Orientation-Dependent Interactions in Polymer Systems. 4. Chain-Length Dependence of the Nematic−Isotropic Transition Behavior of Thermotropic Semiflexible Polymers

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ABSTRACT: The nematic−isotropic transition behavior of semiflexible polymers in the bulk was studied on the basis of three typical models of orientation-dependent interactions (the Onsager−Kimura-type mean-field model, the lattice version of the Onsager model, and the Maier−Saupe-type soft interaction model) and two polymer models (the wormlike chain and the freely jointed chain with randomly distributed joints). The critical value of $x = q/D$ required to stabilize the nematic phase was evaluated as a function of $m = L/q$ for various combinations of the models, where L, q, and D are the contour length, the persistence length, and the diameter, respectively, of the chain. Even though x and x_∞, the value of x at $L \to \infty$, strongly depended on the models, the predicted $\ln(x/x_\infty)$ vs m relations were reasonably model-insensitive, offering a hopefully quantitative interpretation for the known dependence of the transition temperature T_i on chain length. (Note that q and hence x is a function of temperature.) Like T_i, the enthalpy change of transition was predicted to increase with L, approaching a constant value for large L. This behavior originates in the conformational change of semiflexible polymers and is not a characteristic of rigid rodlike molecules.

Introduction

Not a few meltable polymers with relatively stiff backbones form a nematic (or chiral nematic) phase at relatively low temperatures and undergo transformation to the isotropic state when heated above a well-defined transition temperature T_i. Cellulose derivatives,[1,2] poly(*n*-hexyl isocyanate),[3] and others[4] are examples of these thermotropic semiflexible polymers. As in the case of nematic low-mass fluids,[5] the existence of T_i may imply that the order−disorder process involves a change in energy. However, it is important to note that semiflexible polymers change their flexibilities with temperature, often drastically,[4] which is not a main characteristic of low-mass rodlike molecules. An increase in flexibility means an increase in the degree of orientational freedom, which will contribute to the destabilization of nematic ordering. As was stressed by Krigbaum et al.,[4] this mechanism of order−disorder transition involves no change in energy, or more correctly, no change in intermolecular interaction energy, and is unique to chain molecules with a temperature-dependent flexibility. Another notable feature of thermotropic semiflexible polymers is the chain-length dependence of T_i that they commonly show. Namely, it has been observed that as the chain length increases, T_i increases at first and levels off, approaching a constant value for sufficiently long chains.[1−3] We believe that this phenomenon cannot be adequately interpreted without invoking the temperature dependence of chain flexibility, but few theories are available as yet that show this in an explicit fashion permitting a quantitative comparison with experiments.

The main purpose of this work is to develop such a theory. In the absence of statistical models that have been proved to be reliably applicable to solvent-free systems, we will consider two typical and perhaps extreme models to treat the excluded-volume (hard) interaction as well as the Maier−Saupe-type model to treat the energetic (soft) interaction. From a similar standpoint, we will consider both the wormlike chain and the modified freely jointed chain as models for semiflexible polymers. By examining various combinations of these models, we hope to extract information that is as general and as model-independent as possible. The same models have been successfully used to discuss the orientational properties of flexible or non-liquid-crystalline polymers under an external force field.[6−8] This work is a simple extension of the theory to less flexible polymers that can orient spontaneously.

Models

There are three main factors to be considered in the discussion of the nematic−isotropic transition of semiflexible polymers. One is the orientation-dependent excluded-volume effect arising from the competition of molecules for space. This interaction is entropic and termed the packing entropy S_p. S_p is the largest for a perfectly oriented system and the smallest for an isotropic system. The second factor is the orientation-dependent energetic interaction E_o. In the case of the dispersion force considered here, E_o is the largest in the isotropic state, decreasing with an increase in ordering. The third factor, the orientational free energy σ of the chains, increases as the system becomes more ordered, counteracting the first two factors. The free energy ΔF (per chain) excess over that in the isotropic state is given by

$$\Delta F/T = E_o/T - S_p + \sigma \tag{1}$$

where T is the absolute temperature and σ has been reduced by T (in the case of rigid molecules, $-\sigma$ is the orientational entropy). We will assume that the system is incompressible.

Packing Entropy. The first S_p theory was given by Onsager[9] for a "gas" of rigid rods. Since this model is based on the second virial coefficient only, it has a

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questionable applicability to dense systems. Several attempts have been made to modify the model for enhanced applicabilities,[10-13] all of which predict stronger packing effects than the Onsager model but are conceptually difficult to apply to neat fluids because of the singularity that they have near the bulk density. On the other hand, Flory[14] and Di Marzio[15] proposed lattice models. These are liquid theory and conceptually applicable to both solutions and solvent-free systems. It has been pointed out that the Di Marzio model (with a cubic lattice) is essentially the same as the Flory model except for the degrees of approximation.[6] Both of them predict weaker packing effects than the Onsager and other gas theories. Flory and Ronca[5] and Kimura[16] have used with certain modifications the Flory and the Onsager model, respectively, for the analysis of the experimental results on low-mass thermotropics. However, it is not clear at this time which of gas theories or lattice theories provide a better description of real thermotropic systems.

Under these circumstances, we will adopt two closely related but numerically very different models. One is the Onsager-type or mean-field-type[16] model (O model), and the other is the lattice model that we have formulated and termed the "lattice-version-of-Onsager" model (L model).[6] For a neat fluid, they read

$$S_p/nk = (1 - n^{-1})^2 \varrho \qquad \text{O model} \tag{2}$$

$$S_p/nk = \varrho^{-1}[1 - (1 - n^{-1})\varrho] \ln[1 - (1 - n^{-1})\varrho] + (1 - n^{-1}) \qquad \text{L model} \tag{3}$$

where S_p is the packing entropy per chain, k is the Boltzmann constant, and n is the number of submolecules per chain, given by the chain contour length L divided by the (mean) diameter D:

$$n = L/D \tag{4}$$

The ϱ in eqs 2 and 3 is defined by

$$\varrho = 1 - (4/\pi)\langle|\sin \theta_{ij}|\rangle \tag{5}$$

which is zero for the isotropic state and unity for the perfectly ordered state, where θ_{ij} is the angle between bonds i and j, and $\langle\ \rangle$ denotes the mean over all bonds. Here a bond is the vector connecting the centers of two adjacent submolecules in a chain.

The factor ϱ in eq 2 comes from the Onsager model for infinitely long cylinders with a unit core volume fraction of the cylinders, i.e., $\phi = 1$ (cf. eq 13 in ref 6), and the factor $(1 - n^{-1})^2$ in the same equation approximately takes account of the finite-length effect or the effect of the chain ends with indefinite geometry: when $n = 1$, $S_p = 0$ in both eqs 2 and 3, as it should be.[17] Note that eq 3 for small ϱ converges to

$$S_p/nk = (1/2)(1 - n^{-1})^2 \varrho \qquad \text{L model, } \varrho \ll 1 \tag{6}$$

Thus, when ϱ is small, the S_p of the L model is exactly half that of the O model. Clearly, this difference comes from the difference in the excluded volume between the discrete (lattice) and continuous (gas) systems.[6] We also note that Khokhlov and Semenov,[18] in their extension of the Onsager model to solutions of semiflexible polymers, require that the persistence length of the chain be long enough. Perhaps this requirement would not be very important in a dense system, particularly in the bulk where numerous intermolecular contacts occur. In there, the excluded volume effect should be of local nature, insensitive to the overall conformation or flexibility of the chain, and the essential parameter that determines S_p is the distribution of the tangential or bond vectors of the chains, as eqs 2 and 3 suggest (see also ref 6).

Interaction Energy. Maier and Saupe[19] have developed a theory on the orientation-dependent dispersion forces between molecules with anisotropic polarizabilities. Later it was slightly modified by Flory and Ronca,[5] whose result suggests an E_o (per chain) of the form

$$E_o/nkT = -B^*\eta^2 \tag{7}$$

where η is the order parameter

$$\eta = (3/2)\langle\cos^2 \theta_i\rangle - (1/2) \tag{8}$$

with θ_i being the angle between the bond vector i and the director, and B^*T corresponds to the Flory–Ronca $T^*/2$. Here we will adopt eq 7.

Polymer Models. As models for semiflexible polymers, we consider the Kratky–Porod wormlike chain[20] (W chain) and the freely jointed chain (F chain) modified so that short as well as long chains can be treated.[7] This F chain comprises rodlike segments linearly connected by freely rotating joints, but unlike the conventional one, the joints in this chain are *randomly* distributed along the straight rod of length L with a constant joint density of b^{-1}: The average number of joints per chain is thus L/b, and b is the mean segment length of the infinitely long chain, equal to the persistence length q. The mean dimensions of this chain such as the mean-square end-to-end distance and radius of gyration are identical with those of the W chain of length L and persistence length q.[7]

The orientational free energy σ (reduced by T) of the F chain may be given by

$$\sigma = (m + 1)\sigma_r \qquad \text{F chain} \tag{9}$$

with $-\sigma_r$ being the orientational entropy of a rod

$$\sigma_r/k = \int f \ln(4\pi f)\, d\Omega \tag{10}$$

where f is the normalized probability density that a segment lies in the solid angle element $d\Omega$ and m is the mean number of joints per chain or the chain length reduced by q:

$$m = L/q \tag{11}$$

The σ of the W chain has been given in a perturbation expansion for the two limiting cases:[18]

$$\sigma = m\sigma_w - 2k \ln\left[\int (f/4\pi)^{1/2}\, d\Omega\right] \qquad m \gg 1 \tag{12a}$$

$$\sigma = \sigma_r + (2m/3)\sigma_w \qquad m \ll 1 \tag{12b}$$

with

$$\sigma_w/k = (1/8)\int (df/d\theta)^2 f^{-1}\, d\Omega \tag{13}$$

Computation for the Order–Disorder Transition Thresholds

In order to make the calculations feasible, we will adopt the Onsager trial distribution function[9,21]

$$f(\theta) = \left(\frac{\alpha}{4\pi \sinh \alpha}\right) \cosh(\alpha \cos \theta) \tag{14}$$

This distribution is characterized by the single parameter α, in terms of which ϱ, η, and σ_r are given as[9,21]

$$\varrho = \frac{1}{(\sinh \alpha)^2} \sum_{k=0}^{\infty} \frac{2\alpha^{2(k+1)}}{k!(k+2)!} \tag{15}$$

$$\eta = 1 - \left(\frac{3}{\alpha}\right)\left(\frac{\cosh \alpha}{\sinh \alpha}\right) + \frac{3}{\alpha^2} \tag{16}$$

$$\sigma_r/k = -1 + \ln \alpha + \ln\left(\frac{\cosh \alpha}{\sinh \alpha}\right) + \frac{\tan^{-1}(\sinh \alpha)}{\sinh \alpha} \tag{17}$$

Similarly, the integrations in eqs 12a and 13 with eq 14 can be evaluated to obtain the following approximate relations:[21]

$$\int (f/4\pi)^{1/2}\, d\Omega = \alpha/4 \qquad \alpha \gg 1 \tag{18}$$

$$\sigma_w/k = (\alpha - 1)/4 \qquad \alpha \gg 1 \tag{19}$$

The conditions for the nematic–isotropic equilibrium now read

$$\Delta F(\alpha) = 0 \tag{20a}$$

and

$$[\partial \Delta F(\alpha)/\partial \alpha]_{T,V} = 0 \tag{20b}$$

Obviously, ΔF is a function of the four parameters n, m, B^*, and α. Hence, given, e.g., B^* and n, eq 20 can be solved for α and m or x, the axial ratio of persistent segment:

$$x = q/D = n/m \tag{21}$$

We wish to do this for the four combinations of the chain models and the packing models, i.e., F chain/O model, F chain/L model, W chain/O model, and W chain/L model, which will be referred to as the F_O, F_L, W_O, and W_L systems, respectively.

With the σ of the W chain given by eq 12, we can obtain the solutions for a given value of B^* in the form

$$\alpha = \alpha_0 + \delta_1 m \qquad m \ll 1 \tag{22a}$$

$$\alpha = \alpha_\infty + \delta_3 m^{-1} \qquad m \gg 1 \tag{22b}$$

and

$$x = n_0 m^{-1} + \delta_2 \qquad m \ll 1 \tag{23a}$$

$$x = x_\infty + \delta_4 m^{-1} \qquad m \gg 1 \tag{23b}$$

where the subscripts 0 and ∞ denote the rigid rod limit and long-chain limit, respectively: for example, n_0 and x_∞ are the critical axial ratio of the rigid rod and that of the persistent segment of an infinitely long chain, respectively, required to stabilize the nematic phase. These as well as α_0, α_∞, and δ_i are a constant for a given model and B^*. Following Khokhlov and Semenov,[18,21] we assume that the general solution is approximated by a ratio of polynomials, the simplest of such ratios being

$$x/x_\infty = g(m) \tag{24a}$$

$$g(m) = \frac{1 + (\delta_4/x_\infty)m^{-1} + (\delta_2/x_\infty)m^{-2} + (n_0/x_\infty)m^{-3}}{1 + m^{-2}} \tag{24b}$$

It is easily confirmed that eq 24b satisfies eq 23. Similarly, other quantities of interest can be evaluated by using eqs 22 and 23. For example, the order parameter $\eta(\alpha)$ may be approximated by

$$\eta = \frac{\eta_\infty + \lambda_3 m^{-1} + \lambda_1 m^{-2} + \eta_0 m^{-3}}{1 + m^{-3}} \tag{25}$$

where $\eta_\infty = \eta(\alpha_\infty)$, $\eta_0 = \eta(\alpha_0)$, $\lambda_1 = \delta_1(\partial\eta/\partial\alpha)_0$, and $\lambda_3 = \delta_3(\partial\eta/\partial\alpha)_\infty$ with $\partial\eta/\partial\alpha$ obtainable from eq 16. In the case of the F chain, rigorous numerical solutions are obtainable for all m, but because we wished to obtain an analytical solution for convenience, we have adopted the above procedure also for the F chain. A comparison of rigorous and approximate solutions has suggested that the approximate procedure works very well in most cases.

Results and Discussion

Rigid Rod Limit. When q or x becomes infinitely large, the F and W chains tend to the same limit. In this rigid rod limit, therefore, only the difference of the packing models matters. Figure 1 shows the relation between B^* and n_0 for the two packing models. In both models, the critical axial ratio n_0 of the rod decreases with increasing energy parameter B^*, and when $n_0 = 1$, i.e., in the absence of the packing entropy contribution, $B^* = 2.31$. This limit corresponds to the Maier–Saupe (MS) theory.[19] Our value does not exactly agree with the MS value of 2.27[5,19] (in the B^* notation) due to the use of the approximate distribution function of Onsager. The difference is minor, however. When $B^* = 0$, n_0 is 5.50 for the O model and 8.28 for the L model. For n_0 larger than these values, the respective models predict the absolute stability of the nematic phase irrespective of B^* (≥ 0).

The O model here is essentially similar to the Kimura (K) model,[16] in which both soft and hard interactions were considered in a mean-field-type approximation. According to the K model, $n_0 = 5.20$ for $B^* = 0$. The rather small difference between this and the O model value comes partly from the difference in the approximations used and partly from the difference in the geometries of the rod ends assumed in the two models. (The K model treats a spherocylinder, while the O model takes account of the end effect in the form of eq 2, as is suggested by the lattice model, eqs 3 and 6.) The nearest counterpart of the L model may be the Flory–Ronca (FR) theory,[5] which is a combination of the Flory lattice model[14] and the MS-type soft interaction model. The FR value of n_0 for $B^* = 0$ is 6.42.[5,22] The difference between this and the L model values comes mainly from the difference between the two lattice models. (For $n = 1$, for example, $S_p > 0$ in the Flory lattice, while $S_p = 0$ in the L model).

Figure 2 shows the order parameter η of the nematic phase at coexistence as a function of n_0. Both models predict that η increases with increasing n_0. When $n_0 = 1$ or in the MS limit, we have $\eta = 0.393$, which again differs from the MS value of 0.429[5,19] due to the use of the Onsager function. In contrast to the O model that

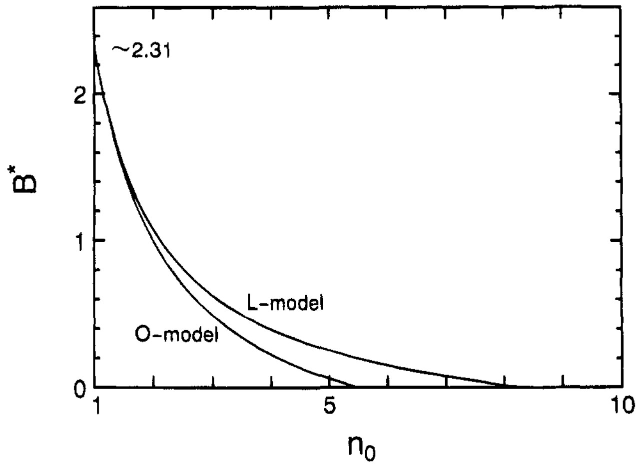

Figure 1. Relation between the critical axial ratio n_0 of the rigid rod ($q = \infty$) and the interaction parameter B^* for the O and L models.

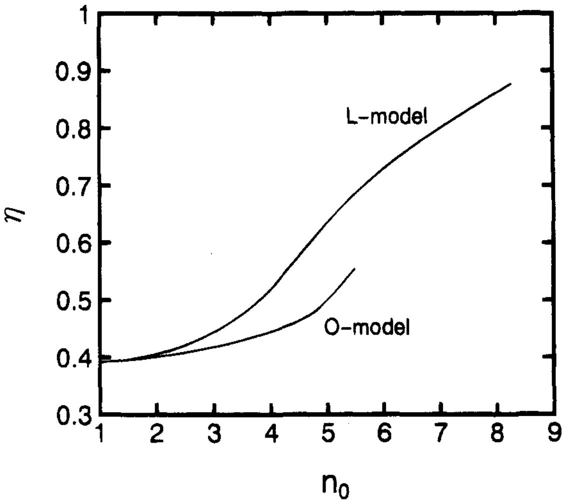

Figure 2. Order parameter $\eta = P_2(\cos\theta)$ as a function of the critical axial ratio n_0 of the rigid rod ($q = \infty$) for the O and L models.

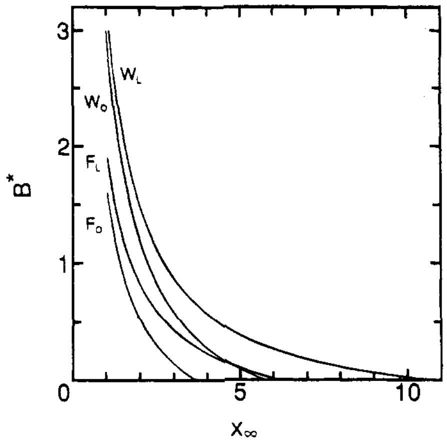

Figure 3. Relation between the critical axial ratio x_∞ of the persistent segment in the infinitely long chain and the interaction parameter B^* for the F_L, F_O, W_L, and W_O systems.

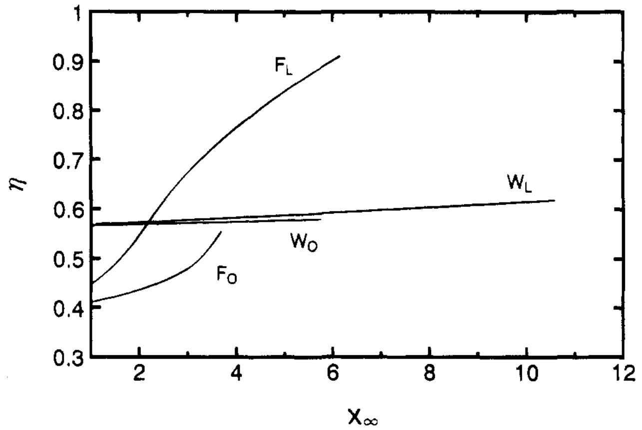

Figure 4. Order parameter $\eta = P_2(\cos\theta)$ as a function of the critical axial ratio x_∞ of the persistent segment in the infinitely long chain for the F_L, F_O, W_L, and W_O systems.

predicts an increase of η with n_0, the K theory predicts a constant η independent of n_0.[16] This is due to the particular approximation used in the K theory. In view of the admirable accuracy of the Onsager distribution function, the prediction of the O model might be more reliable in this particular respect. The L model predicts somewhat smaller η than the FR model,[5] but the general features of the two models are similar.

Long-Chain Limit. When the number of persistent segments, m, becomes infinitely large, ΔF becomes a function of B^*, α, and x only. Figure 3 shows the relation between B^* and the segmental axial ratio x_∞ in this limit for the four combinations of the models. In all cases, x_∞ decreases as B^* increases, as it should be. The values of x_∞ at $B^* = 0$ are 3.68 (F_O), 6.16 (F_L), 5.75 (W_O), and 10.59 (W_L). The x_∞ values for the F_O and F_L models (at $B^* = 0$) are considerably smaller than the corresponding values of n_0 for the O and L models, respectively (see above). This is because the end effect disappears for long chains.

In relation to the F_L and W_L models, we should note that Flory[23] has proposed treating a long semiflexible polymer as a collection of rods having a length equal to the Kuhn length b_K, and combining this freely jointed chain with the Flory lattice model, he predicted that the nematic phase is absolutely stable for $x_K = b_K/D \geq 6.42$. This critical x_K value is identical with the n_0 value of the FR theory and nearly the same as the x_∞ value of the F_L model (with $B^* = 0$). Since $b_K = 2q$ for the W and F chains, it follows that the critical value of x_∞ predicted by Flory is 3.21, about half the F_L value and about one-third the W_L value. Aside from these large numerical differences, it is difficult to model short chains with the Kuhn freely jointed chain with its discrete segment length.

Figure 4 shows the η vs x_∞ relation at coexistence. In the F_L and F_O systems η strongly depends on x_∞, while in the W_L and W_O systems η stays in a narrow range around 0.6 for all x_∞. Values of η larger than about 0.7 are predictable only by the F_L model.

Intermediate-Chain-Length Region. Now we turn to the main subject. We have seen that each of the four models has the critical values of n_0 and x_∞ to stabilize the nematic phase. Here n_0 refers to the critical axial ratio of a rigid rod or a chain molecule with infinitely large q or x. In other words, in order for a molecule of length n_0 to form a nematic phase, its x has to be infinitely large. On the other hand, the critical condition for a long enough chain is that $x = x_\infty$. Therefore, as the chain length increases from n_0 to a very large value with other conditions fixed, the critical value of x has to decrease from infinity to the contant value x_∞. We have evaluated this critical x vs n (or m) relation for the four models.

Figure 5 shows the plot of $\ln(x/x_\infty)$ vs $\log m$ for the case with $B^* = 0$. (To obtain $g(m) = x/x_\infty$ for this case,

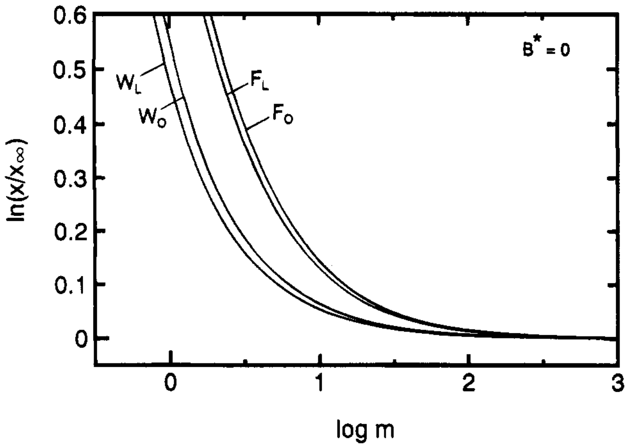

Figure 5. Plot of $\ln(x/x_\infty)$ vs log m at the transition for the F_L, F_O, W_L, and W_O systems with $B^* = 0$.

Table 1. Values of the Parameters in Equations 22–25 for the F_L, W_L, F_O, and W_O Systems with $B^* = 0$

	system			
param	F_L	W_L	F_O	W_O
α_0	23.428	23.428	5.528	5.528
δ_1	4.737	−306.071	0.000	18.754
n_0	8.282	8.282	5.499	5.499
δ_2	6.329	10.984	3.807	3.977
η_0	0.877	0.877	0.555	0.555
α_∞	32.785	6.705	5.528	5.940
δ_3	−19.640	−2.462	0.000	−2.731
x_∞	6.159	10.590	3.681	5.755
δ_4	8.533	5.934	5.681	3.842
η_∞	0.911	0.619	0.556	0.580

eq 24 can be used along with the parameter values listed in Table 1.) The ordinate scale has been reduced by x_∞ so that for $m \to \infty$, $x/x_\infty \to 1$. All the curves show the expected trend that x/x_∞ decreases with increasing m, approaching unity for large m ($>10^2$). Particularly noteworthy is the fact that the differences among the models are rather small in this plot. Above all, the F_L and F_O curves are very close to each other. Similarly, the W_L and W_O curves are nearly the same. This suggests that the x/x_∞ vs m relation is generally insensitive to the models of intermolecular interactions. This can be confirmed in Figure 6, which gives the results obtained for various values of B^*. We see that the plot is virtually independent of B^* in all cases. In Figure 7, the order parameter η is shown as a function of m and B^*.

Correspondence with Real Systems. The m dependence of the critical x predicted by the models offers an important clue for interpreting the chain length dependence of the isotorpization temperature T_i commonly observed in real systems. As noted in the Introduction, the T_i of many semiflexible polymers increases with increasing chain length to approach a constant value T_∞ for sufficiently long lengths. In addition, their flexibilities change with temperature so that the following relation holds at least in a limited range of temperature:

$$\partial \ln q/\partial T = -\beta \tag{26}$$

with β being usually a positive constant. Hence writing

$$\ln(x/x_\infty) = -\beta(T_\infty - T_i) \tag{27}$$

we can recast the $\ln(x/x_\infty)$ vs m curve into a T_i vs L relation by knowing x_∞, β, and T_∞. This provides a powerful means to experimentally test the models and check the reality of the underlying hypothesis of "flexibility induced transition", an origin of thermotropicity unique to semiflexible polymers.

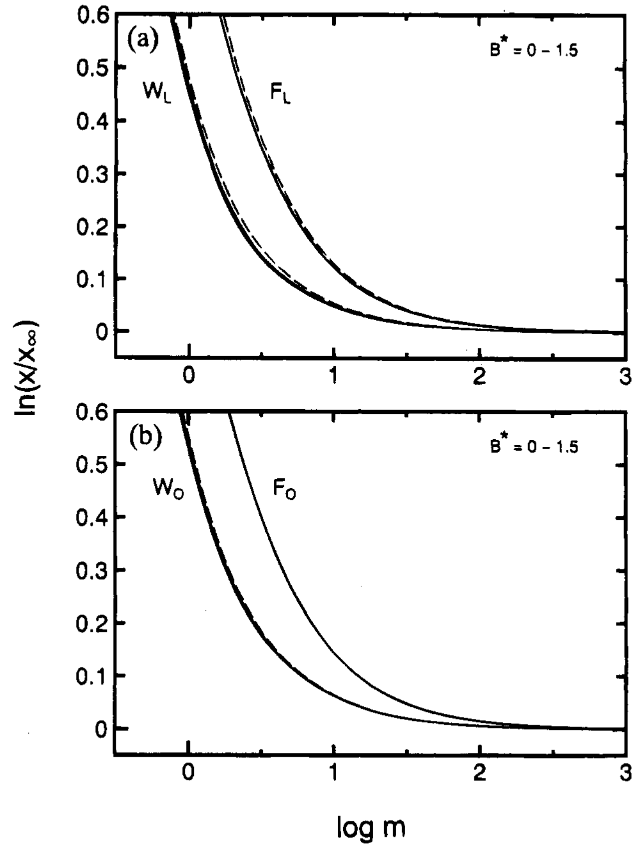

Figure 6. Plot of $\ln(x/x_\infty)$ vs log m at the transition for (a) the F_L and W_L systems and (b) the F_O and W_O systems with $B^* = 0$ (broken line), and 0.5, 1.0, and 1.5 (solid lines).

Another point of particular interest may be the chain length dependence of the transition enthalpy. Since the relaxation of a semiflexible polymer (with a temperature-dependent flexibility) from an oriented conformation in the nematic state to an unrestricted one in the isotropic state must be endothermic, the transition would always accompany a nonzero latent heat ΔH, even when $E_0 = 0$. The component of ΔH arising from this source, ΔH_C, will be absent in rigid rod systems, and hence it is expected that as the chain length increases, ΔH_C per unit chain length will increase from zero to a constant value for long chains.

The theoretical evaluation of ΔH_C, however, encounters the fundamental difficulty that neither the F and W chains nor other chain models devised so far fail to predict the large values of β often observed for thermotropic semiflexible polymers: for example, βT values of 1.6–2.4 (cellulose derivatives)[4,24] and 3.6 (poly(n-hexyl isocyanate))[4] have been reported. The W chain, viewed as a wire with a characteristic bending force constant,[25] has a constant βT of 1, but real polymers with this βT value are rather few. The F chain is even more artificial and difficult to be associated with a temperature-dependent segment length in a consistent fashion. For enhanced applicabilties of the W chain, Ronca and Yoon[26] have introduced a cutoff length to restrict the maximum curvature allowed for the W chain. Combining this new model with the Flory lattice, they developed a theory of nematic–isotropic transition in the bulk polymer, demonstrating the chain length dependence of T_i and ΔH_C. Unfortunately, however, their model is

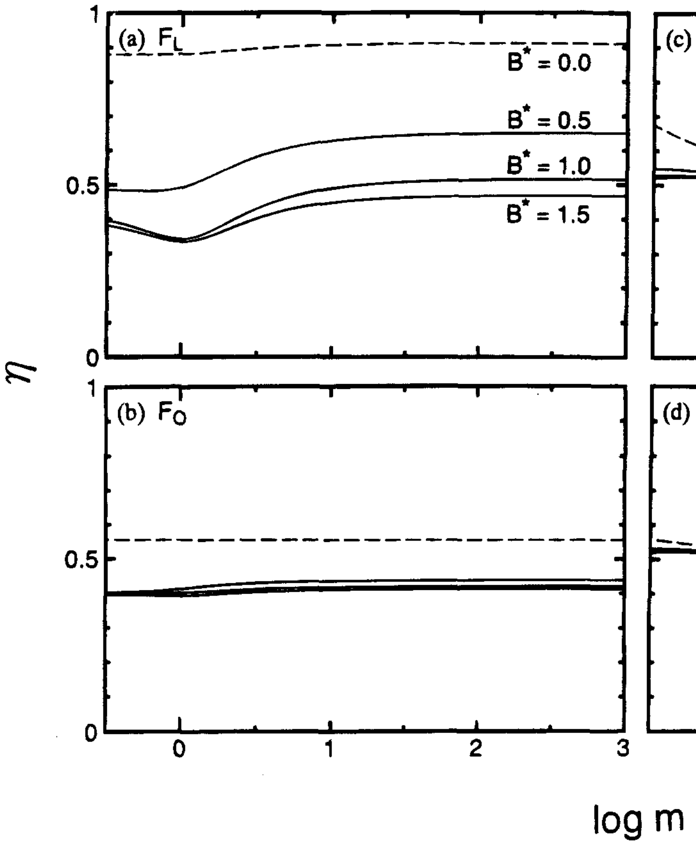

Figure 7. Order parameter $\eta = P_2(\cos\theta)$ as a function of log m for the (a) F_L, (b) F_O, (c) W_L, and (d) W_O systems with $B^* = 0$, 0.5, 1.0, and 1.5 (from top to bottom).

applicable only to polymers with $0 \le \beta T \le 1$.

With these obvious defects of the F and W chains in mind, we write

$$\Delta H = -\left[\frac{\partial(\Delta F/T)}{\partial T^{-1}}\right]_{V,n,\alpha} = \Delta H_E + \Delta H_C \tag{28}$$

where

$$\Delta H_E/nkT_i = B^*\eta^2 \tag{29}$$

is the enthalpy change arising from the soft interaction, and ΔH_C is obtained from

$$-\Delta H_C/k = [\partial\sigma/\partial T^{-1}]_{V,n,\alpha} \tag{30}$$

Writing $\partial\sigma/\partial T^{-1} = (\partial\sigma/\partial m)(\partial m/\partial x^{-1})(\partial x^{-1}/\partial T^{-1})$ and formally evaluating $(\partial\sigma/\partial m)_{V,n,\alpha}$ according to the previous models, we can cast the result in the form

$$\Delta S_C/nk = (\beta T_i\sigma_\infty/x_\infty)h(m) \tag{31}$$

where $\Delta S_C = \Delta H_C/T_i$, $\sigma_\infty = \sigma_r(\alpha_\infty)$ (eq 17) or $\sigma_w(\alpha_\infty)$ (eq 19), β is as given by eq 26, and $h(m)$ is a function of m such that $h(\infty) = 1$ and $h(0) = 0$. As already noted, this discussion is internally consistent only for the W chain (with $\beta T_i = 1$). We have evaluated the $h(m)$ for the W_L and W_O systems according to the interpolation method using a polynomial ratio (see above). Figure 8 shows the $\Delta S_C/nk$ vs m relation thus obtained for the two W chain systems ($\beta T_i = 1$) with several values of B^*. The expected trend that ΔS_C approaches zero for short chains is clear. Also notably, the absolute values of ΔS_C for long chains are fairly large especially when B^* is large. Real systems with $\beta T_i > 1$ can have even greater ΔS_C. The overall entropy change ΔS is given by the sum $\Delta S_E + \Delta S_C$ with $\Delta S_E = \Delta H_E/T_i$ (see eq 29 and Figure 7).

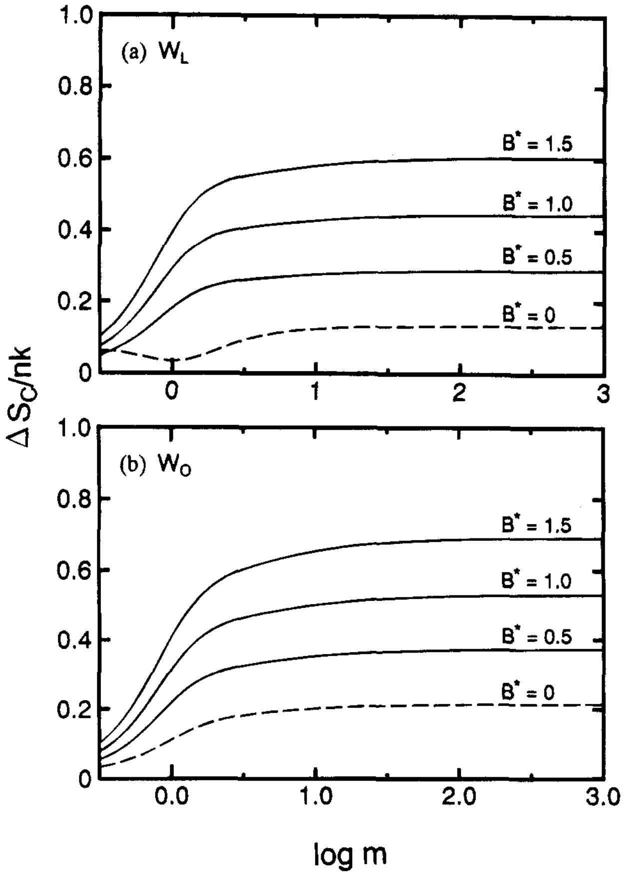

Figure 8. Plot of $\Delta S_C/nk$ vs log m for the (a) W_L and (b) W_O systems with $B^* = 0$, 0.5, 1.0, and 1.5.

To summarize, we have discussed the chain-length dependence of the nematic–isotropic transition behavior of semiflexible polymers in the bulk on the basis of various sets of simple statistical models. Even though the critical values of x depend largely on the models, the ratio x/x_∞ as a function of m shows reasonably weak dependence on the models, indicating some universality of the T_i vs chain-length relation scaled properly. The entropy change ΔS_C related to the chain conformation increases from virtually zero for short chains to an important level, as the chain length increases. These predictions will be quantitatively tested by experiments in a forthcoming paper.[27]

References and Notes

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