}S^{-2}T_{NI}\Delta S_{NI}$$

For a typical example, if $r = t = 3$, $\phi = 0.7$, $S = 0.827$, $\Delta S_{NI} = 7.87$ J K$^{-1}$ mol$^{-1}$ (see Table IV, $\lambda_I = 0.1$), and $T_{NI} = 400$ K, $(\bar{w}_\parallel - \bar{w}_\perp)_{rr} = 8630$ J per mole of monomers. This anisotropic dispersion energy is only about 20–25% of typical molar heats of vaporization for low molecular weight liquids.

When $(\bar{w}_\parallel - \bar{w}_\perp)_{rt}$ and/or $(\bar{w}_\parallel - \bar{w}_\perp)_{tt}$ are nonzero and positive, ordering of the spacer segments can be enhanced in the nematic mesophase and corresponding increases in $S$, $\Delta S_{NI}$, and $d$ can result. Examples where $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} > 0$ and $(\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$ are presented for some hypothetical homologous series in Table IV. In performing these calculations, we have chosen the transition temperatures for each member of the series to be consistent with the ratios $T_{NI}(t)/T_{NI}(1)$ obtained when $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$ for the same series. Also we have maintained constant values for $(\bar{w}_\parallel - \bar{w}_\perp)_{rr}$ and $(\bar{w}_\parallel - \bar{w}_\perp)_{rt}$ for each member of the homologous series. The variation of $S$, $\Delta S_{NI}$, and $d$ between the lowest and highest homologues enlarges relative to the corresponding results determined for the case where $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$. In particular, for the higher homologues the calculated $\Delta S_{NI}$ becomes comparable in magnitude to that measured for the higher even-membered homologues of the polyesters investigated by BT and KWI. The change in the rigidity of the flexible spacer bond segments at the transition as measured by $\Delta(r + 1)$ and $d$ both increase as $(\bar{w}_\parallel - \bar{w}_\perp)_{rt}$ increases for fixed $t$. The nematic–isotropic transition can also disappear for the higher members of these hypothetical homologous series if the transition temperature becomes too small and $(\bar{w}_\parallel - \bar{w}_\perp)_{rt}/T_{NI}$ becomes comparable to or larger than $(\bar{w}_\parallel - \bar{w}_\perp)_{rr}/T_{NI}$. Examples of this behavior are mentioned in the caption of Table IV. The disappearance of an ordered mesophase for the higher members of a homologous series of main-chain mesogenic polyesters has been observed by Blumstein et al. for the $n = 20$ even and $n = 15$ odd members of the polymer homologues based on the polyesters formed from 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and alkanedioic acids.[27] Hence the present theory can correlate under certain conditions with the experimental observation that ordered mesophases can disappear if the constituent monomer units become sufficiently flexible through addition of spacer groups beyond a cutoff value which presumably depends on the nature of the rigid core. The present prediction of ordered mesophase disappearance does not incorporate the possibility that the $T_{NI}$ would become superseded by the crystal–isotropic melting transition.

If $(\bar{w}_\parallel - \bar{w}_\perp)_{rt}$ and/or $(\bar{w}_\parallel - \bar{w}_\perp)_{tt}$ remain constant for each homologue within a series, then odd–even variations in $S$, $S^*$, $\Delta S_{NI}$, and $\Delta H_{NI}$ cannot be generated in the present analysis. However, if odd–even variations in the anisotropic dispersion interactions involving the spacer groups are allowed, then corresponding variations in $S$, $\Delta S_{NI}$, and $\Delta H_{NI}$ can be produced, and some examples are displayed in Table IV. The resultant simulations of odd–even variations in $S$ and $\Delta S_{NI}$ are admittedly incorporated in an ad hoc fashion. The odd–even behavior of the statistical thermodynamic properties of homologous series of low molecular weight nematogens obtained by Marčelja[14] in his self-consistent mean-field analysis of chain ordering ultimately appear from odd–even variations in the anisotropic dispersion energy. The present analysis does not treat the configurational and internal energy of the spacer groups in sufficient detail to justify a similar self-consistent formulation. Also the spacer groups are not considered here in sufficiently sophisticated detail to utilize the rotational-isomeric model[20] to elucidate their conformational behavior in a manner related to that employed by Abe[28] and Yoon and Bruckner.[29]

Table V depicts the dependence of $S$ upon the reduced temperature, $T/T_{NI}$, evaluated from eq 33 with $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$ for $r = 4$, $t = 5$, $\phi = 0.8$, and $M = 3, 5, 10, 25$, and 100. In general, $S$ increases monotonically as $T/T_{NI}$ decreases and the variation is greatest for the $M = 10$ example although the overall change is rather gradual.[25,26] Extension of the spacer groups as measured by $\Delta(r + 1)$ or $d$ also is enhanced as the temperature is lowered.

This analysis endeavors to describe the statistical thermodynamics of linear, thermotropic main-chain polymeric liquid crystalline melts in terms of the segmental composition, structure, and volume fraction of the mesogenic monomers, the degree of polymerization, the anisotropic dispersion interaction energies, the configurational behavior of the polymer chains, and the associated coupling between the mesogenic and polymeric attributes. The anticipated tendency for distortion (i.e., elongation along the preferred direction) of the polymer chain configurations in the ordered mesophase relative to random coil behavior in the isotropic melt[17] is proposed to enhance the ordering of the spacer bond segments in each monomer comprising the chain. This coupling leads to predictions consistent with experiment of substantially larger transition entropies, transition enthalpies, and order parameters for the mesogenic polymers than is customarily measured for low molecular weight nematogens. Neglect of the mesogenic–polymeric correlations generates a theory of polymeric liquid crystals which predicts order parameters and transition entropies for the same $r$ and $\phi$ which are essentially identical with those obtained previously for a fluid of low molecular weight rigid rods.[10] The corresponding prediction that the statistical thermodynamic properties at the nematic–isotropic transition for polymeric liquid crystalline melts and a fluid of disconnected rodlike molecules are nearly identical is then in agreement with the conclusion obtained by Flory[5] but in disagreement with the experimental observations.[2,3]

An enhanced degree of alkyl chain order in the nematic melt of linear polymeric liquid crystals prepared by condensation of 4,4′-dihydroxy-2,2′-dimethylazoxybenzene with the diacid chlorides ClCO–(CH$_2$)$_n$–COCl has indeed been suggested and verified by extensive experimental studies using a variety of techniques such as X-ray diffraction,[30] $^1$H NMR broad-line spectroscopy,[31] magnetic birefringence,[17,32] DSC calorimetry,[2] $^1$H NMR,[1] and re-

## Table V
### Calculated Dependence of $S$, $\Delta(r + 1)$, $S^*$, and $d$ on the Reduced Temperature $T/T_{\text{NI}}$ When $r = 4$, $t = 5$, $\phi = 0.8$, and $(\bar{w}_\parallel - \bar{w}_\perp)_{rt} = (\bar{w}_\parallel - \bar{w}_\perp)_{tt} = 0$ for the Indicated Values of $M$

$(r = 4, t = 5, \phi = 0.8)$

| | $M = 3$ | | | | | $M = 5$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $T/T_{\text{NI}}$ | $S$ | $\Delta(r + 1)$ | $S^*$ | $d$ | $T/T_{\text{NI}}$ | $S$ | $\Delta(r + 1)$ | $S^*$ | $d$ |
| 1.00 | 0.966 | 0.899 | 0.731 | 0.351 | 1.00 | 0.901 | 0.966 | 0.688 | 0.435 |
| 0.95 | 0.975 | 0.913 | 0.739 | 0.356 | 0.95 | 0.925 | 1.025 | 0.711 | 0.453 |
| 0.91 | 0.981 | 0.924 | 0.745 | 0.359 | 0.91 | 0.943 | 1.073 | 0.730 | 0.467 |
| 0.80 | 0.992 | 0.942 | 0.755 | 0.364 | 0.80 | 0.975 | 1.168 | 0.764 | 0.493 |
| 0.67 | 0.998 | 0.952 | 0.760 | 0.367 | 0.67 | 0.994 | 1.228 | 0.785 | 0.509 |

| | $M = 10$ | | | | | $M = 25$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $T/T_{\text{NI}}$ | $S$ | $\Delta(r + 1)$ | $S^*$ | $d$ | $T/T_{\text{NI}}$ | $S$ | $\Delta(r + 1)$ | $S^*$ | $d$ |
| 1.00 | 0.751 | 0.744 | 0.556 | 0.390 | 1.00 | 0.738 | 0.623 | 0.538 | 0.287 |
| 0.95 | 0.773 | 0.795 | 0.577 | 0.412 | 0.95 | 0.753 | 0.651 | 0.551 | 0.304 |
| 0.91 | 0.791 | 0.842 | 0.594 | 0.431 | 0.91 | 0.765 | 0.677 | 0.562 | 0.319 |
| 0.80 | 0.834 | 0.971 | 0.637 | 0.479 | 0.80 | 0.794 | 0.747 | 0.589 | 0.358 |
| 0.67 | 0.883 | 1.161 | 0.691 | 0.538 | 0.67 | 0.827 | 0.847 | 0.621 | 0.409 |

| | $M = 100$ | | |
|---|---|---|---|---|
| $T/T_{\text{NI}}$ | $S$ | $\Delta(r + 1)$ | $S^*$ | $d$ |
| 1.00 | 0.837 | 0.590 | 0.607 | 0.153 |
| 0.95 | 0.845 | 0.603 | 0.614 | 0.163 |
| 0.91 | 0.852 | 0.615 | 0.621 | 0.172 |
| 0.80 | 0.868 | 0.646 | 0.635 | 0.195 |
| 0.67 | 0.887 | 0.688 | 0.652 | 0.228 |
| 0.50 | 0.907 | 0.757 | 0.674 | 0.280 |

cently deuterium NMR.[24,25] Preliminary theoretical investigations have also been initiated concerning the inter- and intramonomer coupling between the orientational alignment of the mesogenic cores and induced conformational changes (e.g., stiffening) of the flexible spacer segments along the backbones of the polymer chains.[9,33]

The present analysis reaffirms the VKS[9] prediction of both weakly and highly anisotropic mesophases. While both analyses employ a completely flexible segment to connect successive monomer units along the chain, this investigation differs from the VKS theory in several respects. For instance, the VKS analysis modifies the Matheson-Flory[6] lattice model treatment of polymeric liquid crystalline solutions to include the self-consistent induced ordering of the spacer segments when nematic ordering is established by performing more careful configurational counting of steric interference. Here the mechanism of conversion of flexible spacer to rigid bond segments is considered to be generated by chain extension which occurs in response to an environmentally induced tension which acts along the backbone of the chain and which arises from nematic ordering of the mesogenic cores. An explicit dependence of the ordering tendency upon the degree of polymerization is introduced through the length-tension relationship (eq 14). No counterpart of this coupling between mesogenic and polymeric attributes appears in the VKS analysis.

The VKS theory pertains to athermal, concentrated ($\phi = 1$) melts and the mesogenic cores require a rather large length-to-breadth ratio, 6.70, to exhibit an isotropic mesophase in the Matheson-Flory approximation. Furthermore, if there is no intrinsic chain stiffness, a minimum length-to-breadth ratio of 14.1 is required for the appearance of a highly anisotropic mesophase. A potential mechanism for incorporating odd-even variations in the statistical thermodynamic properties is also not apparent in the VKS treatment. Presumably, inclusion of anisotropic dispersion interactions in the VKS formulation would generate anisotropic mesophases for shorter mesogenic cores and provide a basis for generating odd-even effects.

The determination of the number of accessible config-

urations of each polymer molecule in the melt might be improved by utilizing either the VKS[9] or the Dowell-Martire[34] approach which includes ordering of the individual bond segments of the spacer groups in evaluating the interference factors. Inclusion of intrinsic stiffness or semiflexibility for the spacer segments might also generate a more realistic physical description of the spacer segments.[9,34] Implementation of these improvements is not anticipated, however, to alter fundamentally the physical description and conclusions obtained from the present treatment.

When both weakly and highly anisotropic mesophases are possible for a given set of values of $r$, $t$, $\phi$, $M$, and the anisotropic dispersion energies, the present analysis does not determine the mesophase of lowest free energy since the free energy densities of both mesophases are equal in the approximation which generates eq 31. The transition temperature for the isotropic-highly anisotropic transition is always appreciably lower than that for the isotropic-weakly anisotropic transition for the same values of $r$, $t$, $\phi$, $M$, and the anisotropic energies.

Recent deuterium[24,25] and proton[1] NMR studies strongly indicate that the poly(methylene) spacers in the nematic state of thermotropic main-chain polyesters assume highly extended configurations, and the measured orientational order parameters range from $\sim 0.7$ to 0.85. These experimental results perhaps might suggest that the highly anisotropic mesophase is a more suitable representation of the ordered melt. However, the lattice model used in this and the VKS analysis permits angles of either $0°$ or $90°$ between adjacent bond segments of the spacer groups while the methylene groups in real polyesters are constrained within small torsional fluctuations to rather definite bond angles of $\sim 110°-120°$.[25] In the highly anisotropic phase the spacer segments are constrained to be collinear along the preferred direction and this restriction undoubtedly promotes an ordering too large when compared to real systems and may render this mesophase an artifact of the model. Thus, with this reservation, the weakly anisotropic mesophase is considered to be a more realistic depiction of the nematic phase of mesogenic polymer melts. The values of the isotropic-weakly an-

isotropic transition entropies and enthalpies are in better agreement with experiment than those values calculated for the highly anisotropic transition, which are more compatible with experimental results for the crystalline–isotropic melt transition.[2,3]

A direct comparison of this formulation with previous theories is difficult because of differences in the models adopted and/or the types of polymeric crystals considered. Ronca and Yoon[7] and ten Bosch, Maissa, and Sixou[8] have investigated semiflexible nematic polymers using a wormlike model for the chain statistics and a Landau–de Gennes mean-field approach, respectively. Since a completely flexible segment is assumed to connect successive monomers, orientational correlations between successive monomers are not propagated through chain stiffness for the polymers considered here, and the persistence length in the isotropic melt is comparable to the largest linear dimension of a monomer unit. The present analysis may become applicable to stiff semiflexible polymers when $r \gg 1$ and $x \rightarrow 0$ and the density change at the order–disorder transition is considered.

Possible extension of this analysis might include investigation of isotropic–smectic and nematic–smectic phase transitions of polymeric liquid crystals by consideration of possible spatial variation in the number density distribution of rigid and flexible segments in the evaluation of the dispersion energy and the short-range configurational free energy contributions. A statistical thermodynamic treatment of comblike polymeric liquid crystals with pendant mesogenic groups attached to the main chain also seems possible by the present methods. Extension to the thermodynamics of solutions of polymeric liquid crystals and the surface adsorption or monolayer behavior of these polymers also appears feasible using appropriate modifications of the present theory.

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