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products were analyzed by reverse-phase HPLC. The chromatography was carried out on a Jones APEX ODS colum with a flow of 1.6 m*l*/min at 25°C. The column was eluted with 5% CH_3CN in 0.1 M triethylammonium acetate buffer.

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Chain Ordering Effects in the Nematic-Isotropic Phase Transition of Polymer Melts

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A statistical theromdynamic theory of theromtropic main-chain polymeric liquid crystalline melts is developed within the framework of the lattice model by a generalization of the well-known procedure of Flory and DiMarzio. According to the results of Vasilenko *et al.*, the theory of orientational ordering in melts of polymers containing rigid and flexible segments in the main chain ᶦᶜ taken into account. When the ordering of flexible segments in the nematic melt is correlated with that of rigid mesogenic groups, the former is assumed to be given as a function of the ordering of rigid mesogenic cores. A free energy density that includes short-range packing contributions is formulated. The properties of the liquid-crystalline transiton are investigated for various cases of the system. The results calculated in this paper show not only the order-parameter values but also the first-order phase transition phenomena that are similar to those observed experimentally for the thermotropic liquid-crystalline polymers and show the transitional entropy terms which actually increase upon orientational ordering. In the orientational ordering values, it is shown that mesogenic groups, flexible segments, and gauche energy (temperature) may be quite substantial. Finally, by using the flexibility term, we predict the highly anisotropic mesophase which was shown by Vasilenko *et al.*

Introduction

Liquid crystalline polymers are largely characterized by the thermotropic mesophases and the lyotropic ones. The hydrocarbon chains in amphiphilic mesophases, such as lipid monolayer and bilayer, are highly ordered near the interfacial plane of the polar head groups. These hydrocarbon chains exhibit the lyotropic liquid crystalline polymers. On the other side, thermotropic liquid crystalline polymers have their mesogenic elements separated by flexible or semiflexible spacer groups, which exhibit anisotropic-isotropic phase transition temperature considerably lower than that required for thermal degradation of the macromolecules. Thermotropic liquid crystalline polymers have several different mesophases according to the molecular configurations-nematic, smectic, and cholesteric polymers.

Not until 1981 was, a paper published by Matheson and Flory[1] in which the liquid crystalline transition in a solution of macromolecules containing rigid rods, freely rotating joints between the rods, and flexible segments was considered on the basis of the well-known lattice method.[2,3] Vasilenko, Khokhlov, and Shibaev (VKS)[4] have extended the Matheson-Flory lattice model treatment to include the induced ordering of the flexible spacer segments in the anisotropic melt. They show that the self-consistent orientational field due to the liquid crystalline order affects the flexible chain segments as well as the rigid groups, leading to straightening and stiffening of the former. The ordering of flexible segments, accompanying the formation of the liquid crystalline phase, is also indicated by some of the experimental results.[5-7] A statistical thermodynamic theory of thermotropic liquid crystalline polymers was developed, by application and extension

of a previously formulated statistical mechanical theory[8] of rigid rodlike fluids by Boehm et al.[9] Boehm et al.[9] assume that the ordering of the mesogenic groups in the nematic melt generates an environmentally induced tension, which acts along the backbone of each chain, and increases the average end-to-end chain length along the preferred direction and assume that an extension or enhanced ordering of the flexible groups in each monomer results. But Boehm's theory formulates a limited condition between an environmentally induced tension and the degree of polymerization. The calculated order parameters are considerably larger than those customarily observed for low molecular weight nematogens where typically $s \simeq 0.4$[10,11] (s: order paramter).

In this paper the case of polymer melts was chosen for the investigation because this case is most interesting with respect to the application of the result to thermotropic liquid crystalline polymeric systems. We consider an orientational ordering in melts of regular copolymers containing stiff and flexible segments in the main chain, taking into account the fact that the properties of flexible segments, as well as of rigid groups, are changed when liquid crystalline order is established. The induced tension of polymer chains are due to the freely rotating chain in the dilute system. The orientational ordering in melts of flexible segments in the main chain is assumed to be given as a function of the ordering of rigid mesogenic cores. Also we assume that one of the $z-1$ sites available to the ith ($i>1$) site occurs with a configurational energy less by an amount ε than the remaining $z-2$ sites, owing to hindrance to free rotation where z is the coordination number.

Here a statistical thermodynamic theory of thermotropic liquid crystalline polymers is developed within the framework of the lattice model by a generalization of the well-known procedure of Flory and DiMarzio.[2,3,13] For the sake of simplicity we confine the present work to athermal polymer melts only. In this case liquid crystalline ordering occurs solely for steric reasons. 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-1 we first describe the model of the polymeric system under investigation. And we describe our method for calculation of the free energy of the liquid crystalline phase, which takes into account the orientational ordering of the flexible segments. In section II-3 we formulate an expression for the free energy of a linear polymeric liquid crystalline melt which includes short-range packing contribution. 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[13,14] on a cubic lattice. And we derive expressions for the changes in order parameter, entropy, and enthalpy of polymer which accompany the anisotropic-isotropic

transition. In section III, we present theoretical predictions of the order parameters at constant volum fraction to be an implicit function of the temperature (ε/kT). Also the calculated values of transition entropy and enthalpy are shown. And, as in the VKS analysis both highly and weakly anisotropic mesophases are predicted. Finally we discuss the obtained results.

Theory of Thermotropic Liquid Crystalline Polymers with Rigid and Flexible Segments in the Main Chain

Model Let us consider a melt of N monodisperse thermotropic liquid crystalline polymer molecules placed on a spatial lattice (a cubic one to be definite). Each molecules consists of a periodically repeating sequence of M monomeric units bonded contiguously, without branching, along a linear chain. Every monomer possess a rigid group of $r+1$ consecutive segments connected to successive, completely flexible segments (t). The molecular volumes of a rigid and a flexible segment are assumed to be comparable, and the total number of segments per polymer chain is

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

Successive monomers are assumed to be always connected by a completely flexible junction segment. Let us assume that the initial segment of the $r+1$ rigid segments is the completely flexible segment which connects adjacent monomers. Let αM ($t+1$) of the flexible segments in a molecule occupy one of the $z-2$ sites available in each case for bent configurations (gauche form), and βM ($t+1$) choose the site corresponding to the energetically favored configuration which perpetuates the direction dictated by the two proceeding segments in each case. For simplicity in the subsequent derivation of the free energy, we restrict the allowed orientations of the rigid groups to three mutually orthogonal directions (1, 2, 3). This restriction permits direct application of Flory-DiMarzio lattice statistics[13,14] to construct an approximate short-range configurational free energy.

Derivation of the Partition Function In this section we consider orientational ordering of linear polymers containing rigid and flexible segments in melts, taking into account the fact that the properties of flexible segments, as well as of rigid ones, are changed when liquid crystalline order is established. In general, at sufficiently high temperatures or low volume fractions 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 volume fraction, alignment of the mesogenic units alone a preferred direction may represent a thermodynamically more stable configuration, and a transition to an ordered nematic melt occurs. In anisotropic-isotropic phase transition of the latter case, the ordering of flexible segments is considered to be that of mesogenic groups. For simplicity we shall assume that $N_1(k)$, $N_2(k)$, and $N_3(k)$ rigid 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, ($-1/2 \leq s \leq 1$) as follows by Boehm et al.[9]
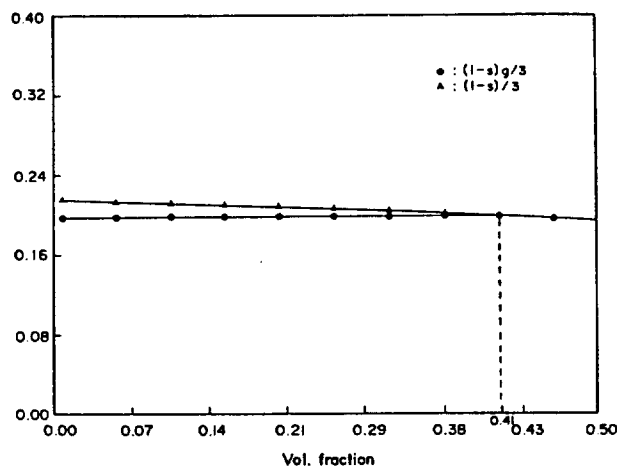
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Figure 1. The varying values of $(1-s)/3$ and $(1-s)g/3$ with respect to the change of volume fraction at $r=10$, $t=6$, and $\varepsilon = 2.5$.

$$N_1(k)=N_2(k)=(1-s)M/3$$

$$N_3(k)=(1+2s)M/3 \tag{2}$$

where $\Sigma_{i=1}^{3}N_i(k)=M$ and $\Sigma_{k=1}^{N}\Sigma_{i=1}^{3}N_i(k)=MN$. Also as the flexible segments were assumed to be dependent upon the rigid ones, the ordering of flexible segments oriented along direction 1 and 2 is considered to be proportional to that of rigid groups.

$$\tilde{N}_1(k)=\tilde{N}_2(k)=(1-s)g/3 \tag{3}$$

Therefore, the ordering fraction of flexible segments along direction 3 is given as follows:

$$\tilde{N}_3(k)=\{1-2(1-s)g/3\} \tag{4}$$

where $\Sigma_{i=1}^{3}\tilde{N}_i(k)=M(t+1)$ and $\Sigma_{k=1}^{N}\Sigma_{i=1}^{3}\tilde{N}_i(k)=NM(t+1)$. But, at higher volume fraction the distribution of flexible segments is equal to that of the rigid groups by Figure 1, that is, the value of factor g is unity. Hence, in this paper we consider that the average ordering of flexible segments is equal to that of the rodlike rigid groups.

$(1-s)$ $(=f_o)$ is defined as the flexibility and $2(1-s)/3$, gauche fraction of flexible segments. The gauche fraction of flexible segments means the cis-form of flexible segments: the flexible segments which are not arranged in the direction of the main chain.

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

$$Q_c(V,\ \tilde{N}_1,\ \tilde{N}_2,\ \tilde{N}_3,\ N_1,\ N_2,\ N_3,\ r,\ t,\ M,\ s,\ \alpha)$$

$$=(N\ !\ )\sum_{\{\tilde{N}_i(1),\ N_i(1)\}}\cdot\sum_{\{\tilde{N}_i\ (2),\ N_i(2)\}}\cdots\cdots\cdots$$

$$\cdots\cdot\sum_{\{\tilde{N}_i(j),\ N_i(j)\}}\prod_{j=0}v_{j+1}(N_i(j+1)) \tag{5}$$

where $\Sigma_{\{\tilde{N}_i(j),\ N_i(j)\}}$ actually denotes the triple sum $\Sigma_{\{\tilde{N}_i(1),\ N_i(1)\}}$ $\cdot\Sigma_{\{\tilde{N}_i(2),\ N_i(2)\}}\cdot\Sigma_{\{\tilde{N}_i(3),\ N_i(3)\}}$ and each term in the multiple sum must satisfy the constraints:

$$\sum_{j=0}^{N-1}N_i(j+1)=\sum_{j=0}^{N-1}\tilde{N}_i(j+1)=N_i\ (i=1,\ 2,\ 3)$$

Also $\Sigma_{i=0}^{3}N_i(j)=M$ and $\Sigma_{i=1}^{3}\tilde{N}_i(j)=M(t+1)$ $(j=1,\ 2,\ \cdots\cdots$ $N)$. The expected number of configurations for molecule $j+1$ will be

$$v_{j+1}=(1/2)\cdot z(V-Lj)[(1-Lj/V)]^{M(t+1)\beta-1}$$

$$\cdot[(z-2)\cdot(1-Lj/V)]^{\alpha M(t-1)}$$

$$\cdot\prod_{i=1}^{3}\{(V-Lj)/[V-r\cdot\textstyle\sum_{k=1}^{j}N_i(k)]\}^{rN_i(j+1)}$$

$$\cdot\exp[-\alpha M(t+1)\varepsilon] \tag{6}$$

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 z is the coordination number of the lattice $(z=6$ for a simple cubic lattice).

Having acknowledged Flory-DiMarzio[13,14] approximations, we proceed in conventional fashion as follows to get the expected number of configurations for molecule $j+1$. The number of sites available to the first segment of molecule $j+1$ will be $V-Lj$, where V is the total number of lattice sites. $(1-Lj/V)^{M(t+1)\beta-1}$ is the probability of vacant adjacent sites which can be occupied by succeeding flexible segment in the *trans* form, $[(z-2)\cdot(1-Lj/V)]^{\alpha M(t+1)}$, that which can be placed by flexible segment in case of bent configurations. The factor $(V-Lj)/(V-r\Sigma_{k-1}^{j}N_i(k))$ denotes the probability of a given vacant site to be adjoined by another in orientation i if $\Sigma_{k=1}^{j}\Sigma_{i=1}^{3}\ N_i(k)=Mj$ rigid rodlike sequences have already been inserted on the lattice. Since no distinction will be made between the alternative directions along the $(j+1)$th molecule, a symmetry number of two will be assigned to each polymer molecule.

Utilization of the random distribution approximation for the flexible segments that was applied to the rigid rodlike groups yields

$$\frac{[M(t+1)]\ !}{\{((1-s)M(t+1)/3)\ !\ \}^2\ \{((1+2s)M(t+1)/3)\ !\ \}} \tag{7}$$

Taking into account Eq. (2)-(7), the configurational partition function of athermal polymer melts under consideration can be written as

$$Q_c=(N\ !\ )^{-1}(z/2)^N\cdot(z-2)^{N[\alpha M(t+1)]}$$

$$\cdot\left[\frac{[M(t+1)]\ !}{\{((1-s)M(t+1)/3)\ !\ \}^2\ \{((1+2s)M(t+1)/3)\ !\ \}}\right]^N$$

$$\cdot\left[\frac{M\ !}{\{((1-s)M/3)\ !\ \}^2\ \{((1+2s)M/3)\ !\ \}}\right]^N$$

$$\cdot[\{(V-rMN(1-s)/3)\ !\ \}^2\{(V-rMN(1+2s)/3)\ !\ \}]$$

$$\cdot[V^{N[M(t+1)-1]}\ (V-LN)\ !\ (V\ !\ )^2]^{-1}$$

$$\cdot\exp[-\alpha MN(t+1)\ \varepsilon] \tag{8}$$

where we have employed $\prod_{j=0}^{N-1}(V-Lj)^L\simeq V\ !\ /(V-LN)\ !$, $\Sigma_{j=0}^{N-1}(V-rjN_i)^{rN_i}\simeq V\ !\ /(V-rN_i)\ !$ $(i=1,\ 2,\ 3)$, and the random distribution approximation for $\{N_i(j)\}$ to evaluate the multiple summation ion Eq. (4).

Application of Stirling's approximation to Eq. (8) gives

$$\ln Q_c=-N\ \ln N+N+N\ \ln(z/2)+\alpha MN(t+1)\ \ln(z-2)$$

$$+[MN(t+1)/3]\cdot\{3\ln3-2(1-s)\ln(1-s)-(1+2s)\ln(1+2s)\}$$

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$+[MN/3] \cdot \{3 \ln 3 - 2(1-s) \ln (1-s) - (1+2s) \ln (1+2s)\}$

$+2(V-rMN(1-s)/3) \ln (V-rMN(1-s)/3)$

$+(V-rMN(1+2s)/3) \ln (V-rMN(1+2s)/3)$

$-(V-LN) \ln (V-LN) - 2V \ln V - NM(t+1)$

$-N[M(t+1)-1] \ln V$

$-\alpha MN(t+1)\varepsilon$ (9)

Helmholtz Free Energy and Thermodynamic Properties of the Liquid Crystalline Polymers at the Phase Transition

Let N_t and $\tilde{N}_t (t=1, 2, 3)$ represent the total number of rodlike groups and flexible segments oriented along direction t, $n_t(=N_t/V)$ and $\tilde{n}_t(=\tilde{N}_t/V)$ represent their corresponding number densities.

Using Wulf and DeRocco method[14] that was based on dividing Helmholtz Free Energy into two parts, we exprss the reduced Helmholtz free energy density as

$f \equiv f(\phi, \tilde{n}_1, \tilde{n}_2, \tilde{n}_3, n_1, n_2, n_3, r, t, M, s, \alpha)$

$\equiv F(V, \tilde{N}_1, \tilde{N}_2, \tilde{N}_3, N_1, N_2, N_3, r, t, M, s, \alpha)/Vk_BT$

$\equiv f_c + f_h$ (10)

where F is the total Helmholtz free energy, f_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 $(\phi, \tilde{n}_1 = \tilde{n}_2 = 0, \tilde{n}_3 = M(t+1)/V, n_1 = n_2 = 0, n_3 = MN/V, s = 1, \alpha = 0)$ to the state $(\phi, \tilde{n}_1, \tilde{n}_2, \tilde{n}_3, n_1, n_2, n_3, s, \alpha)$. Therefore f_c can be rewritten as:

$f_c = f_I(\phi, \tilde{n}_1, \tilde{n}_2, \tilde{n}_3, n_1, n_2, n_3, r, t, M, s, \alpha)$

$\quad -f_{II}(\phi, 0, 0, \tilde{n}_3, 0, 0, n_3, r, t, M, s=1, \alpha=0)$

$f_c \equiv F_c / Vk_BT$ (11)

$f_c = V^{-1} \cdot \ln[Q_c(V, 0, 0, \tilde{N}_3, 0, 0, N_3, r, t, M, s=1)/$

$\quad Q_c(V, \tilde{N}_1, \tilde{N}_2, \tilde{N}_3, N_1, N_2, N_3, r, t, M, s, \alpha)]$ (12)

where $Q_c(V, \tilde{N}_1, \tilde{N}_2, \tilde{N}_3, N_1, N_2, N_3, r, t, M, s, \alpha)$ 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, and $Q_c(V, 0, 0, \tilde{N}_3, 0, 0, N_3, r, t, M, s(=1))$ is the corresponding partition function when all rodlike moieties are aligned along direction 3.

The free energy density f_h pertains to a hypothetical reference state where all rigid, rodlike groups are completely aligned along direction 3. Theoretical calculations of the thermodynamic properties for this system are not available. Pherhaps an appropriate modification of the scaled-particle theory of Cotter and Martire[15,16] for perfectly aligned spherocylinders could be applied.

From Eq. (9) and (12), the total free energy density in units of k_BT is obtained as follows:

$V \cdot f_c = \ln[Q_c(V, 0, 0, NM(t_1+1), 0, 0, NM, r_1, t_1)/$

$\quad Q_c(V, \tilde{N}_1, \tilde{N}_2, \tilde{N}_3, N_1, N_2, N_3, r, t, M, s, \alpha)]$

$= -MN[\alpha(t+1) \ln (z-2) - (t-t_1)(1+\ln V) + (t+2) \ln 3]$

$+NM/3(t+2)[2(1-s) \ln (1-s) + (1+2s) \ln (1+2s)]$

$-2(V-rMN(1-s)/3) \ln (V-rMN(1-s)/3)$

$-(V-rMN(1+2s)/3) \ln (V-rMN(1+2s)/3)$

$+2V \ln V$

$+(V-r_1 MN) \ln (V-r_1 MN)$

$+\alpha MN (t+1) \varepsilon$ (13)

From Eq. (3) the free energy density change at the nematic-isotropic transition is respectively $V \cdot \Delta f = V \cdot (f_c - f_{II})$. Δf is given as follows:

$\Delta f = (t+2)\lambda/r[2(1-s) \ln (1-s) + (1+2s) \ln (1+2s)$

$\quad -3 \ln 3] - 2 \cdot \{1-(1-s)\lambda\} \ln \{1-(1-s)\lambda\}$

$\quad -\{1-(1+2s)\lambda\} \ln \{1-(1+2s)\lambda\}$

$\quad +(1-3\lambda) \ln (1-3\lambda)$

$\quad +2 \cdot (1-s)(t+1)\lambda/r[\varepsilon - \ln(z-2)]]$ (14)

where $\lambda = rMN/3V$ and $\alpha = 2(1-s)/3$.

The order parameter, s, which minimizes the free energy density satisfies

$(\partial \Delta f/\partial s) = 0$

$= (t+2) \ln (z-2) + (t+2) \ln \{(1+2s)(1-s)\}$

$\quad +r \cdot \ln[\{1-(1+2s)\lambda\}/\{1-(1-s)\lambda\}]$

$\quad -(t+1)\varepsilon$ (15)

The enthalpy change in units of k_BT is

$\Delta\varepsilon_c = \Delta E_c / Vk_BT$

$= 2(1-s) \cdot (t+1) \cdot \lambda/r$ (16)

By the thermodynamic connection, the reduced entropy change is calculated.

Results and Discussion

Let us examine in detail Eq. (2)-(4) the distribution, for the rigid rodlike groups and the flexible segments that was given in the section II-2. For the given order parameters (s) the value of the factor g which minimizes the free energy density exhibits '1' in case of the high density system considered in this paper. The case of $r=10$ and $t=6$ is shown in Figure 1. From this result, we can know the fact that the average order parameter of flexible segments is equal to that of rodlike rigid groups.

By using of Eq. (14), we determine the average order parameter (s) of liquid crystalline polymers as a function of r, t, M, and ϕ. Tables 1-4 list results of order parameter and flexibility with variables r and t. If we examine Table 1-4 in more detail at constant volume fraction and given flexible segments, while the rigid rodlike groups increase the order parameter monotonically, the flexibility decreases. For constant volume fraction and rigid rodlike groups, the case is reverse. Each of Tables 1-4 corresponds to each volume fraction 0.80, 0.85, 0.90 and 0.95. While, for case $r=4$

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Table 1. The changes of order-parameter values of rigid segment (r) and flexible segment (t) at $\varepsilon(\varepsilon / k_b T)=2.5$ and ϕ (volume fraction)$=0.80$

r	t	s	α	r	t	s	α
4	1	0.404	0.397	5	1	0.493	0.338
4	2	0.382	0.412	5	2	0.426	0.383
4	3	0.377	0.415	5	3	0.404	0.397
4	4	0.376	0.416	5	4	0.395	0.403
4	5	0.376	0.416	5	5	0.391	0.406
				5	6	0.389	0.407
7	1	0.759	0.161				
7	2	0.557	0.295	6	1	0.619	0.254
7	3	0.480	0.346	6	2	0.483	0.345
7	4	0.447	0.369	6	3	0.438	0.374
7	5	0.429	0.381	6	4	0.419	0.388
7	6	0.418	0.388	6	5	0.408	0.394
7	7	0.412	0.392	6	6	0.403	0.398
7	8	0.407	0.395	6	7	0.399	0.401

Table 3. The changes of the order-parameter values of rigid segment (r) and flexible segment (t) at $\varepsilon(\varepsilon / k_b T)=2.5$ and ϕ (volume fraction)$=0.90$

r	t	s	α	r	t	s	α
4	1	0.441	0.373	5	1	0.569	0.287
4	2	0.399	0.401	5	2	0.455	0.363
4	3	0.387	0.409	5	3	0.420	0.386
4	4	0.382	0.412	5	4	0.406	0.396
4	5	0.381	0.413	5	5	0.398	0.401
				5	6	0.395	0.404
7	1	0.870	0.086				
7	2	0.636	0.243	6	1	0.740	0.174
7	3	0.520	0.320	6	2	0.533	0.311
7	4	0.470	0.353	6	3	0.464	0.357
7	5	0.445	0.370	6	4	0.435	0.377
7	6	0.430	0.380	6	5	0.420	0.387
7	7	0.421	0.386	6	6	0.411	0.393
7	8	0.414	0.390	6	7	0.405	0.396

Table 2. The changes of the order-parameter values of rigid segment (r) and flexible segment (t) at $\varepsilon(\varepsilon / k_b T)=2.5$ and ϕ (volume fraction)$=0.85$

r	t	s	α	r	t	s	α
4	1	0.422	0.386	5	1	0.528	0.315
4	2	0.390	0.407	5	2	0.440	0.373
4	3	0.382	0.412	5	3	0.412	0.392
4	4	0.379	0.414	5	4	0.400	0.400
4	5	0.379	0.414	5	5	0.395	0.404
				5	6	0.392	0.406
7	1	0.819	0.121				
7	2	0.594	0.271	6	1	0.678	0.215
7	3	0.499	0.334	6	2	0.507	0.329
7	4	0.458	0.361	6	3	0.451	0.366
7	5	0.437	0.376	6	4	0.426	0.382
7	6	0.424	0.384	6	5	0.414	0.391
7	7	0.416	0.389	6	6	0.407	0.396
7	8	0.411	0.393	6	7	0.402	0.399

Table 4. The changes of order-parameter values of rigid segment (r) and flexible segment (t) at $\varepsilon(\varepsilon / k_b T)=2.5$ and ϕ (volume fraction)$=0.95$

r	t	s	α	r	t	s	α
4	1	0.463	0.358	5	1	0.618	0.255
4	2	0.408	0.395	5	2	0.473	0.352
4	3	0.392	0.406	5	3	0.430	0.380
4	4	0.386	0.410	5	4	0.411	0.392
4	5	0.383	0.411	5	5	0.402	0.398
				5	6	0.397	0.402
7	1	0.912	0.059				
7	2	0.682	0.212	6	1	0.801	0.133
7	3	0.544	0.304	6	2	0.564	0.291
7	4	0.484	0.344	6	3	0.479	0.347
7	5	0.454	0.364	6	4	0.444	0.371
7	6	0.436	0.376	6	5	0.426	0.383
7	7	0.425	0.383	6	6	0.415	0.390
7	8	0.418	0.388	6	7	0.409	0.394

and $t=1$, the order parameter (s) is 0.404 at $\phi=0.80$, for each of $\phi=0.85$, 0.90 and 0.95 the value s is 0.422, 0.441, and 0.463. And at given volume fraction ($\phi=0.95$), as the rigid rodlike groups vary from $r=4$ to $r=7$, the corresponding values of s exhibit 0.463, 0.618, 0.80, and 0.912. These results illustrate the expected ones well that the increase of the rigid groups number increases the order parameter and that of flexible segments number decreases s. Though the interaction between molecules is not considered, the good results are obtained. Also, from the obtained results we can defer the fact that the rigid groups have greater influence on the order parameter changes than the flexible segments.

It is shown through Figure 2-5 that the steric-hindrance energy-changes for the flexible segments have an effect on the order parameter changes. Figure 2 is the case of $r=10$ and $t=1$. Each case of Figure 3, 4, and 5 is $t=2$, $t=3$, and

$t=4$ at the given rigid group ($r=10$). These results show a first order phase transition for the steric-energy of the flexible segments vs the order-parameter. We can see it very cleary through the Helmholtz free energy change of Figure 6 that the order-parameter changes show the phase transition. Also, at Figure 6 we can calculate the order parameter which minimizes the Helmholtz free energy density. The order paramters calculated by this method show the measured orientational order parameters range of ~ 0.4 to ~ 0.8.[17-19]

As shown in Figure 7, in the molecular ordering region the increase of entropy (S) leads to the decrease of Helmholtz free energy (F) and energy (E).

In any disorder-order phase transition it is crucial to ask at the outset: what is the physical mechanism which allows the free energy (F) to be lowered even as the system loses entropy (S) ? : $F=E-TS$ implies that F is raised as $S(>0)$ decreases. The answer of course is that ordering decreases
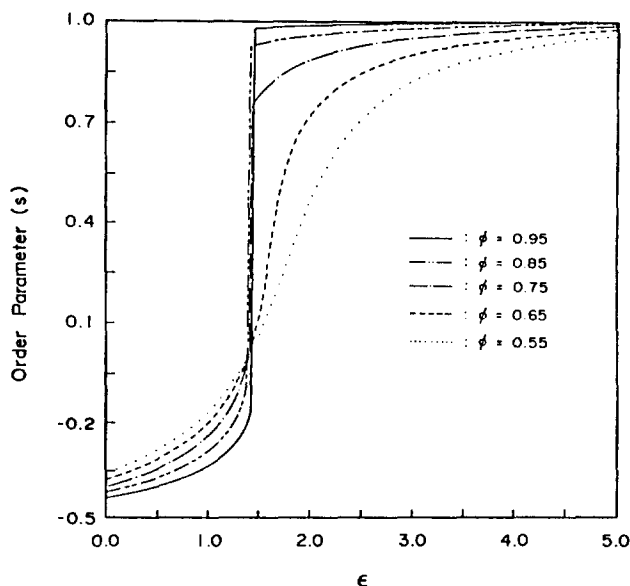
Figure 2. The changes of the order-parameter values with respect to gauche energy (temperature) at $r=10$, $t=1$, and various volume fractions.
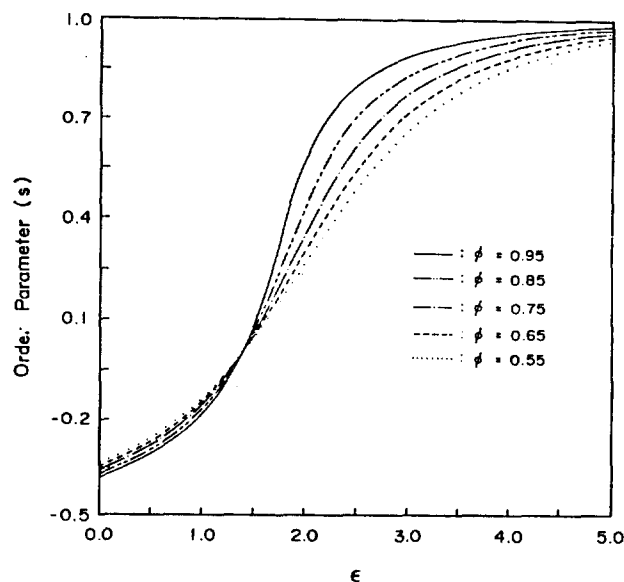

Figure 4. The changes of the order-parameter values with respect to gauche energy (temperature) at $r=10$, $t=3$, and various volume fractions.
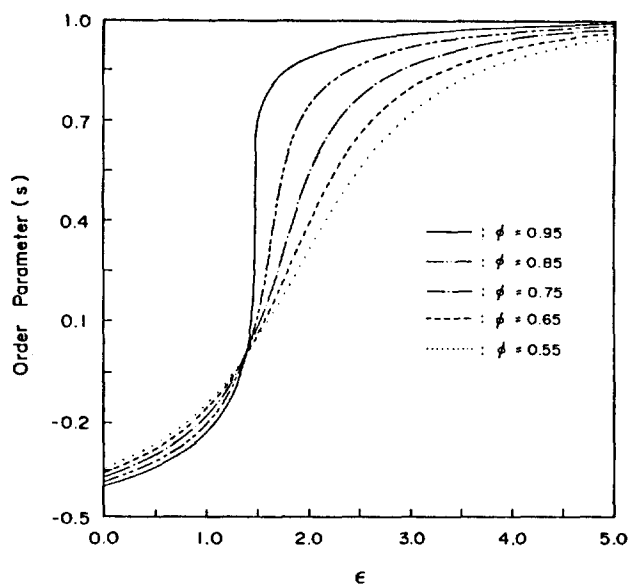

Figure 3. The changes of the order-parameter values with respect to gauche energy (temperature) at $r=10$, $t=2$, and various volume fractions.
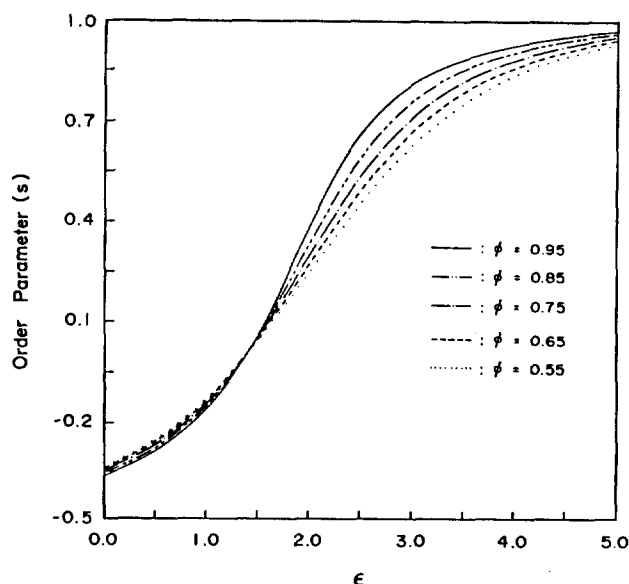

Figure 5. The changes of the order-parameter values with respect to gauche energy (temperature) at $r=10$, $t=4$, and various volume fractions.

not only the entropy but also the energy (E). This is because the molecular arrangement depends on relative orientations and the aligned configurations dominates the system. In fact, there are translational—as opposed to rotational—entropy terms which actually increase upon orientational ordering. That is, as the molecules align, there are more ways to pack them without their bumping into one another. This effect becomes important at high density (low temperature) and helps to stabilize the nematic.

The DSC thermogram of the diacid derivative experimentally investigated by Hoshino *et al.*[20] shows a first order phase transition. Also, for the liquid-crystal-forming molecule

p-Azoxyanisole (PAA) with cooled through 408°K, it undergoes a first-order phase transition to a liquid crystal in which there is a preferred direction for the molecular axes. As mentioned above, the calculated results are in accord with the experimentally observed ones.

The phase diagram which was shown by VKS[4] is obtained by means of the flexibility and gauche fraction of flexible segments. Each of Figure 8-11 presents the calculated phase diagrams for the liquid-crystalline transition for $\phi=0.95$, $\phi=0.90$, $\phi=0.85$, and $\phi=0.80$ with respect to the varying number of flexible segments at the given rigid group. These curves show two different anisotropic phases. The upper one
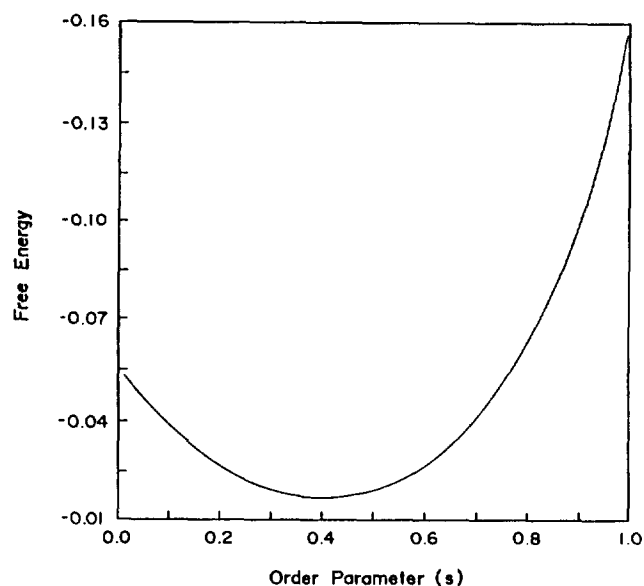
Figure 6. The changes of the reduced Helmholtz free energy density *vs* the order-parameter values.

The reduced Helmholtz free energy density

----- The reduced energy density

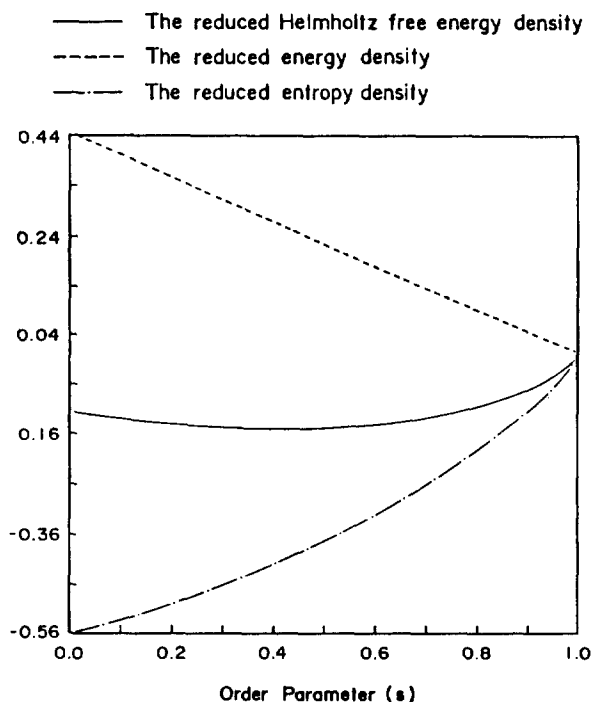—·— The reduced entropy density

Figure 7. The changes of the reduced Helmholtz free energy density, reduced energy, and reduced entropy values with respect to the order-parameter values.

of these phases is called the "weakly anisotropic" one and the lower one, "highly anisotropic" one according to VKS.[4] Figure 12 shows the critical value for the flexible segments increase regardless of the volume fraction of the system.
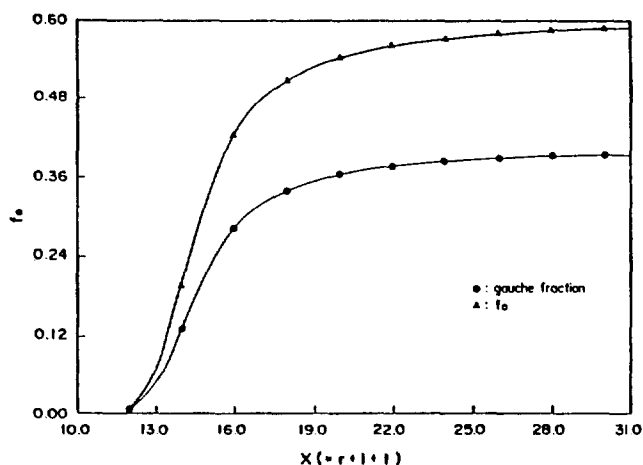
Figure 8. The changes of $(1-s)$ $(=f_o)$ and $2(1-s)/3$ with respect to the varying number of flexible segments at given rigid group and volume fraction, $\phi = 0.95$.
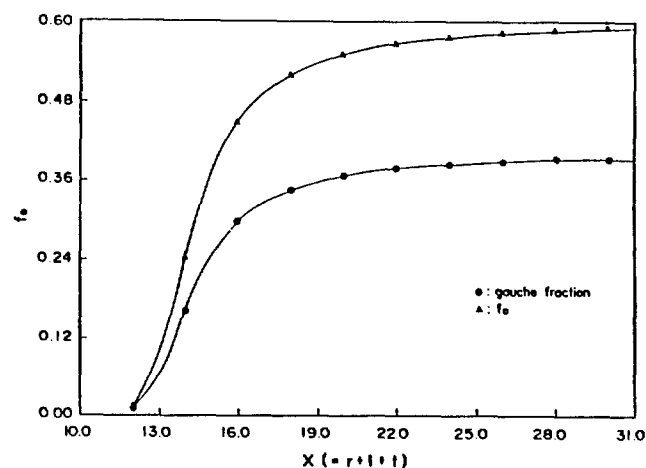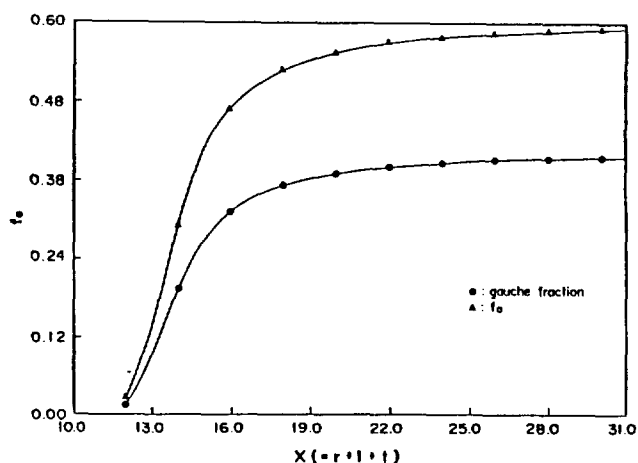

Figure 9. The changes of $(1-s)$ $(=f_o)$ and $2(1-s)/3$ with respect to the varying number of flexible segments at given rigid group and volume fraction, $\phi = 0.90$.
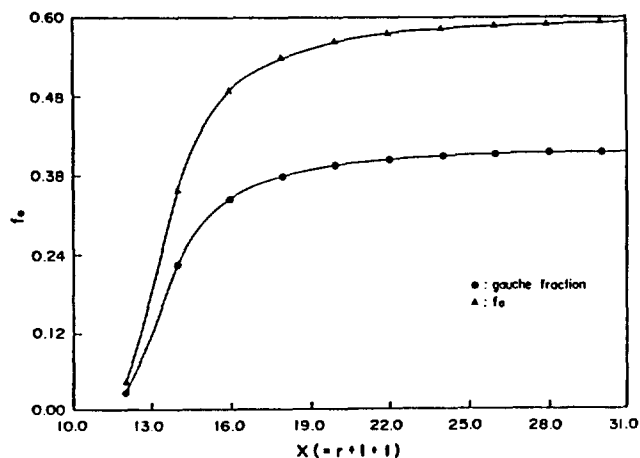

Figure 10. The changes of $(1-s)$ $(=f_o)$ and $2(1-s)/3$ with respect to the varying number of flexible segments at given rigid group and volume fraction, $\phi = 0.85$.

Figure 11. The changes of $(1-s)(=f_o)$ and $2(1-s)/3$ with respect to the varying number of flexible segments at given rigid group and volume fraction, $\phi = 0.80$.
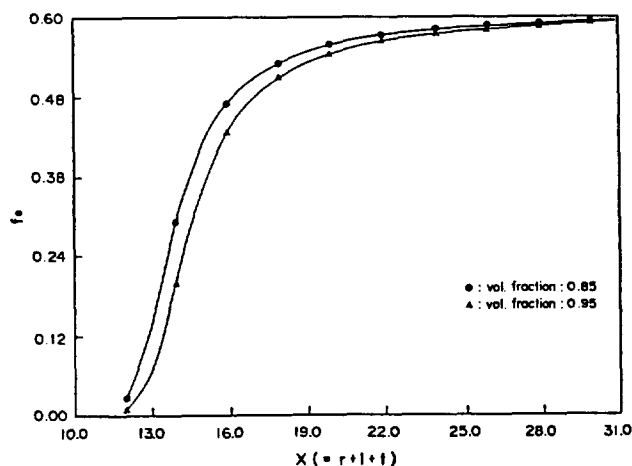

Figure 12. The changes of the flexibility at voulme fractions, $\phi = 0.95$ and 0.85.

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