Macromolecules **1990**, *23*, 5341–5346

A Lattice Model for Segmental Orientation in Deformed Polymeric Networks. 2. Effect of Chain Stiffness and Thermotropic Interactions

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Received January 16, 1990; Revised Manuscript Received May 7, 1990

ABSTRACT: The lattice model of segmental orientation developed in the preceding paper for athermal network chains subject to uniaxial deformation is extended in the present work to the case of (i) Kuhn segments with increased stiffness characterized by a relatively large length-to-width ratio, x, and (ii) thermotropic systems with anisotropic polarizabilities. Those two factors, of entropic and energetic character, respectively, contribute both to a first-order transition from a relatively disordered to a highly oriented structure, upon imposition of an external perturbation. This transition is observed from the abrupt rise in the orientation function accompanying the stretch under well-defined molecular characteristics and environmental conditions.

1. Introduction

The lattice model developed in the preceding manuscript[1] permits a critical assessment of the relative contributions of intermolecular and intramolecular effects on segmental orientation in deformed network chains. The fundamental hypothesis underlying the theory is the approximation of the individual chains by freely jointed Kuhn segments of rodlike character. The concept of equivalent freely jointed chains has proved to be of great utility in gaining insights into the statistical behavior of polymers. Likewise, its adoption for the treatment of segmental orientation in deformed networks reveals that, for relatively flexible chains (i.e. $x \leq 3$, where x is the axial ratio of rodlike Kuhn segments), the intermolecular interferences in the form of competition for space between neighboring chains is only of minor importance compared to the orienting effect of intramolecular origin. In more specific terms, throughout the range of extension ratios $\lambda \leq 5$, the percent increase in the orientation function due to packing constraints does not exceed 15%.[1] This effect is further reduced in swollen networks as expected from the higher free volume allocated to the chains in this latter case.

In the present work we will concentrate on networks having relatively stiffer chains. Cross-linked polyesters with aromatic groups on the main chain constitute an example of such networks. In view of the model developed in the preceding manuscript, an increase in chain stiffness corresponds to an increase in the asymmetry of Kuhn segments composing the chains. It is known that beyond a critical axial ratio x_c, systems of rodlike particles spontaneously split into two phases, differing in the degree of anisotropy.[2-5] Such a phase transition is expected to occur even more easily if the existing entropic driving forces are supplemented by orientation-dependent energetic contributions.[6,7] Here we attempt to visualize the influence of an external perturbation, the uniaxial stretching, on the phase transition behavior of such relatively rigid chains. Both athermal and thermotropic conditions will be explored with the purpose of understanding how orientation on a molecular level is affected by macroscopic parameters such as deformation ratio and temperature.

The organization of the paper is as follows: In the succeeding section, the application of the formulation of ref 1 to the phase equilibrium problem in dry networks will be presented together with its extension to thermotropic systems. An approximate expression for orientation applicable to weakly deformed and relatively flexible chains will be presented in the same section. Illustrative calculations and discussion in section 3 will be followed finally by some concluding remarks.

2. Theory

General Formulation for Athermal Systems. We will consider a system of n_2 monodisperse network chains consisting each of m Kuhn segments with length-to-width or axial ratio x. The orientation of a given segment is characterized by two angles, Ψ_k and ϕ_k. The former represents the azimuthal angle between the rodlike segment and the preferred direction, which is referred to as the domain axis or the nematic director. The latter is the angle of rotation about the domain axis. In order to accommodate the rods within the n_0 sites of a lattice, each rod is approximated by a sequence of y_k submolecules, directed along the domain axis, such that[1-5]

$$y_k = x \sin \Psi_k(|\cos \phi_k| + |\sin \phi_k|) \tag{1}$$

Thus, y_k characterizes the spatial orientation of a given rod and is referred to as its disorientation index. Accordingly, the mean disorientation index for the system of n_2 chains is defined by

$$\bar{y} = \frac{1}{n_2 m} \sum_{l=1}^{n_2} \sum_k n_{l,k} y_k \tag{2}$$

where $n_{l,k}$ indicates the number of segments of the lth chain, whose orientation lies within the kth solid angle.

We will direct our attention to the determination of the orientation function

$$S = \langle P_2(\cos \Psi) \rangle = \frac{3}{2}\langle \cos^2 \Psi \rangle - \frac{1}{2} \tag{3}$$

Here, the brackets refer to the ensemble average over all segments of network chains, Ψ represents the angular

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deviation of rodlike segments from the direction of stretch inasmuch as the domain axis is naturally identified with the direction of stretch. The quantity $\langle \cos^2 \Psi \rangle$ is found from

$$\langle \cos^2 \Psi \rangle = \frac{\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\Psi \cos^2 \Psi \, f(\phi,\Psi)}{\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\Psi \, f(\phi,\Psi)} \quad (4)$$

where $f(\phi,\Psi)$ is the orientational distribution function, which for athermal systems subject to uniaxial deformation assumes the form[1]

$$f(\phi,\Psi) = \sin \Psi \exp[-ax \sin \Psi[|\cos \phi| + |\sin \phi|] + \beta \cos \Psi + \gamma \sin \Psi(\cos \phi + \sin \phi)] \quad (5)$$

with

$$a \equiv -\ln [1 - \upsilon_2(1 - \bar{y}/x)] \quad (6)$$

Here υ_2 is the volume fraction of the network chains, and β and γ are the two Lagrange multipliers to be determined together with $\bar{y}$ from the simultaneous solution of[1]

$$\frac{\lambda}{(3m)^{1/2}} = \frac{\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\Psi \cos \Psi \, f(\phi,\Psi)}{\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\Psi \, f(\phi,\Psi)} \quad (7)$$

$$\frac{1}{(3m\lambda\upsilon_2)^{1/2}} = \frac{\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\Psi \sin \Psi \cos \phi \, f(\phi,\Psi)}{\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\Psi \, f(\phi,\Psi)} \quad (8)$$

and

$$\frac{\bar{y}}{x} = \frac{\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\Psi \sin \Psi[|\cos \phi| + |\sin \phi|] \, f(\phi,\Psi)}{\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\Psi \, f(\phi,\Psi)} \quad (9)$$

Here λ is the extension ratio, i.e., the ratio of the final length to the unswollen, undeformed length. The set of eqs 5–9 applies to athermal systems, i.e., in the absence of intermolecular energetic interactions between neighboring chains. It incorporates both steric or space-filling characteristics of the segment and the additional contribution of the external perturbation to orientation. In the presence of orientation-dependent dispersion interactions between molecules, as occurs in typical nematogens with anisotropic polarizabilities, the above formulation should be modified to include, as well, the energetic contribution to orientation. The treatment presented below for thermotropic systems applies to dry networks inasmuch as in the presence of significant amounts of solvent, polymer–polymer energetic interactions become vanishingly small by the increase in intermolecular distances.

Extension to Thermotropic Systems. Let us consider two cylindrically symmetric subsegments k and l belonging to Kuhn segments that make the respective angles Ψ_k and Ψ_l with the nematic director.[8] The centers of the two subsegments are assumed to be separated by a distance r_{kl}. The interaction ϵ_{kl} between the pair is expressed as[5]

$$\epsilon_{kl} = -C r_{kl}^{-6} \Delta\alpha_k \Delta\alpha_l P_2(\cos \Psi_{kl}) = -C r_{kl}^{-6} \Delta\alpha_k \Delta\alpha_l \left(\frac{3}{2} \cos^2 \Psi_{kl} - \frac{1}{2}\right) \quad (10)$$

where $\Delta\alpha_k$ is the difference between the longitudinal and transverse polarizabilities of subsegment k, Ψ_{kl} is the angle between the axes of the two subsegments, and C is a constant. For a fixed subsegment k, using the addition theorem for spherical harmonics, $P_2(\cos \Psi_{kl})$ averaged out over all possible orientations of subsegment l equates to

$$\langle P_2(\cos \Psi_{kl}) \rangle = \langle P_2(\cos \Psi_l) \rangle P_2(\cos \Psi_k) = S P_2(\cos \Psi_k) \quad (11)$$

Upon substitution of eq 11 into eq 10 and consideration of the interaction between only nearest pairs as the inverse sixth power dependence on separation allows, the average orientation-dependent energy of interaction for a subsegment inclined at an angle Ψ_k to the domain axis takes the form

$$\epsilon(\Psi_k) = -\frac{C z_c S}{r_*^{6} \tilde{V}} \Delta\alpha_k \Delta\alpha P_2(\cos \Psi_k) \quad (12)$$

where z_c is the number of first neighbors surrounding the segment, $\Delta\alpha$ is the mean anisotropy of all segments, r_* is the distance between subsegments for dense packing, and $\tilde{V}$ is a reduced volume, which will be taken as unity throughout the present study, in conformity with previous work.[5] If $\epsilon(\Psi_k)$ is construed as the mean orientational energy of a subsegment, $\Delta\alpha_k$ is also replaced by $\Delta\alpha$, and the average orientation-dependent interaction energy for a Kuhn segment composed of x subsegments becomes

$$E(\Psi_k) = x\epsilon(\Psi_k) = -\frac{k_B T}{\tilde{T}} S P_2(\cos \Psi_k) \quad (13)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and the reduced temperature $\tilde{T}$ is defined by[5,7]

$$\tilde{T} = \frac{k_B T}{x} \left[\frac{C z_c (\Delta\alpha)^2}{r_*^{6}} \right]^{-1} \quad (14)$$

The total contribution to the Helmholtz free energy arising from the above orientation-dependent interactions between the mn_2 Kuhn segments may be written as

$$E_{\mathrm{orient}} = \sum_{l=1}^{n_2} \sum_k n_{l,k} E(\Psi_k) \quad (15)$$

This factor may be incorporated within the orientational partition function, Z_{orient}, which then reads

$$Z_{\mathrm{orient}} = \prod_{j=1}^{n_2} m! \times \prod_k \frac{\left[\frac{1}{4\pi} \sin \Psi_k \, \mathrm{d}\Psi_k \, \mathrm{d}\phi_k \exp\{S \tilde{T}^{-1} P_2(\cos \Psi_k)\} \right]^{n_{j,k}}}{n_{j,k}!} \quad (16)$$

The above expression directly follows from the eq 8 of the preceding paper, in which the solid angle ω_k is replaced by $(1/4\pi) \sin \Psi_k \, \mathrm{d}\Psi_k \, \mathrm{d}\phi_k$ and each angular deviation Ψ_k from the nematic director is weighted by the corresponding Boltzmann factor $\exp\{-\sum_{l=1}^{n_2} n_{l,k} E(\Psi_k)/k_B T\}$.

The combinatorial part of the partition function, Z_{comb}, remains unaffected by the presence of those interactions. The new form of Z_{orient} given by eq 16 is readily inserted in the Helmholtz free energy of mixing ΔA_{m}

$$\Delta A_{\mathrm{m}} = -k_B T(\ln Z_{\mathrm{comb}} + \ln Z_{\mathrm{orient}}) \quad (17)$$

where $\ln Z_{\mathrm{comb}}$ is given by[1]

$$-\ln Z_{\mathrm{comb}} = n_1 \ln \upsilon_1 + n_2 \ln (\upsilon_2/mx) - (n_1 + n_2 m\bar{y}) \ln [1 - \upsilon_2(1 - \bar{y}/x)] + n_2(m\bar{y} - 1) - n_2(m - 1) \ln (z - 1) \quad (18)$$

in which $\upsilon_2 = 1$ is used for thermotropic systems. Minimization of ΔA_{m} following the method of Lagrange multipliers described in detail in the preceding manuscript leads to four nonlinear equations to be solved simultaneously: three of them are in form identical with eqs 7–9 with the exception of the new equilibrium distribution of orientations $f_t(\phi,\Psi)$ replacing $f(\phi,\Psi)$. The subscript t is appended to $f_t(\phi,\Psi)$ to indicate that this distribution function applies to thermotropic systems. It takes the form

$$f_t(\phi,\Psi) = \sin\Psi \exp\{-ax \sin\Psi[|\cos\phi| + |\sin\phi|] + \beta\cos\Psi + \gamma\sin\Psi(\cos\phi + \sin\phi) + S\tilde{T}^{-1}P_2(\cos\Psi)\} \quad (19)$$

and reduces to $f(\phi,\Psi)$ if $T \to \infty$ and $\Delta\alpha \to 0$, as follows from eq 14. Since those equations contain implicitly the orientation function S, self-consistency requires their simultaneous solution with the fourth nonlinear equation

$$S = \frac{\int_0^{2\pi}\mathrm{d}\phi \int_0^{\pi}\mathrm{d}\Psi\, P_2(\cos\Psi)\, f_t(\phi,\Psi)}{\int_0^{2\pi}\mathrm{d}\phi \int_0^{\pi}\mathrm{d}\Psi\, f_t(\phi,\Psi)} \quad (20)$$

It is not difficult to conceive that the set of four nonlinear equations with double integrations is a tough numerical problem. It is interesting to verify, however, that the problem can be simplified to a considerable extent by preaveraging the ϕ dependence prior to numerical integrations over Ψ. Accordingly

$$y_k = (4/\pi)x \sin\Psi_k \quad (21)$$

is adopted instead of eq 1 and γ is equated to 0. This simplification brings about an incomparably large reduction in computation time. The resulting deviation from the exact solution is insignificant for sufficiently large deformations. On the other hand, for small deformations a linearized solution, which closely approximates, the exact solution may be adopted. The latter will be presented below.

In the case of preaveraging, the problem reduces to the simultaneous solution of

$$\frac{\lambda}{(3m)^{1/2}} = \frac{\int_0^{\pi}\mathrm{d}\Psi \cos\Psi\, h(\Psi)}{\int_0^{\pi}\mathrm{d}\Psi\, h(\Psi)} \quad (22)$$

$$\frac{\bar{y}}{x} = \frac{\frac{4}{\pi}\int_0^{\pi}\mathrm{d}\Psi \sin\Psi\, h(\Psi)}{\int_0^{\pi}\mathrm{d}\Psi\, h(\Psi)} \quad (23)$$

and

$$S = \frac{\int_0^{\pi}\mathrm{d}\Psi\, P_2(\cos\Psi)\, h(\Psi)}{\int_0^{\pi}\mathrm{d}\Psi\, h(\Psi)} \quad (24)$$

where the equilibrium distribution of orientations $h(\Psi)$ is given by

$$h(\Psi) = \sin\Psi \exp\left\{-\frac{4}{\pi}ax\sin\Psi + \beta\cos\Psi + S\tilde{T}^{-1}P_2(\cos\Psi)\right\} \quad (25)$$

Equations 22–25 will be the basic equations employed in the calculations. Before proceeding to them an approximate analytical solution will be presented. The applicability of the latter is restricted to a weakly ordered regime.

Approximate Expression for the Orientation Function in Thermotropic Systems. In analogy to the treatment of the preceding paper, for small β, γ, α, and $S\tilde{T}^{-1}$, both numerators and denominators in eqs 7–9 and 20 (with the equilibrium distribution of orientations given by eq 19 inserted in each of them) may be expanded in the Taylor series and truncated after a few leading terms. Thus, in a first approximation we obtain, using $v_2 = 1$

$$\beta \cong (3/m)^{1/2}\lambda \quad (26)$$

$$\gamma \cong (3/m\lambda)^{1/2} \quad (27)$$

$$\frac{\bar{y}}{x} \cong 1 - \frac{ax}{3}\left(\frac{4}{\pi} - 1\right) - \frac{1}{24}(\beta^2 - \gamma^2) - \frac{1}{8}S\tilde{T}^{-1} \quad (28)$$

$$S \cong \frac{1}{8}ax + \frac{1}{15}(\beta^2 - \gamma^2) + \frac{1}{5}S\tilde{T}^{-1} \quad (29)$$

Substituting eq 28 into eq 6 and expanding the logarithm, we obtain

$$a = \frac{\frac{1}{24}(\beta^2 - \gamma^2) + \frac{1}{8}S\tilde{T}^{-1}}{1 - \frac{x}{x_a}} \quad (30)$$

where x_a is the axial ratio beyond which the isotropic phase disappears for an undeformed network. The subscript a refers to the anisotropic single phase prevailing beyond the axial ratio. Equation 30 is used in eq 29 to yield, with the help of eqs 26 and 27

$$S = \frac{1}{5m}\left(\lambda^2 - \frac{1}{\lambda}\right)\left[\frac{u}{1 - \tilde{T}^{-1}u/5}\right] \quad (31)$$

with

$$u \equiv 1 + \frac{5x}{64}\left[1 - \frac{x}{x_a}\right]^{-1} \quad (32)$$

Equation 31 reduces to eq 49 of the preceding paper for $\tilde{T}^{-1} = 0$. This result will be discussed in the last section in relation to an analogous expression obtained by Jarry and Monnerie.[10]

3. Calculations and Discussion

Following the criterion for coexistence of two phases, the differential changes in the respective free energies with respect to any driving force have to be equal to each other, for the two phases in equilibrium. Thus, for conventional biphasic systems where the two phases differ in their composition, equilibrium is achieved when the two partial derivatives of free energies with respect to mole numbers, i.e., by definition the two chemical potentials, equate to each other. In the present work, inasmuch as we confine our attention to dry systems, composition is not the property of interest, but instead the degree of orientation characterized by $\bar{y}$ (or S) distinguishes the two phases. Thus a stable phase is the one whose free energy is minimum with respect to the distribution of orientations. Inasmuch as the method of Lagrange multipliers relies on the differentiation of the free energy with respect to $n_{l,k}$, the resulting set of equations will automatically yield solutions corresponding to an extremum of ΔA_m. More explicitly, let us suppose that we solve the set of eqs 22–24, coupled with eq 25, for the unknowns β, $\bar{y}/x$, and S. The results must necessarily satisfy the condition $\partial\Delta A_m/\partial n_{l,k} = 0$. Whether the solution represents a minimum or a maximum of ΔA_m should be checked to ascertain the stability of the resulting phases. In the presence of more than one free energy minimum, the state with the lowest free energy is the most stable one.

For a clearer understanding of the dependence of the free energy on the orientational distribution of Kuhn segments, preliminary calculations have been performed for the simplest case of athermal and undeformed systems. Chains consisting of $m = 20$ segments have been considered

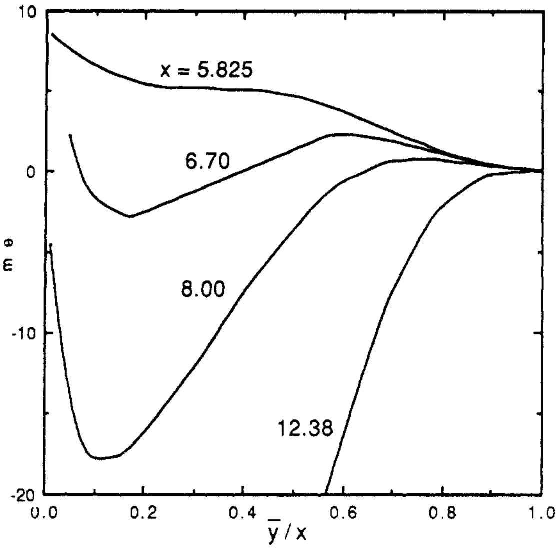

Figure 1. Dependence of the excess free energy with respect to the isotropic state, $(\Delta A_m)_e$, on the normalized disorientation index, $\bar{y}/x$. The curves are obtained for athermal, dry, undeformed network chains consisting each of $m = 20$ Kuhn segments with the indicated various length-to-width ratios x, which are characteristic of chain stiffness.

in the calculations. Figure 1 displays the results obtained for various stiffnesses of Kuhn segments as characterized by the x values 5.825, 6.7, 8.00, and 12.38. The abscissa $\bar{y}/x$ varies from 0, for complete alignment of rods, to 1 for isotropic systems. The ordinate is the excess free energy $(\Delta A_m)_e$ relative to that in the isotropic state, per chain, in dimensionless form. It is obtained from

$$(\Delta A_m)_e = [(\Delta A_m)_{\text{aniso}} - (\Delta A_m)_{\text{iso}}]/n_2 k_B T \qquad (33)$$

The free energies in the anisotropic and isotopic phases $(\Delta A_m)_{\text{aniso}}$ and $(\Delta A_m)_{\text{iso}}$ may be evaluated with the help of eqs 16–18. They differ in their disorientation index, which assumes the value x in the case of isotropic systems. For the particular case of dry, athermal, undeformed networks, this difference reduces to

$$(\Delta A_m)_e = m(\bar{y} - x + \ln 4\pi - \ln Z) \qquad (34)$$

where Z is defined as

$$Z \equiv \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\Psi \sin \Psi \exp\{-ax \sin \Psi[|\cos \phi| + |\sin \phi|]\} \cong 2\pi \int_0^{\pi} \mathrm{d}\Psi \sin \Psi \exp\left\{-\frac{4}{\pi} ax \sin \Psi\right\} \qquad (35)$$

The last equality follows from preaveraging over ϕ. Calculations indicate that, for $x < 5.825$, $(\Delta A_m)_e$ is a strictly monotonically increasing function as $\bar{y}/x$ decreases from 1 to 0 and the isotropic limit is the only state satisfying the requirement $\partial \Delta A_m/\partial n_{l,k} = \partial(\Delta A_m)_e/\partial \bar{y} = 0$. At $x = x_c = 5.825$, a point where both the first and second derivatives of ΔA_m equate to zero is observed. The latter may be found either from the examination of the $(\Delta A_m)_e$ vs $\bar{y}/x$ curve or by the simultaneous solution of eqs 22–24 coupled to eq 25. This corresponds to the first appearance of a new minimum in the free energy, though the latter is a metastable equilibrium state inasmuch as its energy is larger than that of the isotropic state. The corresponding disorientation index and orientation function are 0.330 and 0.847, respectively. As the asymmetry of the Kuhn segments gets larger, the excess energy of the anisotropic phase gradually decreases and equates to that of the isotropic phase at $x = 6.42$. This represents the axial ratio for the first-order phase transition from the isotropic to the anisotropic (nematic) state. Above $x = 6.42$, the free energy of the anisotropic phase is less than that of the isotropic one. Thus the anisotropic phase is the most stable phase, and beyond $x_a = 1/[32/3\pi^2 - 1] = 12.38$ the isotropic minimum totally disappears as indicated by the nonzero slope of $(\Delta A_m)_e$ at $\bar{y}/x = 1$, for $x \geq x_a$.

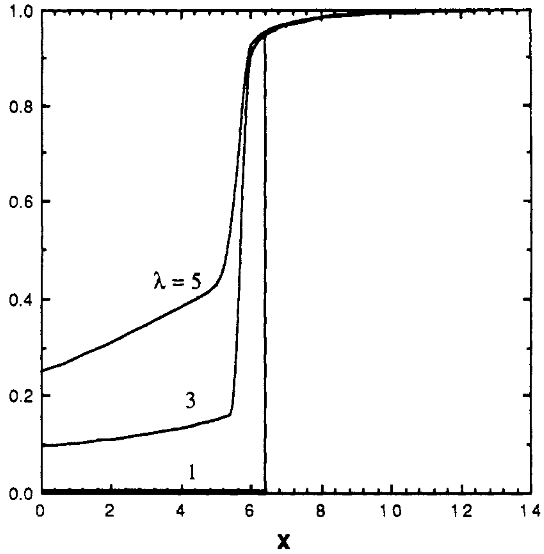

Figure 2. Dependence of orientation function S on the axial ratio x of the Kuhn segments in network chains. Curves are obtained for athermal dry networks with $m = 20$ and subject to uniaxial tension with the indicated extension ratios λ. The networks exhibit a first-order phase transition from isotropic to anisotropic state, as apparent by the abrupt rise in the orientation function.

The above analysis gives a clear picture of the dependence of phase behavior on chain stiffness, in the absence of any external perturbation. The associated change in the orientation function for athermal systems is illustrated in Figure 2 by the curve for which $\lambda = 1$. The latter consists from two parts: The lower part is indistinguishable from the abscissa along $0 \leq x \leq 6.42$. This corresponds to the isotropic phase. The second part of the curve, representative of the highly ordered phase, extends in the range $x \geq 6.42$. The effect of stretching the network is displayed by the upper two curves in Figure 2. They are obtained for $\lambda = 3$ and 5, as indicated by solving eqs 22–24 for the three unknowns β, $\bar{y}$, and S. That the solution set represents a minimum of free energy is verified, each time. An abrupt change in the orientation function is observed at about the same axial ratio in both curves. This is indicative of a crossover from a weakly ordered regime to a highly ordered regime as one treats chains with increasing stiffness. The parts of the curves representative of the weakly oriented regime are clearly discernible for various λ, while the upper parts are almost indistinguishable.

Figure 3 displays the influence of thermotropic interactions on the orientation function. Both of the curves are obtained for $\lambda = 3$ using the same calculation procedure as above. The dashed curve corresponds to the athermal case. The solid curve is obtained for $\tilde{T}^{-1} = 2$. The most striking result is the shifting of the transition to a significantly lower x_c value by the inclusion of thermotropic effects. This shows the importance of anisotropic interactions in orienting network chains. Accordingly, chains with relatively less rigidity, or higher flexibility, are susceptible to exhibiting an oriented structure, provided that the external perturbation is supplemented by thermotropic interactions.

It is noted that, in both Figures 2 and 3, the lower parts of the curves are very closely reproducible by the approxi-

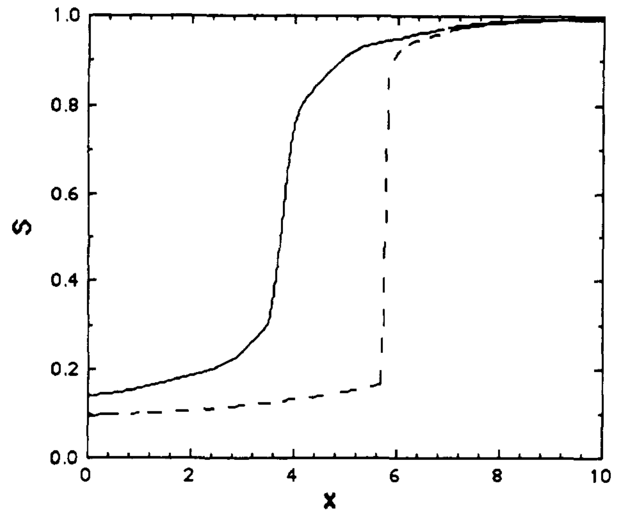

Figure 3. Dependence of orientation function S on the axial ratio x of the Kuhn segments in network chains. Both of the curves are obtained for $\lambda = 3$, $m = 20$. The solid curve is calculated from eqs 22–25, for $\tilde{T}^{-1} = 2$, to illustrate the effect of thermotropic interactions in comparison to the athermal system shown by the dashed curve.

mate expression given by eqs 31 and 32. This expression is not however applicable beyond the crossover region.

Figure 4 illustrates the change in orientation function induced upon stretching of network chains. The curves are plotted for chains varying in stiffness, as indicated by the axial ratio of the corresponding Kuhn segments. Calculations are performed for athermal systems. It is found that for relatively flexible chains S increases smoothly with the extension ratio whereas the sensitivity to external perturbation significantly increases as the chain rigidity approaches the crossover value. In fact for $x = 5.7$ for instance, a transition from a weakly ordered to a highly oriented regime is clearly apparent. Stiffer chains on the other hand exhibit little dependence on the applied stress in the dry state inasmuch as they possess a highly ordered structure even at lowest extensions.

4. Concluding Remarks

The present study demonstrates that a first-order transition from a relatively disordered to a highly ordered structure is expected to occur upon stretching of networks of semirigid chains. The latter is evidenced by an abrupt increase in the orientation function in network chains with sufficiently large stiffness and subject to substantial deformation. The transition is expected to occur more readily in the presence of anisotropic intermolecular interactions favoring parallel alignment of neighboring chains. A homogeneous structure with a definite degree of ordering is predicted to result by the imposition of uniaxial tension. The possibility of obtaining a highly ordered and homogeneous structure may be of significant importance to industrial applications where high-performance polymers are finding increasing use as load-carrying materials.

In the above analysis, attention has been confined to network chains consisting of $m = 20$ Kuhn segments. In conventional networks this value of m is representative of a typical degree of cross-linking. For a fixed degree of cross-linking, m decreases with increasing chain stiffness. A theoretical analysis of the extreme case $m = 1$, i.e., rigid-rod networks where the only freedom lies in the hinging at the junction points, has recently been performed by Vilgis and collaborators.[11] As is apparent from eq 34, an increase in the number m of Kuhn segments is accompanied by a rise in the absolute value of the equilibrium free energy per unit chain, without altering the location of the minima with respect to $\bar{y}$. Thus, for undeformed networks, the coexisting phases exhibit the same orientational structure regardless of the number of Kuhn segments. In deformed networks on the other hand, from the examination of eqs 22–25, one may verify that the dependence on m and λ appears only through the ratio $\lambda/m^{1/2}$, in the left-hand side of eq 22. Accordingly, doubling λ, for instance, has the same effect as reducing m by a factor of 4. Thus, by picking network chains made of a smaller number of Kuhn segments, one may observe the critical transition at considerably smaller extensions.

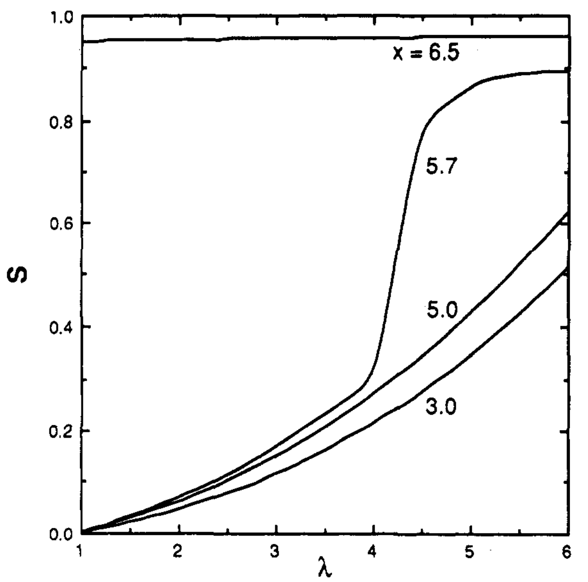

Figure 4. Increase in orientation function with increasing extension ratio. Curves are obtained for dry, athermal network chains. Chains whose Kuhn segments possess axial ratios close to the crossover value 5.825, which corresponds to the first appearance of a new minimum in the undeformed state, exhibit an abrupt rise in the orientation function, indicative of a first-order transition from a weakly ordered to a highly anisotropic regime. The latter is expected to occur at lower axial ratios in the case of thermotropic systems, as follows from Figure 3.

It should be noted that, in a strict sense, the theory applies to chains comprising rigid sequences separated by flexible joints. Accordingly, the recently prepared liquid-crystalline elastomers of polysiloxane,[12] polyacrylate, and polymethacrylate[13] may provide a direct example of such network chains, formed by mesogenic moieties separated by flexible spacers. However, both the originally developed[4] model of rods with flexible joints and its present extension to network chains are expected to be applicable to a broader range of chains, which may be classified as semirigid. The potentiality of the rigid sequences to form a nematic phase is the basic factor leading to a crossover from a weakly ordered to a highly oriented regime, under stress. This point has also been emphasized previously by Warner and collaborators[14,15] and calculations have been provided for both main-chain and side-chain liquid-crystalline networks.

It is interesting to note that, by using the approximation $5x_a/64 \approx 1$, eq 31 may be rearranged to

$$S = \frac{1}{1 - V}\frac{1}{5m}\left(\lambda^2 - \frac{1}{\lambda v_2}\right) \tag{36}$$

with

$$V \equiv \frac{\tilde{T}^{-1}}{5} + \frac{x}{x_a} \tag{37}$$

The present form of orientation function permits a direct comparison with the work of Jarry and Monnerie.[10] In fact, for deformed networks in the Gaussian range, i.e., $\lambda^2/m \ll 1$, Jarry and Monnerie proposed an expression in form identical with eq 36. The quantity V in their work is identified as $U/5$ where U is a parameter characterizing the intensity of interaction. Equation 37, which follows from an approximate solution of the present lattice model, confirms the relationship between V and the prevailing *intermolecular interactions* and *also calls attention to* another effect, still intermolecular in nature but of entropic origin. The latter is the only contributing effect in the case of athermal effects as shown in the preceding manuscript. For gaslike or volumeless networks, as in James–Guth theory, it vanishes, since in this case $x \rightarrow 0$. It is natural that this effect is absent in the expression obtained by Jarry and Monnerie since their treatment relies on the James–Guth three-chain model.

Acknowledgment. It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Grants DMR-15082 (Polymers Program, Division of Materials Research) and INT-8903327 (Sciences in Developing Countries Program).

References and Notes

(1) Erman, B.; Bahar, I.; Kloczkowski, A.; Mark, J. E., preceding paper in this issue.

(2) Flory, P. J. *Proc. R. Soc. London, A* **1956**, *234*, 73.

(3) Flory, P. J. *Adv. Polym. Sci.* **1984**, *1*, 59.

(4) Flory, P. J. *Macromolecules* **1978**, *11*, 1141.

(5) Flory, P. J.; Ronca, G. *Mol. Cryst. Liq.* Cryst. **1979**, *54*, 289.

(6) Flory, P. J.; Ronca, G. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 311.

(7) Warner, M.; Flory, P. J. *J. Chem. Phys.* **1980**, *73*, 6327.

(8) Departing from the Maier–Saupe theory[9] where each molecule is included in its entirety, Flory–Ronca[6] focused on the *interaction* between pairs of "segments", the term segments referring in their work to portions of rods of the size of lattice sites. Here we designate the latter by the term subsegment in order to avoid confusion with the Kuhn segments.

(9) Maier, W. I.; Saupe, A. *Z. Naturforsch. A* **1958**, *13*, 564; **1959**, *14*, 882; **1960**, *15*, 287.

(10) Jarry, J. P.; Monnerie, L. *Macromolecules* **1979**, *12*, 316.

(11) Vilgis, T. A.; Boué, F.; Edwards, S. F. In Molecular Basis of Polymer Networks. *Springer Proceedings in Physics*; Baumgartner, A., Picot, C. E., Eds.; Springer: Berlin, 1989; Vol. 42, p 170.

(12) Finkelmann, H.: Kock, H. J.; Gleim, W.; Rehage, G. *Makromol Chem., Rapid Commun.* **1984**, *5*, 287.

(13) Zentel, R.; Reckert, G. *Makromol. Chem.* **1986**, *187*, 1915. Canessa, G.; Reck, B.; Reckert, G.; Zentel, R. *Makromol. Chem., Macromol. Symp.* **1986**, *4*, 91.

(14) Warner, M. In *Side Chain Liquid Crystal Polymers*; McArdle, C. B., Ed.; Chapman & Hall: New York, 1989; p 7.

(15) Warner, M.; Gelling, K. P.; Vilgis, T. A. *J. Chem. Phys.* **1988**, *88*, 4008.