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Statistical Thermodynamic Theory of the Collapse Transition of Thermotropic, Main-Chain Mesogenic Polymer Molecules in Infinitely Dilute Solution

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ABSTRACT: A statistical thermodynamic theory of an isolated thermotropic, main-chain, nematogenic polymer molecule in a single structureless solvent environment is developed by application of Flory–Dimarzio lattice statistics to a simple lattice model formulation of the polymer molecule-entrained solvent system. The polymer molecule consists of M contiguously bonded monomeric units, each of which possesses $r + 1$ consecutive rigid rodlike segments followed by t connected flexible segments. An isotropic, effective solvent–polymer segment interchange energy and a long-range pairwise anisotropic dispersion energy between the rodlike monomer groups define the energetics of the model. The most important result is the prediction of a first-order transition between a collapsed globule, where the mesogenic moieties exhibit an anisotropic orientational distribution, and either an isotropic collapsed globule or a swollen coil. The rigidity or anisotropy of the individual monomeric units, the solvent quality, and the strength of the anisotropic dispersion interactions are all important influences on the transition, and their respective roles are investigated in detail. In particular, order parameters, the polymer segment density, and energy changes accompanying the transition are determined for a variety of theoretical polymer–solvent systems. Possible experimental methods of detection of the anisotropically collapsed state for a nematogenic polymer in dilute solution are suggested.

I. Introduction

An isolated, flexible polymer chain swells in a good solvent and collapses in a poor one.[1,2] The transition from a good to a poor solvent environment is usually achieved by a temperature change or by adjusting the solvent composition in mixed solvents. The transition from an expanded coil to a collapsed globule has been extensively analyzed theoretically in the mean-field approximation,[3,4] through computer simulation using either Monte Carlo methods[5,6] or exact enumeration procedures,[7,8] and by scaling arguments[9–11] and renormalization group techniques.[12] Experimental observation of the coil–collapsed globule transition has been performed by employing a variety of techniques such as conventional light scattering,[13,14] elastic neutron scattering[15] and inelastic light scattering.[16–18] A recent review by Williams, Brochard, and Frisch provides an excellent summary of theoretical and experimental advances in the field.[19]

In recent years considerable effort has been expended in the synthesis and physical characterization of the properties of flexible and semiflexible thermotropic polymeric liquid crystals.[20] In particular nematic polyesters formed by condensation of 4,4′-dihydroxy-2,2′-dimethylazoxybenzene[21] or 4,4′-dihydroxybiphenyl[22] with homologous series of alkanedioic acids have been extensively studied in the melt. Here we present an analysis of the statistical thermodynamic properties of very dilute solutions of flexible main-chain thermotropic nematic polymer molecules in an isotropic, single-solvent environment. In a poor solvent collapse of an isolated mesomorphic polymer coil to a globule is anticipated to promote nematic ordering of the mesogenic moieties along the chain to facilitate packing. Hence this investigation concentrates on the dependence of the proposed ordering upon the structure of the constituent monomers, the solvent quality, and possible anisotropic pairwise interactions between different mesogenic groups along the chain.

The analysis is implemented by application and extension of a recent formulation of the polymer collapse problem developed by DiMarzio[23] to an isolated mesogenic polymer molecule that consists of a periodically repeating sequence of monomer units, each composed of a rigid, rodlike group of $r + 1$ contiguous segments aligned along a certain direction connected to t successive, completely flexible segments (flexible spacer). The number of distinguishable chain configurations and, hence, the configurational partition function are estimated using Flory–DiMarzio lattice statistics[24,25] applied to a simple cubic lattice. Minimization of the resulting free energy generates a pair of coupled equations that determines the equilibrium volume fraction of polymer segments, ϕ, and the order parameter, S, of the mesogenic moieties as a function of r and t, the solvent quality, and the strength of the anisotropic dispersion interactions. The possibility of nematic ordering (i.e.; $S \neq 0$) in a collapsed globule is predicted to occur under certain circumstances, and the transition to an anisotropically collapsed globule from either an isotropically collapsed globule or extended coil is thermodynamically first order in three dimensions.

Grosberg and Khokhlov[26,27] have predicted the occurrence of intramolecular liquid crystalline ordering of a mesogenic macromolecule in very dilute solution by generalization of either the Onsager[28] or Flory lattice model[29] theory of nematic ordering in solutions of long rigid rodlike molecules to very long macromolecules composed of mesogenic monomers of very large length-to-breadth ratio (i.e., large r). Under these conditions a first-order coil-collapsed globule transition is predicted to occur at temperatures above the Θ temperature and $\phi \rightarrow 1$ and $S \rightarrow 1$ within the globule, independent of the specific structural properties of the macromolecule. While these general conclusions are asymptotically correct, they do not provide a detailed description of the statistical thermodynamic properties of the globular state of many typical mesogenic main-chain polymers composed of monomers with relatively modest length-to-breadth ratios (e.g., $r < 10$). The nematic polyesters synthesized from 4,4′-dihydroxy-2,2′-dimethylazoxybenzene or 4,4′-dihydroxybiphenyl mentioned previously fall into this category. Collapsed globules of such liquid crystalline polymers possess intermediate values of ϕ and S ($0 < \phi, S \leq 1$), and the transition may occur above or below the Θ temperature, depending on the monomer structure and the strength of the intramolecular anisotropic dispersion interaction between mesogenic moieties.

More detailed numerical predictions of the statistical thermodynamic properties of isolated thermotropic nematic polymer molecules in solution appear in section II.

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Most results correspond to the limit of infinite molecular weight, although the analysis is also applicable to finite molecular weight polymers. Whenever possible comparisons between the predictions of the present analysis with those obtained by Grosberg and Khokhlov[26,27] are made.

In section III, possible modes of experimental detection of an anisotropically collapsed polymer molecule are mentioned and potential extensions to other related problems are discussed. For instance, a potential application of the theory to chromatographic separation by liquid and/or supercritical fluid chromatography of nematogenic homopolymers exists.[30] Also discussed are limitations and possible extensions of this work that are suggested by the analysis of Grosberg and Khokhlov.

Appendix A provides a derivation of the simple form of the dispersion interaction energy utilized in the present analysis. Appendix B establishes the necessary and sufficient conditions required for the state of statistical thermodynamic equilibrium of an isolated mesogenic polymer molecule immersed in a solvent.

II. Theory

We consider an infinitely dilute solution of mesogenic polymer molecules that individually consist of a periodically repeating sequence of M monomeric units bonded contiguously, without branching, along a linear chain. Each monomeric unit possesses a rigid rodlike moiety of $r + 1$ contiguous segments connected to t successive, completely flexible segments, and $L = M(r + t + 1)$ represents the total number of segments per polymer molecule. The rigid-core and flexible segments and the solvent molecules are assumed to have comparable molecular volumes but chemically different properties.

An isolated polymer molecule immersed in a favorable solvent environment swells by solvent uptake, and the volume fraction $\phi = L/V$ of polymer segments is small, where V represents the number of lattice sites occupied by the polymer chain and associated solvent molecules in the swollen coil. Furthermore an infinite number of equally probable orientations of the mesogenic groups is anticipated for the expanded coil. However, at lower temperatures the solvent may become sufficiently poor that the polymer coil will expel solvent from its interior by collapsing its dimensions and thus increasing ϕ substantially. In the collapsed state, alignment of the mesogenic groups along a preferred direction (or set of nearly equivalent directions) facilitates packing and may represent a thermodynamically more stable configuration. The subsequent analysis is simplified by restricting the allowed orientations of the rigid segments to three mutually orthogonal directions (1, 2, 3). This restriction permits direct application of Flory–DiMarzio lattice statistics[24] to the derivation of the configurational partition function, Q_c, of the nematic polymer molecule and the entrained solvent molecules. The partition function, Q_c, enumerates the number of distinguishable ways $L = M(r + t + 1)$ contiguous segments can be incorporated sequentially on a cubic lattice of V sites such that only single-segment occupancy per site is allowed.

The total number, N_k, $k = 1, 2, 3$, of rodlike mesogenic moieties oriented along direction k can be expressed in terms of an average order parameter, S, $(-{}^1/_2 \leq S \leq 1)$ as $N_1 = N_2 = (1 - S)M/3$ and $N_3 = (1 + 2S)M/3$, where $\sum_{k=1}^{3} N_k = M$ as required. When $S = 0$, $N_1 = N_2 = N_3$, which corresponds to an isotropic distribution of mesogenic groups; when $1 \geq S \geq 0$, preferred alignment along direction 3 occurs. If $\upsilon_{j+1}{}^{(i)}(\{N_i(j)\})$ denotes the number of ways the $(j + 1)$ monomeric group can be placed on the lattice with the $(j + 1)$ mesogenic group oriented along direction i, given that j consecutive monomers have been successfully introduced according to a prescribed sequence of orientations of the preceding rigid units specified by $\{N_i(j)\}$, then

$$Q_c(V, N_1, N_2, N_3) = Vc(c - 1)^{-2} \sum_{\{N_i\}}{}' \prod_{j=0}^{M-1} \prod_{i=1}^{3} \upsilon_{j+1}{}^{(i)}(\{N_i(j)\})$$

where c is the coordination number of the lattice ($c = 6$ for a cubic lattice) and the summation $\sum'_{\{N_i\}}$ extends over all possible orientational sequences of the rodlike moieties consistent with the constraints $\sum_{k=1}^{M} N_i(k) = N_i$, $i = 1, 2, 3$, where $N_i(k) = \delta_{ik}$, the Kronecker delta. We propose that

$$\upsilon_{j+1}{}^{(i)}(\{N_i(j)\}) = \{(c - 1)(1 - (r + t + 1)j/V)\}^{t+1}[(V - (r + t + 1)j)/(V - r\sum_{k=1}^{j} N_i(k))]^{rN_i(j+1)}$$

The factor $(1 - (r + t + 1)j/V)(c - 1)$ is the number of vacant adjacent sites that can be occupied by either a completely flexible segment or the initial segment of a rigid rod sequence of $r + 1$ segments that are in contiguous alignment along an allowed direction. The factor $(V - (r + t + 1)j)/(V - r\sum_{k=1}^{j} N_i(k))$ denotes the probability that a given vacant site is adjoined by another in orientation i after j rodlike moieties have already been placed on the lattice.

We assume that the $N_1 = (1 - S)M/3$, $N_2 = (1 - S)M/3$, and $N_3 = (1 + 2S)M/3$ rodlike groups with orientations 1, 2, and 3, respectively, are randomly distributed along the polymer chain. The partition function may then be simplified to

$$Q_c(V, S, L) = c(c - 1)^{M(t+1)-2}[M!/(((1 - S)M/3)!)^2((1 + 2S)M/3)!]((V - r(1 - S)M/3)!)^2(V - r(1 + 2S)M/3)!/(V - L)!(V!)^2V^{M(t+1)-1} \quad (1)$$

where we have employed $\prod_{j=0}^{M-1}(V - (r + t + 1)j)^{r+t+1} = V!/(V - L)!$ and after assuming that $\sum_{k=1}^{j} N_i(k) = jN_i/M$, $\prod_{j=0}^{M-1}(V - rjN_i/M)^{rN_i/M} = V!/(V - rN_i)!$ for $i = 1, 2, 3$, and we have also expressed the N_i in terms of the order parameter S. The factor $c(c - 1)^{-2}$ refers to the fact that after the first segment has been placed on the lattice there are c nearest-neighbor sites available for the second segment. For all remaining flexible segments there are $c - 1$ available adjacent sites; hence the factor $(c - 1)^{-1}$ corrects for overcounting this factor in the definition of $\upsilon_{j+1}{}^{(i)}(\{N_i(j)\})$.

In the limit when $r = 0$ and $S = 0$, $Q_c = Q_c\,(V, M\,(t + 1)) \rightarrow (c/(c - 1)^2)(c - 1)^{M(t+1)}(M!/((M/3)!)^3)V!/(V - M\,(t + 1))!V^{M(t+1)-1}$, which is essentially the Flory–Huggins result for the number of distinguishable configurations that a completely flexible polymer molecule of $M(t + 1)$ segments can assume without steric hindrance on a cubic lattice of V sites.[31] When $t = 0$, $Q_c = Q_c(V, S, M(r + 1)) = c(c - 1)^{M-2}M!((V - r(1 - S)M/3)!)^2((V - r(1 + 2S)M/3)!)/2V^{M-1}(V!^2)(((1 - S)M/3)!)^2\,((1 + 2S)M/3)!(V - M(r + 1))!$, which is the configurational partition function derived from DiMarzio lattice statistics for M connected rigid rods of $r + 1$ segments whose orientations are uncorrelated between successive monomers along the chain.

The total canonical partition function for a given V and S can be expressed as[32]

$$Q(\beta, V, S, L) = Q_c(V, S, L) \exp((L^2/V)(\chi + \chi_A S^2))P(V, S) \quad (2)$$

where $\beta = 1/kT$ and where

$$\chi = ((r + 1)^2\chi_{rs} + t^2\chi_{ts} + t(r + 1) \times (\chi_{rs} + \chi_{ts} - \chi_{rt}))/(r + t + 1)^2$$

with $\chi_{ab} = \beta(w_{ab} - (w_{aa} + w_{bb})/2)$ $(a, b = r, t, s)$ and $\chi_A = -((r + 1)/(r + t + 1))^2|\beta w_A|$ respectively represent a net isotropic interchange energy between rigid-core type segments (r), flexible segments (t), and solvent molecules (s) and a total anisotropic pairwise dispersion interaction between mesogenic moieties. The interaction energies w_{ab} (a, $b = r, t, s$) and w_A represent the total pairwise interaction potential between segments and/or solvent molecules integrated over all allowed intermolecular separations. An explicit determination of the energetic contributions appears in Appendix A.

The function $P(V, S)$ represents the probability that the polymer coil in the presence of solvent occupies a volume V. The function $\ln P(V, S)$ is proportional to the entropy of deformation of the polymer coil due to swelling or contraction in the solvent. We assume that $P(V, S)$ can be determined from the configurational statistics obtained from the trajectories generated by a particle executing a biased random walk on a three dimensional cubic lattice and that all chain configurations generated in this manner possess the same internal energy. If, on the average, for each M steps taken by the biased "random walker" ($N_1 = N_2 = (1 - S)M/3$ and $N_3 = (1 + 2S)M/3$ steps of equal length, $((r + t + 1)b^2)^{1/2}$, are taken parallel or antiparallel along directions 1, 2, and 3, respectively, then the normalized probability density distribution is

$$P(V, S) = (3/2\pi Lb^2)^{3/2}(1 - S)^{-1}(1 + 2S)^{-1/2} \times \exp(-(3/2Lb^2)((R_1{}^2 + R_2{}^2)(1 - S)^{-1} + R_3{}^2(1 + 2S)^{-1}))$$

where $R_i{}^2$ ($i = 1, 2, 3$) represents the square of the distance along direction i. Here b is the length of an individual cubic lattice site and a Gaussian statistical root-mean-square length, $(r + t + 1)^{1/2}b$, has been employed to estimate the effective length of a monomer unit (composed of both rigid and flexible segments) along the specified directions 1, 2, and 3. We also assume that the ratio of the hydrodynamic volume of the coil to the volume of a lattice site, b^3, provides an estimate of the number of lattice sites accessible to an isolated polymer molecule and its associated solvent environment;[23] hence $V = (R_1{}^2R_2{}^2R_3{}^2)^{1/2}/b^3$. Furthermore we assume that the ratios $R_i{}^2/R_3{}^2$ ($i = 1, 2$) are identical with the ratio of the mean-square distances: $R_i{}^2/R_3{}^2 = \langle R_i{}^2\rangle/\langle R_3{}^2\rangle = (1 - S)Lb^2/3/(1 + 2S)Lb^2/3 = (1 - S)/(1 + 2S)$, where $\langle R_j{}^2\rangle = \int d^3R\, R_j{}^2P(V, S)$ ($j = 1, 2, 3$). Hence we can then express

$$V = ((1 - S)/(1 + 2S))R_3{}^3/b^3 \tag{3}$$

and

$$P(V, S) = (\tfrac{3}{2}\pi Lb^2)^{3/2}(1 - S)^{-1}(1 + 2S)^{-1/2} \exp(-(9/2L)(1 + 2S)^{-1/3}(1 - S)^{-2/3}V^{2/3}) \tag{4}$$

Substitution of eq 1 and 4 into eq 2, calculation of $\ln Q$, and application of Stirling's approximation lead to

$$\begin{aligned}\ln Q(V, S) ={}& \\ &\ln Q_c(V, S) + L^2(\chi + \chi_A S^2)/V + \ln P(V, S) = \\ &\ln (c(c - 1)^{-2}) + (M(t + 1) - 1) \ln (c - 1) - (2M/3)(1 - S) \ln ((1 - S)/3) - ((1 + 2S)/3)M \ln ((1 + 2S)/3) + 2(V - r(1 - S)M/3) \ln (V - r(1 - S)M/3) + \\ &(V - r(1 + 2S)M/3) \ln (V - r(1 + 2S)M/3) - (V - L) \ln (V - L) - (2V + M(t + 1) - 1) \ln V + \\ &L^2 (\chi + \chi_A S^2)/V + \tfrac{3}{2} \ln (\tfrac{3}{2}\pi Lb^2) - \ln ((1 - S) \times (1 + 2S)^{1/2}) - (9/2L)V^{2/3}(1 + 2S)^{-1/3}(1 - S)^{-2/3}\end{aligned} \tag{5}$$

We seek the values of V and S that minimize the free energy, $-kT \ln Q(V, S)$. Thus

$$\begin{aligned}\partial \ln Q/\partial V = 0 ={}& 2 \ln (1 - y(1 - S)\phi) + \ln (1 - y(1 + 2S)\phi) - \ln (1 - \phi) + (3y - 1 + L^{-1})\phi - \\ &\phi^2(\chi + \chi_A S^2) - 3L^{-4/3}\phi^{1/3}(1 + 2S)^{-1/3}(1 - S)^{-2/3}\end{aligned} \tag{6}$$

and

$$\begin{aligned}\partial \ln Q/\partial S = 0 ={}& \\ &\ln [(1 - S)/(1 + 2S)] + r \ln [(1 - y\phi(1 - S))/(1 - y\phi(1 + 2S))] + r\phi\chi_A S/y + L^{-1}(3/2)ry^{-1}S(1 - S)^{-1}(1 + 2S)^{-1} - \\ &(9/2)Sr/(y\phi^{2/3}L^{4/3}(1 + 2S)^{4/3}(1 - S)^{5/3})\end{aligned} \tag{7}$$

where we have introduced the equilibrium polymer volume fraction $\phi = L/V$ and have set $y \equiv r/3(r + t + 1)$. Clearly $\phi = 0$ is always a solution (usually trivial unless $L \to \infty$) to eq 6, and $S = 0$ always satisfies eq 7. However, solutions to eq 6 and 7 where $\phi \neq 0$ and $S \neq 0$ are also possible under certain conditions. Physically acceptable solutions of V or $\phi = L/V$ and S that simultaneously satisfy eq 6 and 7 and maximize $\ln Q$ must also satisfy the requirements

$$(\partial^2 \ln Q/\partial S^2)(\partial^2 \ln Q/\partial V^2) - (\partial^2 \ln Q/\partial S\, \partial V)^2 > 0$$

and

$$\partial^2 \ln Q/\partial S^2 < 0 \qquad \partial^2 \ln Q/\partial V^2 < 0 \tag{8}$$

A more detailed discussion of the implications of eq 8 appears in Appendix B.

Whether an isolated polymer molecule in solution is an expanded coil or collapsed globule depends on the value of χ. If the polymer is swollen by solvent uptake, ϕ is small and expansion of the logarithmic terms in eq 6 leads to

$$\begin{aligned}3(1 + 2S)^{-1/3}(1 - S)^{-2/3}\phi^{-5/3}L^{-4/3} - \phi^{-1}L^{-1} ={}& \\ &(1 - 3y^2)/2 - \chi - (\chi_A + 3y^2)S^2 \\ &+ \sum_{k=3}^{\infty} k^{-1}\phi^{k-2}(1 - (2(1 - S)^k + (1 + 2S)^k)y^k)\end{aligned} \tag{6$'$}$$

Introduction of the expansion factor $\alpha = R_3/\langle R_3{}^2\rangle^{1/2} = R_3L^{-1/2}((1 + 2S/3)^{-1/2}/b$, which is related to the volume fraction by

$$\phi^{-1} = \alpha^3L^{1/2}(1 + 2S)^{1/2}(1 - S)3^{-3/2} \tag{9}$$

and substitution of eq 9 into eq 6$'$ yields after rearrangement

$$\begin{aligned}\alpha^5 - \alpha^3 ={}& 3^{3/2}(1 - S)^{-1}(1 + 2S)^{-1/2}L^{1/2}((1/2) \times (1 - 3y^2) - \chi - (\chi_A + 3y^2)S^2) + \sum_{k=3}^{\infty} L^{1/2}k^{-1}(\alpha^{-3}L^{-1/2}(1 + \\ &2S)^{-1/2}(1 - S)^{-1}3^{3/2})^{k-2}(1 - (2(1 - S)^k + (1 + 2S)^k)y^k)\end{aligned} \tag{6$''$}$$

Also series expansion of the logarithmic terms involving ϕ in eq 7 gives

$$\begin{aligned}0 ={}& \ln ((1 - S)/(1 + 2S)) + 3\phi S(ry + (r + t + 1)\chi_A) + \\ &\sum_{k=2}^{\infty} rk^{-1}y^k\phi^k((1 + 2S)^k - (1 - S)^k) + (3/2y)rS/L(1 - S)(1 + 2S) - (9/2y)rS\phi^{-2/3}L^{-4/3}(1 + 2S)^{-4/3}(1 - S)^{-5/3}\end{aligned} \tag{7$'$}$$

For isolated polymer molecules with large L in a good solvent environment defined by the criterion $1 - 3y^2 - 2(\chi + (\chi_A + 3y^2)S^2) > 0$, $\alpha > 1$ and for large L, eq 6$''$ reduces to $\alpha^5 = 3^{3/2}(1 - S)^{-1}(1 + 2S)^{-1/2}L^{1/2}((1/2)(1 - 3y^2) - (\chi + (\chi_A + 3y^2)S^2))$ and $\alpha \sim L^{0.1}$, which is the familiar Flory result,[1,2] and $\phi \sim L^{-0.8}$ (see eq 9), which is very small for large L. In the limit of a polymer coil of large L in a good solvent eq 7$'$ reduces to $\ln ((1 - S)/(1 + 2S)) + 3\phi S(yr + (r + t + 1)\chi_A) - (9/2y)rS\phi^{-2/3}L^{-4/3}(1 + 2S)^{-4/3}(1 - S)^{-5/3} = 0$. The last two terms decrease as $L^{-0.8}$, and $S = 0$ is the only solution if $(ry + (r + t + 1)(\chi_A - (9/2))) < 1$, which should be satisfied unless χ_A is abnormally large.

When $S = 0$, $1 - 3y^2 - 2\chi > 0$, and L is large, eq 6$''$ reduces to

$$\alpha^5 - \alpha^3 = 3^{3/2}L^{1/2}((1/2)(1 - 3y^2) - \chi) \tag{6$'''$}$$

which is essentially the conventional Flory equation for the expansion factor for a swollen polymer coil in a good solvent where $2\chi < 1 - 3y^2$. If the coil possessed only flexible segments $r = 0$ and $y = 0$, and $\chi \equiv \chi_{ts} < {}^1/_2$ (see Appendix A) represents the usual Flory condition for a good solvent. When the polymer has a rigid mesogenic group incorporated into the basic monomer unit, $y > 0$, and the transition from a poor to a good solvent (i.e., the Θ temperature) occurs at higher temperatures than for completely flexible polymers since $\chi \propto T^{-1} < (1 - 3y^2)/2$. Nematic polymers composed of rigid monomeric groups with $r \gg 1$ and $t \simeq 0$ have $y = r/3(r + 1) \sim {}^1/_3$, and they simulate rigid rodlike polymers. Since for a good solvent $\chi < {}^1/_3$ for these type of polymers, one anticipates comparatively low solubility in conventional solvents at ordinary temperatures. This prediction is consistent with the poor solubility observed for rigid, fibrous nematogenic polymers such as Kevlar at ordinary temperatures in almost all solvents.

When $1 - 3y^2 - 2\chi = 0$, the solvent approaches its Θ temperature and eq 6″ with $S = 0$ can be approximated by $\alpha^5 - \alpha^3 - 3^{1/2}(1 - 3y^3)\alpha^{-3} = 3^{3/2}L^{1/2}((1/2)(1 - 3y^2) - \chi)$ + terms of $O(L^{-1})$ by retaining only the leading term of the summation in eq 6″. The quantity $B_3 = 3^{1/2}(1 - 3y^3)$ corresponds to the configurational contribution of the third osmotic virial coefficient in a free energy expansion of the monomer concentration in the coil. An interaction contribution to B_3 that is a function of χ is not included here. The value of B_3 ranges between $8 \times 3^{1/2}/9 = 1.54$ and $3^{1/2} = 1.73$ and always exceeds the two critical values 0.038[9] and 0.028[33] reported in the literature and below which a discontinuous first-order coil–globule transition is possible. Thus the polymer coil is predicted in this model to make a smooth transition from the expanded to the collapsed state upon cooling through the Θ temperature.[9,33]

When $\chi + (\chi_A + 3y^2)S^2 \geq \chi > (1 - 3y^2)/2$, the composite solvent–polymer segment interchange energy is no longer favorable and an isolated polymer molecule expels solvent within its interior by shrinking its dimensions relative to those in its swollen and/or Θ state. The local volume fraction of polymer segments increases significantly as the transition to a collapsed globular state occurs. The much denser packing of polymer segments tends to promote ordering of the mesogenic moieties along a preferred direction. In poor solvents eq 6 and 7 must be solved in general for ϕ and S simultaneously without approximation as a function of χ, χ_A, r, t, and L, and the resulting solution(s) must satisfy eq 8 to be physically acceptable. However, if $L \rightarrow \infty$ and $\chi + (\chi_A + 3y^2)S^2 - (1/2)(1 - 3y^2) \gtrsim 0$, eq 6′ or 6″ can be utilized to obtain

$$\phi = 3^{3/2}\alpha^{-3}L^{-1/2}(1 + 2S)^{-1/2}(1 - S)^{-1} = 3(\chi + (\chi_A + 3y^2)S^2 - (1/2)(1 - 3y^2))/(1 - 3y^3(1 + 6S^2 + 2S^3)) \quad (10a)$$

or

$$R_3 = \alpha\langle R_3{}^2\rangle^{1/2} = b\{L(1 + 2S)/3(1 - S)\}^{1/3}((\chi + (\chi_A + 3y^2)S^2 - (1/2)(1 - 3y^2))/(1 - 3y^3(1 + 6S^2 + 2S^3))^{-1/3}) \quad (10b)$$

where we have recalled that $\langle R_3{}^2\rangle^{1/2} = b((1 + 2S)L/3)^{1/2}$. The latter result reveals the familiar $L^{1/3}$ dependence of the end-to-end distance or radius of gyration of a collapsed polymer globule.

It is instructive to investigate eq 6 and 7 and their solutions in the limit $L \rightarrow \infty$ and when $\chi_A = 0$, for then eq 7 can be employed to express ϕ directly in terms of S as

$$y\phi = (1 + 2S)^{-1}(1 - ((1 - S)/(1 + 2S))^{1/r})/(1 - ((1 - S)/(1 + 2S))^{1+1/r}) \quad (11a)$$

It is convenient to introduce the function

$$h = h(S) = ((1 - S)/(1 + 2S))^{1/r} \quad (12)$$

Clearly as $0 \leq S \leq 1$, $1 \geq h \geq 0$, and in terms of h, $S = (1 - h^r)/(1 + 2h^r)$, $1 - S = 3h^r/(1 + 2h^r)$, and $1 + 2S = 3/(1 + 2h^r)$, eq 11a becomes

$$y\phi = (1 + 2h^r)(1 - h)/3(1 - h^{r+1}) \qquad (h \neq 1) \quad (11b)$$

and eq 6 can be expressed in terms of h ($\chi_A = 0$ and $L \rightarrow \infty$)

$$\chi = \frac{9y^2(1 - h^{r+1})^2}{[(1 + 2h^r)(1 - h)]^2}\left\{3 \ln\left[\frac{1 - h^r}{1 - h^{r-1}}\right] + \ln h - \ln\left[1 + \frac{(1 + 2h^r)(1 - h)}{3y(1 - h^{r+1})}\right] + (1 - (3y)^{-1})\frac{(1 + 2h^r)(1 - h)}{1 - h^{r+1}}\right\} \quad (13)$$

Provided $(1 + 2h^r)(1 - h)/3y(1 - h^{r+1}) < 1$ (which corresponds to $\phi < 1$), χ is a concave function of h for $0 < h < 1$ and the critical value of χ, χ_c, necessary to generate a collapsed state can be determined from the value of $h = h_c$ $0 < h_c < 1$ that renders χ a minimum; that is, $\chi_c = \chi(h_c, r, y)$ where h_c is the solution to

$$\frac{\partial\chi}{\partial h} = 0 = [2rh_c{}^{r-1} - 1 + (r + 1)h_c{}^r[3y\phi_c - 2]] \times \left\{2\left(3 \ln\left(\frac{1 - h_c{}^{r+1}}{1 - h_c{}^r}\right) + \ln(1 - \phi_c) - \ln h_c\right) - (3y - 1)\phi_c + \phi_c(1 - \phi_c)^{-1}\right\} + 3y\phi_c h_c{}^{-1}(1 - h_c{}^r)^{-1}[1 - (3r + 1)h_c{}^r - 2h_c{}^{2r+1} + (3r + 2)h_c{}^{r+1}] \quad (14)$$

where ϕ_c is evaluated from eq 11b when $h = h_c$. Also the solution to eq 14 must satisfy the condition $\phi_c \equiv (1 + 2h_c{}^r)(1 - h_c)/3y(1 - h_c{}^{r+1}) \leq 1$, otherwise a nematically ordered collapsed polymer globule is impossible when $\chi_A = 0$. For a given r the condition $\phi_c \leq 1$ will be violated whenever t or y becomes too large or small, respectively. A determination of the largest value of t for a given r and $|\beta w_A|$ where an ordered polymer is possible can be obtained by finding the smallest value of $y = r/3(r + t + 1)$ that yields an $S \neq 0$ solution of eq 7 when $\phi = 1$ ($\chi \rightarrow \infty$). This calculation requires numerical methods and is rather lengthy to perform. An approximate upper limit on the value of t for a given r where nematic ordering is impossible irrespective of χ when $\chi_A = 0$ can be deduced by setting $h_c = 1$ in the condition $\phi_c \leq 1$ to obtain $t \leq (r + 1)(r - 3)/3$. In reality, this result underestimates the largest value of t for a given r necessary for disappearance of nematic order.

When $\chi \rightarrow \infty$, $\phi_c = 1$, $\chi_A = 0$, and $t = 0$, ordering is possible only if $r \geq r(\min) = 2.607$ and $S \geq S(\min) = 0.569$. When r exceeds $r(\min)$, $S \neq 0$ solutions are possible for $1 \geq \phi \geq \phi_c$ and $\chi \geq \chi_c$ where $\phi_c < 1$ and $\chi_c < \infty$. If r becomes sufficiently large, an anisotropic solution is possible for $\chi \leq \chi_\Theta = (1 - 3y^2)/2$. For example, when $r = 6$, $t = 0$, and $\chi_A = 0$, $S \neq 0$ solutions exist if $\chi \geq 0.348$, which is smaller than $\chi_\Theta = 0.378$, which is the Θ condition threshold for isotropic collapse for a polymer composed of monomers with $r = 6$ and $t = 0$. This example suggests anisotropic collapse can occur above the Θ temperature. However, when $\chi_A = 0$ and $r < 6$, ordering is predicted only at temperatures below the corresponding Θ temperature

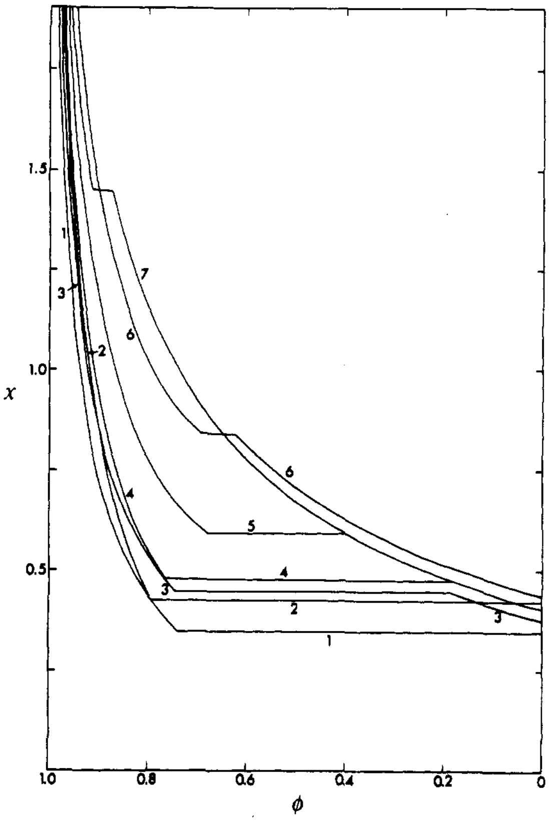

Figure 1. ϕ–χ curves calculated for the following sets of values for r, t, and $|\beta\omega_A|$, respectively: 1 (8, 0, 0); 2 (2, 0, 0.5); 3 (6, 0, 0); 4 (3, 0, 0.25); 5 (6, 1, 0); 6 (6, 3, 0); 7 (3, 0, 0). The horizontal lines represent the first-order transition from either an extended (curve -1) or a collapsed isotropic globule (curves 2–7) to an anisotropically ordered collapsed globule. The corresponding set of values of S, χ, ϕ, ϕ_0, and $\Delta E/V$ respectively at the transition are as follows: 1 (0.999, 0.346, 0.734, 0, –0.19); 2 (0.979, 0.423, 0.794, 6 × 10^{-5}, –0.57); 3 (0.993, 0.446, 0.746, 0.190, –0.19); 4 (0.973, 0.478, 0.767, 0.195, –0.35); 5 (0.949, 0.590, 0.683, 0.400, –0.11); 6 (0.770, 0.840, 0.691, 0.621, –0.041); 7 (0.787, 1.44, 0.910, 0.872, –0.050).

for isotropic collapse. In Table I, some typical results are recorded for χ_c, h_c, S_c, ϕ_c, and χ_Θ as functions of r and t which illustrate the possibilities for $\chi_A = 0$ and $L \rightarrow \infty$. The results in Table I indicate that the asymptotic limits $\phi \rightarrow 1$ and $S \rightarrow 1$ for the anisotropic globule predicted by Grosberg and Khokhlov are not simultaneously attained for the listed examples but rather for any selected value of r ϕ increases and S decreases monotonically toward and away from unity, respectively, as t increases (i.e., as the monomer becomes more flexible). Also for $t = 0$, S increases toward unity and ϕ decreases as r increases.

An isotropic solution to eq 6 and 7 is always possible in either an expanded or collapsed state, and under conditions where $S \neq 0$ solutions exist. The observed equilibrium state is that of minimum free energy. The ordered state is thermodynamically more stable for a selected set of values of χ, y, r, χ_A, and L if $V^{-1}(\ln Q)\phi, S) - \ln Q(\phi_0, 0)) > 0$ where explicitly from eq 5 (if $\phi_0 \neq 0$)

$$\begin{gathered}V^{-1}(\ln Q(\phi, S) - \ln Q(\phi_0, 0)) = \\ -2(1 - S)\phi y r^{-1} \ln (1 - S) - (1 + 2S)\phi y r^{-1} \times \\ \ln (1 + 2S) + 2(1 - y\phi(1 - S)) \ln (1 - y\phi(1 - S)) + \\ (1 - y\phi(1 + 2S)) \ln (1 - y\phi(1 + 2S)) - \\ 3(\phi/\phi_0)(1 - y\phi_0) \ln (1 - y\phi_0) - \\ (1 - \phi) \ln (1 - \phi) + (\phi/\phi_0)(1 - \phi_0) \ln (1 - \phi_0) + \\ (\phi^2 - \phi\phi_0)\chi + \chi_A S^2\phi^2 - L^{-1}(\phi \ln (\phi/\phi_0) + \\ \phi \ln (1 - S) + (\phi/2) \ln (1 + 2S) + (9/2)L^{-1/3}\phi^{1/3} \times \\ (1 + 2S)^{-1/3}(1 - S)^{-2/3} - (9/2)L^{-1/3}(\phi/\phi_0){\phi_0}^{1/3}) \quad (15)\end{gathered}$$

Table I
Critical Values of h_c, S_c, ϕ_c, and χ_c Calculated from Eq 11–14 and $\chi_\Theta = (1 - 3y^2)/2$ for the Listed Values of r and t When $\chi_A = 0$[a]

r	t	h_c	S_c	ϕ_c	χ_c	χ_Θ
2.607	0	0.541	0.569	1.000	∞	0.413
3	0	0.539	0.642	0.882	1.349	0.406
4	0	0.510	0.821	0.720	0.678	0.393
4	1	0.650	0.605	0.806	1.109	0.426
4	2	0.701	0.511	0.934	1.938	0.446
5	0	0.512	0.902	0.639	0.462	0.384
5	1	0.627	0.757	0.664	0.717	0.415
5	2	0.706	0.610	0.725	0.931	0.435
5	3	0.747	0.525	0.808	1.189	0.449
5	4	0.765	0.485	0.896	1.627	0.458
5	5	0.772	0.468	0.985	3.269	0.466
6	0	0.527	0.938	0.582	0.348	0.378
6	1	0.617	0.850	0.587	0.547	0.406
6	2	0.687	0.739	0.612	0.693	0.426
6	3	0.740	0.629	0.655	0.821	0.440
6	4	0.774	0.549	0.711	0.952	0.450
6	5	0.793	0.502	0.772	1.111	0.458
6	6	0.803	0.476	0.836	1.328	0.464
6	7	0.809	0.461	0.900	1.677	0.469
6	8	0.813	0.452	0.964	2.490	0.473
8	0	0.566	0.969	0.501	0.229	0.368
8	2	0.677	0.878	0.498	0.480	0.412
8	4	0.751	0.748	0.527	0.634	0.437
8	6	0.804	0.611	0.577	0.754	0.453
8	8	0.834	0.521	0.643	0.871	0.463
8	10	0.849	0.475	0.716	1.011	0.470
8	14	0.860	0.438	0.866	1.495	0.480
8	17	0.863	0.430	0.979	2.995	0.484
10	0	0.602	0.981	0.445	0.168	0.362
10	5	0.766	0.818	0.451	0.548	0.435
10	10	0.848	0.583	0.528	0.727	0.462
10	15	0.878	0.470	0.644	0.898	0.475
10	20	0.887	0.435	0.766	1.145	0.483
10	25	0.890	0.422	0.890	1.643	0.487
10	29	0.891	0.418	0.989	3.567	0.490
20	0	0.720	0.996	0.295	0.069	0.349
100	0	0.906	0.999	0.095	0.011	0.337

[a] For a given r ($r \leq 10$), the largest listed value of t corresponds to the largest integral t, $[t]$, that leads to an anisotropically ordered collapsed globule. Comparison with the approximation $t = (r + 1)(r - 3)/3$ gives the following sets (r, $[t]$, t), (3, 0, 0), (4, 2, $^5/_3$), (5, 5, 4), (6, 8, 7), (8, 17, 15), and (10, 29, $^{77}/_3$).

The transition from either a swollen polymer coil or a collapsed globule with $S = 0$ to a collapsed globule with $S \neq 0$ is first order, and the energy evolved is $\Delta E/V = -\phi(\phi - \phi_0)\chi - \chi_A\phi^2S^2 \leq 0$ since χ, χ_A, and $\phi - \phi_0$ are generally nonnegative.

Figure 1 depicts ϕ–χ and ϕ_0–χ curves calculated from eq 6 and 7 when $L \rightarrow \infty$ and $\chi_A = 0$ for isolated polymer molecules composed of monomers with the following sets of r, t values: (6, 0), (6, 1), (6, 3), (8, 0), and (3, 0). When $\chi > \chi_c$ there are in general three sets of (S, ϕ) values that satisfy eq 6 and 7, including the isotropic state (0, ϕ_0). The state with intermediate values of S and ϕ never satisfies the criteria given by eq 8 and thus does not correspond to a state that represents an absolute free energy minimum. Either the isotropic state or the state with the maximum values of S and ϕ maximize ln Q, and eq 15 must then be utilized to ascertain the thermodynamically favored configuration. When $\chi_A = 0$ and for integral values of r in the range $2.607 \leq r \leq 7$, irrespective of the value of t, the analysis predicts that polymer collapse into an isotropic globule always precedes an anisotropic collapse to a more densely packed molecule as the temperature or solvent quality is reduced (i.e., as χ increases) even if an ordered state is possible for $\chi < \chi_\Theta$. When $r = 8$ and $t = 0$ ($L \rightarrow \infty$, $\chi_A = 0$) direct collapse to an anisotropically ordered globule is predicted to occur for $\chi \simeq 0.35$, where

Table II

Values of S, ϕ, ϕ_0, χ, and $\Delta E/V$ at the Transition from either an Extended Coil or a Collapsed Isotropic Globule to an Anisotropically Ordered Globule for $r = 3$ and $|\beta w_A| = 0.5$ or $|\beta w_A| = 0.25$ and the Indicated Values of t[a]

t	χ_A	S	ϕ	ϕ_M	ϕ_0	χ	χ_Θ	$\Delta E/V$
				$r = 3$, $\lvert\beta w_A\rvert = 0.5$				
0	0.500	0.998	0.779	0.354	0.000	0.225	0.406	−0.439
1	0.320	0.976	0.697	0.443	0.091	0.472	0.440	−0.347
2	0.222	0.911	0.654	0.531	0.367	0.627	0.458	−0.196
3	0.163	0.696	0.650	0.620	0.520	0.760	0.469	−0.098
4	0.125	0.677	0.686	0.708	0.632	0.895	0.477	−0.060
5	0.0988	0.595	0.748	0.797	0.725	1.057	0.481	−0.038
6	0.0800	0.542	0.821	0.886	0.807	1.27	0.485	−0.030
7	0.0661	0.527	0.900	0.974	0.897	1.70	0.488	−0.020
				$r = 3$, $\lvert\beta w_A\rvert = 0.25$				
0	0.250	0.974	0.768	0.536	0.205	0.483	0.406	−0.348
1	0.160	0.842	0.718	0.669	0.544	0.750	0.440	−0.152
2	0.111	0.665	0.763	0.804	0.717	1.02	0.458	−0.064
3	0.0816	0.575	0.867	0.938	0.856	1.44	0.469	−0.034
4	0.0625	0.538	0.984		0.983	3.18	0.477	−0.021

[a] The corresponding values of ϕ_M obtained from eq 17 are also included for comparison and they underestimate (overestimate) the actual value of ϕ at the transition for the smaller (larger) values of t considered. The corresponding values of $\chi_\Theta = (1 - 3y^2)/2$ where isotropic collapse commences are also provided for comparison.

$\chi_c = 0.228 < \chi < \chi_\Theta = 0.368$. Furthermore direct anisotropic collapse from a swollen coil is predicted for $r \geq 8$ and for sufficiently small values of t. The values of χ for selected sets of r and t values where transition to an anisotropically ordered state occurs always exceed the minimum values of χ_c necessary for anisotropic collapse, as indicated in the legend of Figure 1. The results for $r = 6$ and $t = 0, 1, 3$ when $\chi_A = 0$ depicted in Figure 1 reveal that the transition to an ordered, collapsed state occurs at larger values of χ as the flexibility of the constituent monomers increases while the corresponding volume fraction change, $\phi - \phi_0$, decreases. The value of S at the transition also decreases as t increases for a fixed r and χ_A (e.g., $r = 6$ and $\chi_A = 0$ in Figure 1). For a given χ_A and t, the transitional order parameters increase monotonically with r, and this is illustrated in the legend of Figure 1. Also for a given r, t, and χ_A, the order parameter of the rigid rodlike moieties in the anisotropically collapsed globule increases monotonically as χ increases or equivalently as the temperature decreases.

When $\chi_A \neq 0$ and $L \rightarrow \infty$, analysis of eq 6 and 7 becomes slightly more difficult. It would be most desirable to determine the solutions, S and ϕ, to these equations for preselected values of χ and χ_A for polymer molecules structurally characterized by their values of r and y. It turns out, however, to be somewhat more convenient to utilize eq 6 and 7 to solve for χ and S in terms of preselected values of ϕ and χ_A. One can express eq 7 rewritten in terms of $S = (1 - h^r)/(1 + 2h^r)$ as

$$h = f(h, \phi, \chi_A, r, y) = (1 + 2h^r - 3y\phi) \times (1 + 2h^r - 3y\phi h^r)^{-1} \exp(-\phi\chi_A y^{-1}(1 - h^r)/1 + 2h^r) \quad (16)$$

Clearly $h = 1$ ($S = 0$) always satisfies eq 16. Nontrivial roots in the range $0 < h < 1$ are also possible provided $\phi\chi_A/y$ is sufficiently large. Once h or S has been determined by solution of eq 16 for prescribed values of χ_A and ϕ, the corresponding value of χ can be obtained from eq 6 in the limit $L \rightarrow \infty$.

An estimate of the minimum value of ϕ, ϕ_M, for specified $|\beta w_A|$, r, and y, which is required for the appearance of a nontrivial, ordered solution to eq 16, can be derived from solving the equation, $\partial f/\partial h|_{h=1} = 1$, which gives

$$\phi_M = (y^{-1} + 3y{\chi_A}^{-1}(1 + r^{-1}) - ((y^{-1} + 3y{\chi_A}^{-1}(1 + r^{-1}))^2 - 12r^{-1}{\chi_A}^{-1})^{1/2})/2 = (1 + (3(1 + r^{-1})|\beta w_A|)^{-1}) - ((1 + ((3(1 + r^{-1})|\beta w_A|)^{-1})^2 - 4r/3(r + 1)^2|\beta w_A|)^{1/2})/2y \quad (17)$$

The condition $\partial f/\partial h|_{h=1} = 1$ is clarified from a graphical depiction of the left- and right-hand sides of eq 16 plotted as a function of h ($0 \leq h \leq 1$). If ϕ is too small, the right-hand side always exceeds h except at $h = 1$ the isotropic solution. However, as ϕ increases the right-hand side eventually intersects the line $f(h) = h$, and this occurs approximately when the slope of the right-hand side approaches unity at $h = 1$. Values of ϕ_M for $r = 3$ and $|\beta w_A| = 0.5, 0.25$ as a function of t are included in Table II. For a fixed r and y, ϕ_M decreases as χ_A increases as anticipated. However, for fixed r and $|\beta w_A|$, ϕ_M increases with increasing t.

Eventually for a family of polymeric liquid crystalline molecules whose monomeric units belong to a homologous series (i.e., fixed r and variable t in the present context) there exists a limiting value of t that depends on r and $|\beta w_A|$ above which an ordered collapsed polymer globule is impossible. This limiting value can be determined again by finding the smallest value of y that gives an $S \neq 0$ solution of eq 7 when $\phi = 1$. For example, when $r = 3$ the maximum values of t for which an ordered globule is possible when $|\beta w_A| = 0, 0.25$, and 0.5 are $t = 0.551, 4.22$, and 8.37, respectively.

Figure 2 depicts ϕ–χ curves for polymer molecules composed of monomers with $r = 3$ and integral values of t in the range $0 \leq t \leq 7$ (thus simulating a homologous series) with $|\beta w_A| = 0.5$ and when $L \rightarrow \infty$. When $|\beta w_A| = 0.5$ and $t = 0$, a transition to an ordered collapsed state is predicted to occur for $\chi < \chi_\Theta = 0.406$, indicating that the anisotropic interactions dominate and tend to promote alignment of the rodlike moieties incorporated along the chain through collapse of the coil in an otherwise favorable solvent environment. For fixed $|\beta w_A|$ and r, the transition to an anisotropic collapsed globule occurs for increasing values of χ as t increases and eventually an isotropic collapse precedes the transition to an ordered state. Table II reveals that S, $\phi - \phi_0$, and $\Delta E/V$ at the transition decrease systematically as t increases in a homologous monomeric series. The volume fraction ϕ at the transition passes through a minimum as a function of t. When $|\beta w_A| > 0$, anisotropic collapse is also predicted to be possible for a polymer composed of monomers with $r < r(\text{min}) = 2.607$. A $\phi - \chi$ curve for $r = 2$, $t = 0$, and $|\beta w_A| = 0.5$ is included in Figure 1 for illustration.

III. Discussion

Possible experimental methods of detection of an an-

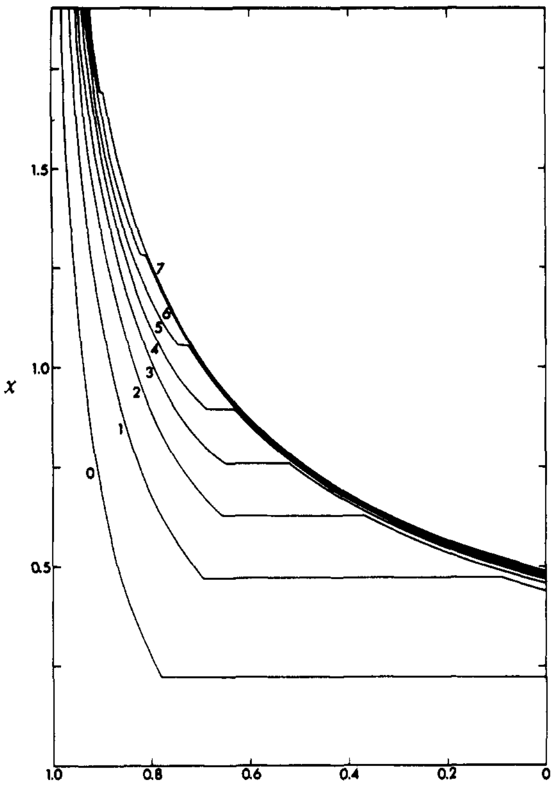

Figure 2. ϕ–χ curves calculated for $r = 3$, $|\beta w_A| = 0.5$, and $t = 0, 1, 2, 3, 4, 5, 6, 7$. The horizontal lines represent the first-order transition from either and extended coil ($t = 0$) or a collapsed isotropic globule ($t = 1 \ldots 7$) to an anisotropically ordered collapsed globule. The parameters characterizing the transition are provided in Table II.

isotropically collapsed nematogenic polymer molecule may involve analysis of depolarized laser light scattering employing high-quality polarizers or application of laser light scattering to the measurement of scattered photon–time correlations which relate to dynamical orientational fluctuations which are optically anisotropic.[34] It might prove convenient to perform low-angle laser light scattering in order to eliminate intramolecular interference effects. Fluorescence polarization measurements that utilize either the rigid rodlike moieties (typically fluorescent in UV) or incorporated fluorescent probe molecules as the fluorescent species may also provide information about the anisotropy of a collapsed polymer through measurement and analysis of the polarization of the emission.[35] Fluorescence microscopy, which has been successfully utilized to detect the substantial anisotropic ordering of condensed forms of DNA which appear in polyethylene oxide solutions (ψ condensation),[36] may also provide a potential method of detection for sufficiently large anisotropic globules. These or other conceivable detection techniques are complicated by the necessary requirement of maintaining extremely dilute polymer solutions in order to prevent interpenetration of different polymer molecules and possible aggregation. The signals are weak from very dilute solutions and the technique employed must be sufficiently sensitive to generate data with a reasonable signal-to-noise ratio.[19]

The results of the present analysis are generally applicable in the limit $L \rightarrow \infty$, and comparison with experiment may be more reliable for extremely dilute solutions of high molecular weight polymers of low polydispersity, which is a formidable requirement. The extended coil and/or collapsed isotropic globule–anisotropic collapsed globule transitions are mollified as L decreases and presumably harder to detect experimentally. While optimal correlation between theory and experiment encourages the use of high molecular weight samples of narrow polydispersity, the dilute solution limit decreases as $L^{-0.8}$, and the corresponding detection limit diminishes rapidly with increasing L.[11]

Quantitative improvements to the present analysis of the coil–globule transition may require inclusion of a surface free energy contribution to globule formation, especially when the finite L limit is considered.[26,27] Indeed the surface free energy contribution may be greater or, at least, comparable to the elastic deformation free energy contribution.[26,37] However, the isotropic–anisotropic globule transition predicted for main-chain mesogenic polymers composed of monomers having stiff and flexible spacer units of comparable dimensions (i.e., $r \lesssim t$) may involve only a small change in the surface free energy at the transition, especially if the anisotropic globule remains nearly spherical. This may be a reasonable supposition for the nematic polyesters mentioned in the Introduction.

Induced stiffening of the flexible spacer groups may also occur from the action of the intramolecular anisotropic self-consistent field that arises when a liquid crystalline globule is formed.[38] This may lead to changes in the statistical thermodynamic properties of the globules, such as odd–even effects in homologous series,[21,22] and may have to be included for a more complete description.

One reasonably direct extension of the present analysis is to include binary solvent mixtures and/or anisotropic solvents that may undergo an isotropic–nematic transition. Utilization of binary solvent systems provides a more convenient method for controlling the variation of χ by changing solvent composition at constant temperature than is afforded by temperature variation in single-solvent systems, which is practically limited by the temperature range where the solvent remains liquid. A statistical thermodynamic analysis of dilute solutions of polymeric liquid crystalline molecules in nematogenic solvents may also prove informative. Presumably both short- and long-range anisotropic interactions and short-range packing effects between the nematogenic solvent molecules and the rodlike moieties incorporated along the chain would play dominant roles in determining the statistical thermodynamics of such mixtures. An investigation of the structure and statistical thermodynamics behavior of gels composed of cross-linked mesogenic polymers in various solvents and solvent mixtures also seems possible with the present approach.[39–41]

The present analysis can also be extended to isolated two-dimensional polymeric liquid crystalline molecules in the presence of solvent. This may have application to dilute monolayers of such polymers adsorbed on a surface or retained at a chromatographic stationary phase surface or an interfacial layer. In the two-dimensional case, the transition of an isotropic extended and/or collapsed globular disk to an anisotropic collapsed disk may be second order in nature.[42]

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Appendix A

If pairwise additive polymer–polymer segment, polymer segment–solvent molecule and solvent–solvent interactions are assumed, then the dispersion energy between an individual mesogenic polymer molecule of $L = M(r + t + 1)$ segments and associated monomeric solvent molecules may be expressed as[43]

$$E = (\beta/2V)(\sum_{i=1}^{3}\sum_{j=1}^{3}\int\int \mathrm{d}^3\mathbf{R}\,\mathrm{d}^3\mathbf{R}'\,n_{ir}(\mathbf{R})w^*{}_{ij;rr}(\mathbf{R} - \mathbf{R}', \Omega_i, \Omega_j)n_{jr}(\mathbf{R}') + \sum_{i=1}^{3}\int\int \mathrm{d}^3\mathbf{R}\,\mathrm{d}^3\mathbf{R}'\,n_{ir}(\mathbf{R})w^*{}_{rt}(\mathbf{R} - \mathbf{R}')n_t(\mathbf{R}') + \sum_{i=1}^{3}\int\int \mathrm{d}^3\mathbf{R}\,\mathrm{d}^3\mathbf{R}'\,n_{ir}(\mathbf{R})w^*{}_{rs}(\mathbf{R} - \mathbf{R}')n_s(\mathbf{R}') + \int\int \mathrm{d}^3\mathbf{R}\,\mathrm{d}^3\mathbf{R}'\,(n_t(\mathbf{R})w^*{}_{tt}(\mathbf{R} - \mathbf{R}')n_t(\mathbf{R}') + n_t(\mathbf{R})w_{ts}{}^*(\mathbf{R} - \mathbf{R}')n_s(\mathbf{R}') + n_s(\mathbf{R})w^*{}_{ss}(\mathbf{R} - \mathbf{R}')n_s(\mathbf{R}'))) \quad \text{(A-1)}$$

Here $n_{kr}(\mathbf{R})$, $k = 1, 2, 3$, $n_t(\mathbf{R})$, and $n_s(\mathbf{R})$ respectively denote the average number densities of rodlike moieties in orientation k, flexible segments, and solvent molecules in a region of the polymer coil localized about $\mathbf{R}$; also $w^*{}_{ij;rr}(\mathbf{R}, \Omega_i, \Omega_j)$, $w^*{}_{rt}(\mathbf{R}) \equiv w^*{}_{tr}(\mathbf{R})$, $w^*{}_{rs}(\mathbf{R}) \equiv w^*{}_{sr}(\mathbf{R})$, $w^*{}_{tt}(\mathbf{R})$, $w^*{}_{ts}(\mathbf{R}) \equiv w^*{}_{st}(\mathbf{R})$, and $w^*{}_{ss}(\mathbf{R})$ respectively represent generally negative pair interaction energies between two rigid rod groups in orientations i and j (i.e., solid angles Ω_i and Ω_j about a fixed reference axis), a rigid group and a flexible segment, a rigid group and a solvent molecule, two flexible polymer segments, a flexible segment and a solvent molecule, and two solvent molecules where each pair of moieties is separated by a distance $\mathbf{R}$ between centers. We assume that

$$(r + 1)^{-2}w^*{}_{ij;rr}(\mathbf{R}, \Omega_i, \Omega_j) = w^*{}_{\parallel}(\mathbf{R})\delta_{ij} + w^*{}_{\perp}(\mathbf{R})(1 - \delta_{ij}) \quad \text{(A-2)}$$

where $w^*{}_{\parallel}(\mathbf{R})$ 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 (on a cubic lattice) consistent with a center of mass separation $\mathbf{R}$ between the pair. An explicit determination of $w^*{}_{\parallel}(\mathbf{R})$ and $w^*{}_{\perp}(\mathbf{R})$ is not required in the analysis.[43]

If the densities $n_{kr}(\mathbf{R})$, $k = 1, 2, 3$, $n_t(\mathbf{R})$ and $n_s(\mathbf{R})$ are spatially uniform throughout the domain occupied by the polymer coil and we set $n_{1r} = n_{2r} = (1 - S)M/3V$, $n_{3r} = (1 + 2S)M/3V$ where $\sum_{k=1}^{3} n_k = M/V$, $n_t = tM/V$, and $n_s = 1 - (L/V) \equiv \phi_s$, then substitution into eq A-1 using A-2 gives

$$\beta E = (\beta/2V)(M^2(r + 1)^2(\bar{w}^*{}_{\parallel} + 2\bar{w}^*{}_{\perp})/3 + M^2(r + 1)^2S^22(\bar{w}^*{}_{\parallel} - \bar{w}^*{}_{\perp})/3 + 2M^2(r + 1)tw_{rt} + 2M(r + 1)\phi_s w_{rs} + M^2t^2w_{tt} + 2Mt\phi_s w_{st} + \phi_s{}^2w_{ss}) \quad \text{(A-3)}$$

where $\bar{w}^*{}_{\parallel} = \int_{\parallel}\mathrm{d}^3\mathbf{R}\,w^*{}_{\parallel}(\mathbf{R})$, $\bar{w}^*{}_{\perp} = \int_{\perp}\mathrm{d}^3\mathbf{R}\,w^*{}_{\perp}(\mathbf{R})$, $(r + 1)w_{rt} = \int\mathrm{d}^3\mathbf{R}\,w^*{}_{rt}(\mathbf{R})$, $(r + 1)w_{rs} = \int\mathrm{d}^3\mathbf{R}\,w^*{}_{rs}(\mathbf{R})$, $w_{tt} = \int\mathrm{d}^3\mathbf{R}\,w^*{}_{tt}(\mathbf{R})$, $w_{st} = \int\mathrm{d}^3\mathbf{R}\,w^*{}_{st}(\mathbf{R})$, $w_{ss} = \int\mathrm{d}^3\mathbf{R}\,w^*{}_{ss}(\mathbf{R})$, and $\phi_s = 1 - \phi$. The notation $\int_{\parallel}$ $(\int_{\perp})$ denotes that the integration extends over all nonoverlapping configurations of two interacting rigid rod moieties with $\parallel$ $(\perp)$ axes of symmetry which are always aligned along either 1, 2, or 3. Introduction of $w_{rr} = (\bar{w}^*{}_{\parallel} + 2\bar{w}^*{}_{\perp})/3$, $w_{\mathrm{A}} = (\bar{w}^*{}_{\parallel} - \bar{w}^*{}_{\perp})/3$, and the segment volume fractions $\phi_r = M(r + 1)/V = (r + 1)\phi/(r + t + 1)$, $\phi_t = Mt/V = t\phi/(r + t + 1)(\phi_r + \phi_t + \phi_s = 1)$ into eq A-3

$$\beta E = \beta V(\phi_r{}^2w_{rr}/2 + \phi_r{}^2w_{\mathrm{A}}S^2 + \phi_r\phi_t w_{rt} + \phi_s\phi_r w_{sr} + \phi_s\phi_t w_{st} + \phi_s{}^2w_{ss}/2 + \phi_t{}^2w_{tt}/2) \quad \text{(A-3')}$$

or

$$E = V(\phi_r{}^2S^2w_{\mathrm{A}} + \phi_r\phi_t(w_{rt} - (w_{rr} + w_{tt})/2) + \phi_r\phi_s(w_{rs} - (w_{rr} + w_{ss})/2) + \phi_t\phi_s(w_{st} - (w_{ss} + w_{tt})/2) + (\phi_r w_{rr} + \phi_t w_{tt} + \phi_s w_{ss})/2)$$

and in more compact form

$$\beta E = -V\phi^2(\chi_{\mathrm{A}}S^2 + \chi) + \beta V\phi((r + 1)w_{rs} + tw_{st})/(r + t + 1)^{-1} + \beta V(1 - \phi)w_{ss}/2 \quad \text{(A-4)}$$

where we have defined $\chi_{\mathrm{A}} = -(r + 1/r + t + 1)^2\beta w_{\mathrm{A}}$ and $\chi = (r + t + 1)^{-2}((r + 1)^2\chi_{rs} + t^2\chi_{st} + (r + 1)t(\chi_{rs} + \chi_{st} - \chi_{rt}))$, where $\chi_{ab} = (w_{ab} - (w_{aa} + w_{bb})/2)$ $a, b = r, t, s$. The last three terms $\beta V\phi((r + 1)w_{rs} + tw_{st})/(r + t + 1) + \beta V(1 - \phi)w_{ss}/2 \equiv \beta L((r + 1)w_{rs} + tw_{st})/(r + t + 1) + \beta(V - L)w_{ss}/2$ are essentially constant energy terms that can be eliminated from the analysis by selecting an energy scale where $w_{ss} = 0$.

Appendix B

For solutions V and/or $\phi = L/V$ and S of eq 6 and 7 to be physically acceptable and maximize $\ln Q$ requires that the conditions stipulated in eq 8 $\partial^2 \ln Q/\partial S^2\,(\partial^2 \ln Q/\partial V^2) - (\partial^2 \ln Q/\partial S\,\partial V)^2 > 0$ and simultaneously $\partial^2 \ln Q/\partial S^2 < 0$ and $\partial^2 \ln Q/\partial V^2 < 0$ be satisfied. Explicit evaluation of the required derivatives from eq 5 gives in general

$$\partial^2 \ln Q/\partial V^2 = V^{-1}(\phi^2(-1 + y\phi(2 + S) + y^2(3(1 + 2S^2)(1 - \phi) - \phi^2(1 - S)(1 + 2S)) - 3y^3\phi(1 - \phi)(1 - S)(1 + 2S))/((1 - y\phi(1 - S))(1 - y\phi(1 + 2S))(1 - \phi)) + 2\phi^2(\chi + \chi_{\mathrm{A}}S^2) - \phi L^{-1} + \phi^{1/3}L^{-4/3}(1 + 2S)^{-1/3}(1 - S)^{-2/3}) \quad \text{(B-1)}$$

$$\partial^2 \ln Q/\partial S^2 = 2Lyr^{-1}(-3(1 - S)^{-1}(1 + 2S)^{-1} + 3(1 - y\phi)ry\phi(1 - y\phi(1 - S))^{-1}(1 - y\phi(1 + 2S))^{-1} + ry^{-1}\phi\chi_{\mathrm{A}} + (3r/2y)(L^{-1}(1 + 2S^2)((1 - S)^{-2}(1 + 2S)^{-2}) - (\phi^2L^4(1 - S)^8(1 + 2S)^7)^{-1/3}(3 + 4S + 8S^2))) \quad \text{(B-2)}$$

and

$$\partial^2 \ln Q/\partial S\,\partial V = \partial^2 \ln Q/\partial V\,\partial S = -6(y\phi)^2S(1 - y\phi(1 - S))^{-1}(1 - y\phi(1 + 2S))^{-1} - 2\chi_{\mathrm{A}}S\phi^2 - 6(\phi/L^4(1 + 2S)^4(1 - S)^5)^{1/3} \quad \text{(B-3)}$$

When $S = 0$ eq B-1, B-2, and B-3 respectively reduce to

$$\partial^2 \ln Q/\partial V^2 = V_0{}^{-1}(\phi_0{}^2(2\chi + 3y^2(1 - y\phi_0)^{-1} - (1 - \phi_0)^{-1}) - \phi_0/L + \phi_0{}^{1/3}L^{-4/3}) \quad \text{(B-1')}$$

$$\partial^2 \ln Q/\partial S^2 = 2Lyr^{-1}(-3(1 - y\phi_0(r + 1))/(1 - y\phi_0) + ry^{-1}\phi_0\chi_{\mathrm{A}} + (3r/2y)(L^{-1} - 3\phi_0{}^{-2/3}L^{-4/3})) \quad \text{(B-2')}$$

$$\partial^2 \ln Q/\partial S\,\partial V = \partial^2 \ln Q/\partial V\,\partial S = 0 \quad \text{(B-3')}$$

where $\phi_0 \equiv L/V_0$ is the corresponding solution of eq 6 when $S = 0$. When $L \rightarrow \infty$ and $\chi_{\mathrm{A}} = 0$, an isotropic solution is only possible provided $0 \leq \phi_0 \leq (r + 1)^{-1}y^{-1} = 3(1 + t/r + 1)/r$, otherwise $\partial^2 \ln Q/\partial S^2 > 0$. Clearly as r increases and $t = 0$ or $t \ll r + 1$, the upper limit of the range of values of ϕ_0 where an isotropic solution exists decreases essentially as $3r^{-1}$. Also when $L \rightarrow \infty$, $S = 0$, $\partial^2 \ln Q/\partial V^2 < 0$ provided $3y^2(1 - y\phi_0)^{-1} - (1 - \phi_0)^{-1} + 2\chi < 0$. If $\phi_0 \rightarrow 0$ this condition reduces to $\chi < (1 - 3y^2)/2$, which is the criterion for a good polymer solvent. In general, $\phi_0 \leq ((3y^2 + 2\chi(1 + y) - y) - ((3y^2 + 2\chi(1 + y) - y)^2 - 8\chi y(2\chi + 3y^2 - 1))^{1/2})/4\chi y$ for $\partial^2 \ln Q/\partial V^2 < 0$ when $S = 0$. When $y = {}^1/_3$, which is the maximum allowed value, $\phi_0 < 2 - (1 + 1/\chi)^{1/2}$ in order to ensure that $\partial^2 \ln Q/\partial V^2 < 0$.

Whenever both isotropic and nematic solutions to eq 5 and 6 are possible and physically acceptable in that eq 8 is satisfied, then the thermodynamically more stable state corresponds to that which maximizes $\ln Q$.

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Novel Approach for the Processing of Thermotropic Liquid-Crystal Polymers. 1. Thermodynamics and Solid-State Transesterification

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ABSTRACT: The phase diagram has been obtained for poly(bisphenol E isophthalate-*co*-naphthalate) in a para-substituted phenyl ester of terephthalic acid, bis(*p*-(methoxycarbonyl)phenyl) terephthalate. This binary system exhibits miscibility in a nematic phase and does not form cocrystals. The crystal-to-nematic phase transition has been characterized by the temperature and heat of transition data and by the Flory–Huggins theory for the melting point depression of a polymer–diluent system. From the extrapolated melting point depression data, the heat of fusion of the crystal–nematic phase transition for the polyester is found to be 20.3 ± 0.6 cal/g. The eutectic composition is ~24 wt % polymer at 247 °C with a eutectic heat of transition of ~20 cal/g. The heat of fusion of bis(*p*-(methoxycarbonyl)phenyl) terephthalate is ~30.0 cal/g for the crystal–nematic phase transition. The phase behavior was examined at high copolyester content with three different molecular weights of BPE/I/N20. These blends were subsequently transesterified in the solid state at 220 °C, and the changes in phase transitions are reported. The phase behavior and transesterification were characterized by DSC, TGA, polarized light microscopy, X-ray diffraction, and dilute-solution viscometry. The thermodynamic criteria for the melting point depression and the kinetics of transesterification are also reported for the utilization of this new processing technique.

Introduction

Background. The fundamental investigation and potential industrial use of thermotropic liquid crystal polymers (TLCP) are beset by difficulties. These rigid extended chain structures have a high axial ratio and a low entropy of "melting" (transition to the liquid-crystal phase). This puts the transition from the semicrystalline to liquid-crystal phase above temperatures for significant thermal and/or oxidative degradation. However, rigid extended chain, wholly aromatic structures are required for enhanced mechanical properties, particularly high-tensile moduli.

An approach for lowering the crystal–mesophase temperatures of these aromatic polyesters is via the incorporation of asymmetric units, kinks, and flexible bonds.[1] These additions to the original rigid TLCP may disrupt crystalline order and increase the number of possible conformations in the liquid-crystal state and lower the

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