*Macromolecules* **1995,** *28,* 4299–4302

# Multistage Cross-Linking of Nematic Networks

**G. C. Verwey and M. Warner***

*Cavendish Laboratory, University of Cambridge, Madingley Road,*
*Cambridge CB3 0HE, England*

*Received November 21, 1994; Revised Manuscript Received February 10, 1995*[⊗]

ABSTRACT: Nematic polymer melts, cross-linked in their isotropic phase, typically form polydomain nematic rubbers and gels. Such elastomers, if strained and then further cross-linked, form nematic monodomain elastomers with interesting mechanical and thermal properties. We calculate the elastic free energy of a network which has undergone multiple cross-linking and obtain the surprising result that it is identical in form to that for a sample once cross-linked from an oriented nematic monodomain. Gaussian elasticity thus predicts that it is impossible to permanently imprint complex structure (including, for instance, biaxiality) into a nematic elastomer by imposing a complex sequence of strains interspersed by cross-linking stages. A multistage cross-linked network should therefore exhibit the same behavior as a single-stage system, including recently predicted and observed nematic transitions in response to imposed strains.

## I. Introduction

Polymer liquid crystals are of particular interest because their behavior is determined by both the entropy-driven disordering that occurs in a polymer and the ordering typical of liquid crystals, leading to molecular shape change on orientational ordering. Long ago de Gennes[1,2] noted that molecular shape change would lead to dramatic effects if the chains were cross-linked to form elastomers. In addition to the normal properties of conventional elastomers, nematic elastomers can undergo spontaneous distortions due to applied stress or a phase change. Work has been done using various molecular models: e.g., the freely jointed rod[3] and worm chains.[4] However, the details are unimportant here as they all lead to the same simple modifications of Gaussian elasticity theory. We require only the measure of the anisotropy of the network. For the Gaussian-distributed chain conformations necessary for rubber elasticity this measure is the persistence length tensor, $\mathbf{l}$, that describes chain shape, $\langle R_i R_j \rangle = {}^1/_3 l_{ij} L$, with the arc length of a chain being $L$.

Experiments have been done both with monodomain samples made by cross-linking a field-oriented nematic melt[5] and by use of two-stage cross-linking with an elastic deformation of the intermediate state, creating a final monodomain sample.[6,7] Theoretical work has so far been confined to the albeit rich area of cross-linking field oriented nematic melts. It therefore seemed appropriate to extend the theory to multiple-stage cross-linking. We predict here, within Gaussian elasticity, that multiply cross-linked *monodomain* networks behave qualitatively as the simpler networks once-cross-linked in the nematic phase. It is likely though where polydomains have been involved at any stage that effects are more subtle.

This paper presents an unexpected result—that cross-linking a Gaussian network in a series of steps has little nematic effect. One cannot create complex states of nematic order, for instance, biaxiality, by applying a sequence of noncoaxial and biaxial strains during cross-linking. This perhaps confounds one's intuition since the mechanical history determines the relaxed shape of an elastomer.

Our purpose is 2-fold: (i) to expose this result that many readers may find counterintuitive and (ii) to suggest that deviations from this simplifying result are possibly due to non-Gaussian effects that apply to both conventional and nematic elastomers. These include entanglements, higher order correlations in chain statistics, and fluctuations in cross-linking density. They motivate most current investigations of networks, and it is possible that nematic networks, because of their complexity and delicacy, will throw light on such non-Gaussian effects. There is an increasing number of experimental results on monodomain samples of greatly differing genesis and on polydomain samples which confront theory with these issues.

The complex and subtle effects found in nematic solids, as against isotropic and conventional anisotropic solids, rest in the nematic order, an internal degree of freedom that is free to adjust (rotate and change its magnitude) as external forces are applied. It is predicted[8] and found[9] that the director can undergo discontinuous transitions or, by rotating the director suitably with few mechanical constraints applied, that such solids can deform at little energetic cost.[10,11] All this principally arises because of the chain of connection between molecular orientation and shape and in turn the relation of molecular to macroscopic shape. Rotating chains by applying a macroscopic strain creates order before a subsequent cross-linking stage. We are therefore centrally concerned in this paper with anisotropic chains in a multistage cross-linking process of network formation. This is in essence an extension of the classical calculation of Scanlon to the richer case of nematic elastomers.

In section II we give a general analysis of the free energy of a nematic/isotropic network cross-linked in an arbitrary number of stages. Technical details are provided in an appendix. In section III we illustrate these principles in a network twice-linked in the isotropic state (and then cooled to the nematic state), corresponding to the important experimental procedure of Finkelman *et al.*[6,7]

## II. Gaussian Elasticity for Multiply Cross-Linked Nematic Networks

Polymer elasticity derives from chains increasing their free energy via the reduction in entropy as they get stretched. This can easily be calculated if we

---

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1995.

0024-9297/95/2228-4299$09.00/0

assume the chains obey Gaussian statistics. A further approximation is often made—that of an affine deformation where the chain ends are fixed to junction points which then deform uniformly with the solid. This overrestricts the positions of chains, overestimating the free energy. However, corrections for fluctuations in the position of junction points within this nematic–Gaussian theory are as discussed by Flory and others for conventional Gaussian theory of phantom networks. Fluctuations merely introduce a numerical prefactor to the free energy which has no effect on the overall behavior of the networks. The free energy calculation of once-linked systems was extended to doubly cross-linked networks by Scanlon.[12] Here (see the appendix) we extend the multiple-stage cross-linking calculation to include tensors of strain $\lambda$ and of persistence lengths $\mathbf{l}$ of a general nondiagonal nonuniaxial structure. Experimental and theoretical studies of nematic networks have revealed an extraordinary richness of instabilities and transitions which emerge when $\lambda$ and $\mathbf{l}$ have this more complex structure.

From the appendix, the multiple cross-linking free energy is:

$$\frac{2F}{kT} = \frac{N_t\phi}{2}\left(\mathrm{Tr}[\mathbf{A}\cdot\lambda^T\cdot\mathbf{l}^{-1}\cdot\lambda] + \ln\left[\frac{\det \mathbf{l}}{a^3}\right]\right) \tag{1}$$

where the tensor $\mathbf{A}$ is given by:

$$\mathbf{A} = \sum_i \frac{N_i}{N_t}(\lambda_i^T\cdot\mathbf{l}_i^{-1}\cdot\lambda_i)^{-1} \tag{2}$$

$\mathbf{A}$ contains all the information about cross-linking and is therefore fixed, leaving only $\mathbf{l}$ and $\lambda$ to vary subsequently. The stages of cross-linking start at the initial network formation, $i = 0$, where we define $\lambda = 1$, and proceed through the first intermediate stage $i = 1$ etc. At the $i$th stage the deformation is $\lambda_i$, the persistence tensor is $\mathbf{l}_i$ and $N_i$ links per unit volume are made ($N_t$ being the total number of cross-links made; the links are of functionality $\phi$; thus, the number of strands is $N_t(\phi/2)$). The persistence tensor, $\mathbf{l}$, may be the result of relaxation or rotation depending on the strains applied and the current temperature. Its elements can easily be calculated in a model[3,13] or simply measured. At low temperatures the nematic order is relatively rigid, consequently $\mathbf{l}$ rotates without changing the magnitude of the nematic anisotropy. The $a^3$ term in the log can be arbitrarily chosen (it is an additive constant in the free energy). We have adopted the monomer length $a$.

If we only have one cross-linking step, then $\mathbf{A} = \mathbf{l}_0$ and we recover the free energy equation for a once-cross-linked network:[8]

$$\frac{2F}{kT} = \frac{N_t\phi}{2}\,\mathrm{Tr}[\mathbf{l}_0\cdot\lambda^T\cdot\mathbf{l}^{-1}\cdot\lambda] + \frac{N_t\phi}{2}\ln\left[\frac{\det \mathbf{l}}{a^3}\right] \tag{3}$$

Note that eq 3 has great similarities to eq 1, with $\mathbf{A}$ fulfilling the role of the initial shape tensor.

The sample will spontaneously adopt a relaxed state, $\lambda_r$, with respect to the initial state. From the relaxed state we can measure the effective distortions $\lambda'$, whence the total distortion is $\lambda = \lambda'\lambda_r$. The relaxation $\lambda_r$ must be volume preserving (as all distortions of elastomers are). Insertion of $\lambda_r = \mathbf{l}^{1/2}\cdot\mathbf{A}^{-1/2}/(\det[\mathbf{l}^{1/2}\cdot\mathbf{A}^{-1/2}])^{1/3}$ in eq 1 yields:

$$\frac{2F}{kT} = \frac{N_t\phi}{2}\left(\frac{1}{[\det[\mathbf{l}^{1/2}\cdot\mathbf{A}^{-1/2}]]^{2/3}}\,\mathrm{Tr}[\mathbf{l}] + \ln\left[\frac{\det \mathbf{l}}{a^3}\right]\right) \tag{4}$$

This is the lowest energy (the relaxed state) consistent with volume preservation. The $\mathbf{l}$ in eq 3 or eq 1 in this circumstance is the shape tensor current at relaxation. The tensor $\mathbf{l}^{1/2}$ has the property $\mathbf{l}^{1/2}\cdot\mathbf{l}^{1/2} = \mathbf{l}$ and is best considered in its diagonal frame.

Inserting $\lambda = \lambda'\cdot\lambda_r$ into eq 1 gives:

$$\frac{2F}{kT} = \frac{N_t\phi}{2}\left(\frac{1}{[\det[\mathbf{l}^{1/2}\cdot\mathbf{A}^{-1/2}]]^{2/3}}\,\mathrm{Tr}[\mathbf{l}\cdot\lambda'^T\cdot\mathbf{l}'^{-1}\cdot\lambda'] + \ln\left[\frac{\det \mathbf{l}}{a^3}\right]\right) \tag{5}$$

where $\mathbf{l}'$ is the shape tensor after $\lambda'$ has been applied to the relaxed state (for instance, at lower temperatures it might simply be a rotated version of $\mathbf{l}$).

The free energy is now superficially like that of a once-linked system (eq 3), but there are subtle differences. The effective number of strands in front of the Tr[...] term, $N_{\mathrm{eff}}(\phi/2)$, is $N_{\mathrm{eff}}(\phi/2) = N_t(\phi/2)\det[\mathbf{A}\cdot\mathbf{l}^{-1}]^{1/3}$ which is not the same as the actual number $N_t(\phi/2)$ which is the prefactor of the ln[det] term. This discrepancy from eq 3 has consequences for the structure of the Landau theory of such networks. A subject we shall return to in future work.

The strain part of the free energy equation (eq 5) is, however, identical to that of a once-cross-linked network, and we can predict that it should have the same behavior under imposed strains. We thus expect a multiply cross-linked network to exhibit soft deformations and discontinuous director rotations just like a once-cross-linked network.[8,9,11]

Of course, the strain history is still present in eq 5, it resides in $\mathbf{l}$ which is determined by minimizing eq 4 over choices of $\mathbf{l}$. Since eq 5 depends only on det $\mathbf{A}$ rather than the elements of $\mathbf{A}$, and only on det $\mathbf{l}$, the minimal $\mathbf{l}$ cannot be biaxial. Thus, it is important to note that although one could set up biaxial cross-linking conditions, e.g., by imposition of strains, and hence a biaxial $\mathbf{A}$, the memory of this will be lost by relaxation of $\lambda_r$ and of $\mathbf{l}$ and the nematic state will be uniaxial unless there is some intrinsic biaxiality. Similarly, the isotropic state will remain truly isotropic when relaxed—there will be no residual nematic order arising from any sequence of strains imposed during cross-linking. All these conclusions are from within Gaussian elasticity.

### III. Example of a Network Twice-Cross-Linked in the Isotropic State

Here we consider the simple uniaxial example of a sample twice-cross-linked in the isotropic state with $N_0$ cross-links at $\lambda = \mathbf{I}$ and $N_1$ cross-links at $\lambda = \lambda_1$. All the matrices are diagonal, and we will denote the diagonal elements, e.g., $\mathbf{l} = l_\parallel$ and $l_\perp$ for the parallel and perpendicular components. We let $\lambda_{1\parallel} = \alpha$, and so $\lambda_{1\perp} = 1/\sqrt{\alpha}$. We have $\mathbf{A} = ((N_0/N_t)\mathbf{I} + (N_1/N_t)(\lambda_1^T\lambda_1)^{-1})a$, where $a$ is the step length in the isotropic state, that is, the length which underpins the lengths $l_\parallel$ and $l_\perp$ of the nematic state. Since $\mathbf{l} = a\mathbf{I}$ and $\lambda_r = (\mathbf{l}^{1/2}\cdot\mathbf{A}^{-1/2})/(\det[\mathbf{l}^{1/2}\cdot\mathbf{A}^{-1/2}])^{1/3}$, the relaxed isotropic i state is given by

$$\lambda = \lambda_r^{\,i} = \frac{\mathbf{A}^{-1/2}}{(\det \mathbf{A}^{-1/2})^{1/3}} \tag{6}$$

giving:

$$\lambda_{\mathrm{r}\parallel}{}^{\mathrm{i}} = \frac{(N_0 + N_1\alpha)^{1/3}}{(N_0 + N_1/\alpha^2)^{1/3}} \tag{7}$$

$$\lambda_{\mathrm{r}\perp}{}^{\mathrm{i}} = \frac{(N_0 + N_1/\alpha^2)^{1/6}}{(N_0 + N_1\alpha)^{1/6}} \tag{8}$$

and on cooling to the nematic state n we expect a relaxed state with

$$\lambda = \lambda_{\mathrm{r}}^{\mathrm{n}} = \frac{\mathbf{l}^{1/2}\cdot\mathbf{A}^{-1/2}}{\det[\mathbf{A}^{-1}\cdot\mathbf{l}]^{1/6}} \tag{9}$$

giving:

$$\lambda_{\mathrm{r}\parallel}{}^{\mathrm{n}} = \frac{(N_0 + N_1\alpha)^{1/3} l_\parallel{}^{1/3}}{(N_0 + N_1/\alpha^2)^{1/3} l_\perp{}^{1/3}} \tag{10}$$

$$\lambda_{\mathrm{r}\perp}{}^{\mathrm{n}} = \frac{(N_0 + N_1/\alpha^2)^{1/6} l_\perp{}^{1/6}}{(N_0 + N_1\alpha)^{1/6} l_\parallel{}^{1/6}} \tag{11}$$

Note that if $\mathbf{l}$ is unknown, then it may be calculated from the shape change of the sample on cooling from the isotropic to nematic state:

$$l_\parallel/l_\perp = (\lambda_\parallel{}^{\mathrm{i-n}})^3 \tag{12}$$

where $\lambda_\parallel{}^{\mathrm{i-n}}$ is the spontaneous extension, in the direction parallel to the director, on cooling from the isotropic to nematic state.

The free energy equation for subsequent deformation is:

$$\frac{2F}{kT} = \frac{(N_0 + N_1\alpha)^{2/3}(N_0 + N_1/\alpha^2)^{1/3}(\phi/2)}{l_\parallel{}^{1/3} l_\perp{}^{2/3}} \mathrm{Tr}[\mathbf{l}_{\mathrm{r}}\cdot\lambda'^{T}\cdot\mathbf{l}^{-1}\cdot\lambda'] \tag{13}$$

where $\mathbf{l}_{\mathrm{r}}$ is the value that $\mathbf{l}$ would take at the current temperature but with the sample relaxed (i.e., no applied stress).

## IV. Conclusions

We have calculated the properties of multistage cross-linked monodomain nematic elastomers using a Gaussian theory of rubber elasticity extended to account for nematic order. Gaussian theory makes several clear predictions, not all apparently in accordance with experiment. Thus nematic elastomers represent an interesting test of what has been the fundamental approach to elastomers for the last 50 years.

We have found that the *form* of the free energy of a monodomain nematic elastomer cross-linked in a series of steps is identical to that of a monodomain once-cross-linked in the nematic state. As in conventional networks formed by multistage cross-linking the strain history is recorded in the sample in that it determines the final relaxed shape. The imposed strains can also effect the magnitude of the resulting nematic order in the nematic state, but also as in conventional systems it cannot induce permanent order into the isotropic state. This is perhaps not a surprise given the stress-optical theorem, but it is in apparent disagreement with the experiments of Finkelmann *et al.*[6,7] that observe a small residual order in the isotropic state. It is also possible that incomplete relaxation as cross-linking proceeds is possible for this discrepancy.

We have also shown that even a biaxial strain history during cross-linking leaves the relaxed nematic elastomer uniaxial, hence our conclusion that all histories lead to a free energy of the same monodomain form.

It remains to discuss the experiments which show that networks formed in the isotropic state form polydomains when cooled to the nematic state. Large stresses are required before these align and form a monodomain.[6,14] If each separate domain *independently* behaved as the monodomain samples we have described above, then only small stresses would be required for alignment. However, given the intimate contact of the domains, they must mutually resolve their strains and such systems require a more involved treatment than offered above.

Another interesting test of the calculations we have presented is whether monodomain samples achieved by twice cross-linking in the isotropic state should resemble those created by once cross-linking a nematic monodomain melt. To our knowledge experiments on single and multistep cross-linked samples have been performed under very different conditions of temperature relative to their nematic–isotropic transitions and thus have not yet presented a conclusive test of theory.

**Acknowledgment.** This research has been supported by EPSRC and Unilever Plc.

## Appendix: Generalized Version of Scanlon's Calculation

Scanlon in his paper[12] derives an expression for the free energy of a double-cross-linked Gaussian network (given diagonal extensions) using the affine approximation.

The following is a generalization of the calculation to include nontrivial tensor strains $\lambda$ and persistence lengths $\mathbf{l}$. The key point is a substitution to separate the position vectors into their average value and a fluctuation. We use a very similar notation and approach to Scanlon in his paper.

We consider a strand of the network currently spanning from $\mathbf{x}_0$ to $\mathbf{x}_n$. The current extension is $\lambda$, taken with respect to the initial conditions and hence $\mathbf{x}_n = \lambda\cdot\mathbf{x}_n{}^0$ where $\mathbf{x}_n{}^0$ is the initial position of the strand end (when it was originally cross-linked into the network). At an intermediate distortion $\lambda_1$, the $j$th monomer (currently at $\mathbf{x}_j$) was cross-linked into the network at the second cross-linking stage. At that time it was at $\mathbf{x}_j{}^1 = \lambda_1\cdot\lambda^{-1}\cdot\mathbf{x}_j$ (where we have taken $\mathbf{x}_j$ back to its original position $\mathbf{x}_j{}^0 = \lambda^{-1}\cdot\mathbf{x}_j$ and by applying $\lambda_1$ then taken $\mathbf{x}_j{}^0$ to $\mathbf{x}_j{}^1$).

The current entropy from the two substrands $(\mathbf{x}_j - \mathbf{x}_0)$ and $(\mathbf{x}_n - \mathbf{x}_j)$ formed by the second cross-linking is:

$$\frac{S}{k} = -\left\langle \frac{3\mathbf{x}_j\cdot\mathbf{l}^{-1}\cdot\mathbf{x}_j}{2aj} + \frac{3(\mathbf{x}_n - \mathbf{x}_j)\cdot\mathbf{l}^{-1}\cdot(\mathbf{x}_n - \mathbf{x}_j)}{2a(n-j)} \right\rangle_{0,1} - \ln\left(\frac{\det \mathbf{l}}{a^3}\right) \tag{A1}$$

We have taken (for each substrand) the log of the anisotropic Gaussian distribution of the form

$$P = C(\det \mathbf{l})^{-1/2} \exp\left[-\frac{3}{2an}\mathbf{x}_n\cdot\mathbf{l}^{-1}\cdot\mathbf{x}_n\right] \tag{A2}$$

with the step length tensor $\mathbf{l}$ specifying the current average square dimensions

$$\langle(\mathbf{x}_n)_i(\mathbf{x}_n)_j\rangle = {}^1/_3 nal_{ij} \qquad \text{(A3)}$$

where $n$ is the number of monomer units in a strand and $a$ is the length of a monomer. The average $\langle\cdots\rangle_{0,1}$ is over the link positions $\mathbf{x}_j^1$ at the second formation and over $\mathbf{x}_n^0$ at the initial formation. We first average over the second links. The conditional probability of finding the $j$th unit of a chain at $\mathbf{x}_j$ given the $n$th unit is at $\mathbf{x}_n$ is the probability of going from $\mathbf{x}_n$ to $\mathbf{x}_j$ times the probability of going from there to $\mathbf{x}_n$, normalized by the probability of going from $\mathbf{x}_0$ to $\mathbf{x}_n$:

$$P = C\exp\left[-\frac{3}{2aj}\mathbf{x}_j\cdot\mathbf{l}^{-1}\cdot\mathbf{x}_j - \frac{3}{2a(n-j)}(\mathbf{x}_n-\mathbf{x}_j)\cdot\mathbf{l}^{-1}\cdot(\mathbf{x}_n-\mathbf{x}_j) + \frac{3}{2an}\mathbf{x}_n\cdot\mathbf{l}^{-1}\cdot\mathbf{x}_n\right] \qquad \text{(A4)}$$

Substituting $\mathbf{z} = \mathbf{x}_j - (j/n)\mathbf{x}_n$ gives:

$$P = C\exp\left[-\frac{3n}{2j(n-j)a}\mathbf{z}\cdot\mathbf{l}^{-1}\cdot\mathbf{z}\right] \qquad \text{(A5)}$$

The entropy (eq A1) can be rearranged by transforming to the $\mathbf{x}^1$ variables from the $\mathbf{x} = \boldsymbol{\lambda}\cdot\boldsymbol{\lambda}_1^{-1}\cdot\mathbf{x}^1$ and then, in order to average over the second links, from $\mathbf{x}_j^1$ to $\mathbf{z}^1 = \mathbf{x}_j^1 - (j/n)\mathbf{x}_n^1$:

$$\frac{S}{k} = -\frac{3}{2a}\operatorname{Tr}\{\boldsymbol{\lambda}_1^{-1T}\cdot\boldsymbol{\lambda}^T\cdot\mathbf{l}^{-1}\cdot\boldsymbol{\lambda}\cdot\boldsymbol{\lambda}_1^{-1}\}\left\langle\frac{n}{j(n-j)}\mathbf{z}^2 + \frac{(\mathbf{x}_n^{\,1})^2}{n}\right\rangle_{0,1} - \ln\left(\frac{\det\mathbf{l}}{a^3}\right) \qquad \text{(A6)}$$

and then, using the $\mathbf{z}^1$ version of eq A5 with $\mathbf{l}_1$ current at the second cross-linking, we obtain:

$$\frac{S}{k} = -\operatorname{Tr}\{\boldsymbol{\lambda}_1^{-1T}\cdot\boldsymbol{\lambda}^T\cdot\mathbf{l}^{-1}\cdot\boldsymbol{\lambda}\cdot\boldsymbol{\lambda}_1^{-1}\}\left({}^1/_2\mathbf{l}_1 + \left\langle\frac{3(\mathbf{x}_n^{\,1})^2}{2an}\right\rangle_0\right) - \ln\left(\frac{\det\mathbf{l}}{a^3}\right) \qquad \text{(A7)}$$

The end of the strand, $\mathbf{x}_n'$, was fixed at the initial stage; that is, one should write $\mathbf{x}_n^1 = \boldsymbol{\lambda}_1\mathbf{x}_n^0$ in the above and then average using the span probabilities applicable before cross-linking:

$$P(\mathbf{x}_n^{\,0}) = C\exp\left[-\frac{3}{2na}\mathbf{x}_n^{\,0}\cdot\mathbf{l}_0^{-1}\cdot\mathbf{x}_n^{\,0}\right] \qquad \text{(A8)}$$

whence overall the entropy becomes

$$\frac{S}{k} = -{}^1/_2\operatorname{Tr}[\boldsymbol{\lambda}_1^{-1T}\cdot\boldsymbol{\lambda}^T\cdot\mathbf{l}^{-1}\cdot\boldsymbol{\lambda}\cdot\boldsymbol{\lambda}_1^{-1}\mathbf{l}_1 + \boldsymbol{\lambda}^T\cdot\mathbf{l}^{-1}\cdot\boldsymbol{\lambda}\cdot\mathbf{l}_0] - \ln\left(\frac{\det\mathbf{l}}{a^3}\right) \qquad \text{(A9)}$$

This equation has three completely independent parts: the entropy contribution due to the second cross-linking, the entropy contribution due to the first cross-linking, and det($\mathbf{l}$). Note that the det term involves only the current persistence tensor.

To sum up the effects of many stages, we note that the second term in eq A9 is present for each strand created in the initial process. This contribution remains whether or not a second stage link is inserted into the strand or not, the second stage contribution being the first term of eq A9. For each strand created there is a $-({}^1/_2)\ln(\det(\mathbf{l})/a^3)$ contribution. If there were initially $N_0$ cross-links of functionality $\phi$, then $N_0(\phi/2)$ strands were thereby created. Similarly the $N_1$ second stage links created $N_1(\phi/2)$ strands, each contributing to the first term of eq A9 and a $-(1/2)\ln(\det(\mathbf{l})/a^3)$ term. Ultimately one obtains:

$$F = \frac{kT}{2}\left(\frac{N_0\phi}{2}\operatorname{Tr}[\mathbf{l}_0\cdot\boldsymbol{\lambda}^T\cdot\mathbf{l}^{-1}\cdot\boldsymbol{\lambda}] + \frac{N_1\phi}{2}\operatorname{Tr}[\boldsymbol{\lambda}_1^{T-1}\cdot\mathbf{l}_1\cdot\boldsymbol{\lambda}_1^{-1}\cdot\boldsymbol{\lambda}^T\cdot\mathbf{l}^{-1}\boldsymbol{\lambda}] + \frac{(N_0+N_1)\phi}{2}\ln\left(\frac{\det\mathbf{l}}{a^3}\right)\right) \qquad \text{(A10)}$$

The result (eq A10) can easily be generalized to multiple cross-links as at each stage one can split up the contributions into entropy due to previous cross-links and that due to those currently being made. For convenience we may put all the cross-link information into one matrix, $\mathbf{A}$, leaving the current variables outside. The ln(det $\mathbf{l}$) term is only important if the magnitude of $\mathbf{l}$ is changing. One then finally obtains:

$$\frac{2F}{kT} = \frac{N_t\phi}{2}\left(\operatorname{Tr}[\mathbf{A}\cdot\boldsymbol{\lambda}^T\cdot\mathbf{l}^{-1}\cdot\boldsymbol{\lambda}] + \ln\left(\frac{\det\mathbf{l}}{a^3}\right)\right) \qquad \text{(A11)}$$

$$\mathbf{A} = \sum_i\frac{N_i}{N_t}(\boldsymbol{\lambda}_i^T\cdot\mathbf{l}_i^{-1}\cdot\boldsymbol{\lambda}_i)^{-1} \qquad \text{(A12)}$$

## References and Notes

(1) de Gennes, P.-G. *C.R. Acad. Sci. Ser.* **1975**, *B281*, 101.
(2) de Gennes, P.-G. *Polymer Liquid Crystals*; Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic: New York, 1982.
(3) Abramchuk, S. S.; Kockhlov, A. R. *Dokl. Akad. Nauk SSSR* **1988**, *297*, 385. [Translation: *Dokl. Phys. Chem.* **1988**.]
(4) Warner, M.; Gelling, K. P.; Viglis, T. A. *J. Chem. Phys.* **1988**, *88*, 4008.
(5) Davis, F. J.; Gilbert, A.; Mann, J.; Mitchell, G. R. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 1455.
(6) Kupfer, J.; Finkelmann, H. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 717.
(7) Kupfer, J.; Finkelmann, H. *Macromol. Chem. Phys.* **1994**, *195*, 1353.
(8) Bladon, P.; Terentjev, E. M.; Warner, M. *Phys. Rev. E* **1993**, *47*, 3838.
(9) Mitchell, G. R.; Davis, F. J.; Guo, W. *Phys. Rev. Lett.* **1993**, *71*, 2947.
(10) Zentel, R. *Liq. Cryst.* **1986**, *1*, 589.
(11) Warner, M.; Bladon, P.; Terentjev, E. M. *J. Phys. II (Fr.)* **1994**, *4*, 93.
(12) Scanlan, J. *Trans. Faraday Soc.* **1961**, *57*, 839.
(13) Wang, X. J.; Warner, M. *J. Phys. A* **1986**, *19*, 2215.
(14) Zentel, R. *Makromol. Chem.* **1987**, *188*, 665.

MA946184H