Macromolecules 1988, *21*, 3107-3111

Rubber Elasticity: A Phenomenological Approach Including Orientational Correlations

B. Deloche

Laboratoire de Physique des Solides, CNRS, LA2, Universite de Paris XI, Orsay 91405, France

E. T. Samulski*

Department of Chemsitry and Institute of Materials Science, U-136, University of Connecticut, Storrs, Connecticut 06268.

Received June 1, 1987; Revised Manuscript Received March 18, 1988

ABSTRACT: A modest alteration of the classical description of rubber elasticity to include segment–segment (and segment–solvent) orientational correlations satisfactorily reproduces stress–strain data in uniaxially deformed samples and yields a *solvent-dependent* maximum in the dilation modulus of isotropically swollen networks.

I. Introduction

Gottlieb and Gaylord have recently contrasted theoretical models of rubber elasticity by carefully examining their agreement with experiment.[1,2] Their comparisons focused on two aspects of network behavior: (1) the elastic response of the network to uniaxial deformations; (2) the dilation phenomena exhibited by networks undergoing isotropic swelling. Insofar as these two aspects of network elasticity constitute valid criteria for evaluating theory, these authors were able to discriminate among the various theories and thereby consider long-standing questions in this field, namely, the role of polymer chain entanglements and the validity of the assumed separability of elastic and mixing contributions to the network free energy. In this report we examine these two aspects of network elasticity in the context of a model that we developed to describe deformed networks.[3] This model was formulated explicitly to include molecular orientational correlations among pairwise interacting species—chain segments and segment–solvent pairs (in swollen networks). The specifics of our model have their origins in a proposition advanced by de Gennes[4] to account for a hypothetical isotropic-to-nematic phase transition that might be induced by mechanically deforming a network composed of nematogenic polymers, i.e., polymers containing anisometric monomers (mesogenic "cores") in the backbone of the chain. In such a deformed network interactions among anisometric segments would couple the segment orientational order to the stress field created in the network. The consequence of these enhanced orientational correlations among segments is a precipitous increase in orientational order above some critical degree of network deformation.[4]

Our initial motivation for exploring de Gennes' analysis of the nematogenic network derived from attempts to explain experimental NMR observations on networks composed of nonmesogenic (i.e., Gaussian) chains. In both dry and partially swollen networks we demonstrated that orientational correlations between chain segments[5] (and also between segments and solvent probe molecule[3,6]) are generated in uniaxially deformed networks. Hence, our effort to model these observations included in the free energy of the stressed network orientational interactions between segments (solvent) that are coupled to the strain. Herein we reconsider this effort in the context of modeling rubber elasticity because it appears that even in the absence of macroscopic network anisotropy caused by external perturbations, there is NMR evidence for segmental orientational correlations in conventional elastic networks subjected to isotropic dilation on swelling.[7] It is our contention that this evidence is also understandable via modeling of the type we introduced previously.[3] Additionally, when we analyze our modeling using Gottlieb and Gaylord's criteria, it exhibits a high degree of agreement with experiment. The results of including orientational correlations in the network free energy suggest that these correlations may underlie the peculiar behavior exhibited by elastic networks, namely, the explicit form of the stress–strain curve for uniaxially strained rubbers and the appearance of a *solvent-dependent* maximum in the dilation modulus of swollen rubbers.

II. Stress–Strain Behavior

In this section we reexamine the phenomenological description of uniaxially deformed rubbers including the effects of short-range orientational correlations among the chain segments (and solvent molecules) in the elastic network. Such correlations are introduced in terms of an orientational field sampled by the segments and the solvent. The magnitude of such a field is coupled to the applied strain and is characterized by a macroscopic orientational order parameter $S = \langle P_2(\cos\theta)\rangle$, where θ is the angle between the optic axis of the deformed network and the symmetry axis of the segment (solvent); uniaxial symmetry is assumed for these species. Recalling the lattice model description of a partially swollen elastic network,[4,8] the chain free energy per site is given by (see eq 7 in ref 3):

$$\frac{F(T,\varphi,\lambda)}{kT} = (1-\varphi)\log(1-\varphi) - f\frac{a^3}{kT}(\lambda-1) + \varphi(1-\varphi)\chi_0 + \tfrac{1}{2}\frac{\varphi}{N}r^2\left[\lambda^2(1-\mathrm{ES}+\ldots) + \frac{2}{\lambda}\left(1+\frac{\mathrm{ES}}{2}+\ldots\right)\right] + \frac{AS^2}{2} \quad (1)$$

where T is the temperature, φ is the volume fraction of polymer (the fraction of lattice sites, each with volume a^3, that is occupied by chain segments), and λ is the deformation ratio; $r^2 = R^2/R_0^2$ is the ratio of the mean-square end-to-end distance of a chain having N segments to its mean-square value in the absence of constraints. The first three terms represent the classical contributions: the translational entropy of the solvent, the nominal stress f induced in the network by the strain λ (low deformation limit, $\lambda < 2$), and the contribution from the Flory interaction parameter χ_0. The fourth term is the standard form

---

* Present address: Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290.

0024-9297/88/2221-3107$01.50/0 © 1988 American Chemical Society

of the elastic entropy of an elongated chain modified by the coupling of segment orientations to the deformation. In this term we include only the first-order correction to the entropy: $-ES\lambda^2$ ($E > 0$) is the decrement in the elastic entropy caused by the chain segments' enhanced propensity to align in the direction of the uniaxial orientational field; $ES/2\lambda$ is the corresponding effect in the perpendicular directions.[4] The inclusion of higher order corrections (S^2) to the entropy lead to negligible contributions $O(\lambda^6/N^3)$ to the true stress and the nominal force discussed below, particularly in the low deformation limit ($\lambda^2/N < 1$).[3] The last term in the equation, quadratic in S, comes from an explicit correction of the three usual interaction parameters, χ_{ij}, due to orientational correlations among intrinsically anisotropic species in the deformed network (see Appendix). The coupling constants A and E may be dependent on T and φ. Finally, here and throughout this paper we adhere to the practices of previous investigators addressing this general question and do not include non-Gaussian corrections that originate from the effects of very high deformations (at the limiting chain extensiblity).

These two seemingly innocuous modifications of F, the orientation–deformation coupling and the self-energy in the orientational field, were initially considered by us in order to explain solvent orientation in elongated networks.[3] At that time we also noted that these modifications manifest themselves in the stress–strain relationship. For example, the expression for the free energy in eq 1 yields the following true stress t:

$$t = kT\frac{\varphi}{Na^3}r^2\left[(\lambda^2 - \lambda^{-1}) - \frac{1}{4}\frac{\varphi E^2 r^2}{NA\lambda^2}(2\lambda^3 + 1)(\lambda^3 - 1)\right] \quad (2)$$

Clearly, orientational correlations reduce the chain stiffness, and consequently the true stress is attenuated relative to that derived from the classical description of rubber elasticity. Similar expressions for t were derived by Tanaka and Allen[9] and Jarry and Monnerie[10] based on the same considerations but different procedures. These investigators examined their respective expressions for the stress from the point of view of providing a microscopic explanation of the Mooney–Rivlin equation, but they did not quantitatively contrast them with experiment. Indeed both groups of investigators reasoned that the $1/N$ factor in the correction term makes this correction irrelevant. However, recent NMR investigations of networks as a function of cross-link density[11] suggest that the other quantities in the coefficient of the correction term exhibit a dependence on N. Explicitly, the ratio $E/A = N^{\alpha}$ ($\alpha < 0$), and consequently, the coefficient of the second term in eq 2 may not be negligible as previously suggested. Moreover, by rewriting eq 2 to get the so-called reduced nominal stress $[f^*]$ and merely interpreting the result as a parametric relationship between $[f^*]$ and λ, we find

$$[f^*] = \frac{t}{(\lambda^2 - \lambda^{-1})} = X\left[1 - \frac{X}{Y}\,\frac{(2\lambda^3 + 1)}{\lambda}\right] \quad (3)$$

The two parameters X and Y depend on the network characteristics (degree of cross-linking, swelling, etc.) and on the constants A and E related to the strength of the couplings we have introduced. However, independent of these details it is instructive to test the compatibility of the form of $[f^*]$ with experimental data. In Figure 1 we demonstrate that the expression for $[f^*]$ (eq 3 with $X = 0.12$ and $Y = 0.004$) does indeed represent stress–strain data[12] over a wide range of deformation (both tension, $\lambda^{-1} < 1$, and compression, $\lambda^{-1} > 1$) with an accuracy comparable to the best examples of the multiparameter models considered by Gottlieb and Gaylord in their comparison of theory and experiment.[1]

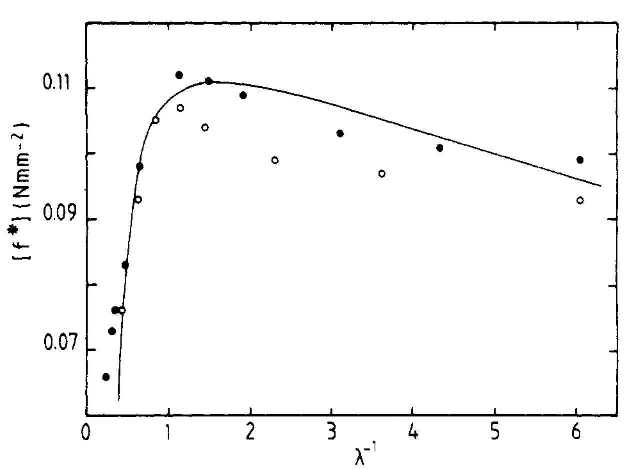

Figure 1. Reduced force $[f^*]$ is shown as a function of the reciprocal of the extension ratio λ for uniaxial extension ($\lambda^{-1} < 1$) and for uniaxial compression ($\lambda^{-1} > 1$). The experimental data are from measurements on PDMS networks (see ref 12, Figure 3); the solid line is computed with eq 3 with $X = 0.12$ and $Y = 0.004$.

III. Swelling Behavior

Preliminary Remarks. As mentioned in the Introduction, NMR observations prompted us to consider orientational correlations in uniaxially deformed networks. These observations were in the form of incompletely averaged, tensorial nuclear interactions (deuteron quadrupolar or proton dipolar interactions). Specifically, the reorientational diffusion of both chain segments and solvent probes becomes biased as the network is deformed, and as a consequence the tensorial nuclear interactions are no longer motionally averaged to zero. In the deuterium NMR spectra of suitably labeled species this residual anisotropy manifests itself as a quadrupolar splitting that is an increasing function of the deformation ratio. A resolved quadrupolar splitting appears because of the *macroscopic* homogeneity of the stress field established by a uniaxial deformation. In this macroscopic, anisotropic phase molecular species exercising rapid motion average tensorial nuclear interactions and give a residual interaction along the principal strain direction; the observed magnitude of the splitting depends on the angle Ω between the strain direction and the magnetic field; i.e., the splitting is proportional to $P_2(\cos\Omega)$.

If, for example, one establishes a distribution of orientations (Ω_i) for i locally anisotropic domains in an otherwise macroscopically isotropic network, a superposition of quadrupolar splittings would be observed (i.e., a powder pattern). It is this kind of local anisotropy—isotropically distributed—that appears to be present in networks at high degrees of swelling. In Figure 2 we depict schematically two stages that are proposed to occur when a network is swollen.[14] In stage I, the entangled, cross-linked chains expand and separate from one another insofar as it is possible under the constraints of permanent entanglements and covalent cross-link junctions; this stage is referred to as "disinterspersion". In stage II the separated chains extend as additional solvent is absorbed. Although not explicitly shown in Figure 2, at all stages there will of course be segments of many different chains in the volume pervaded by a single (illustrated) "test" chain.

Stage II may be simply viewed as a regime wherein chain elongation takes place as topologically neighboring junc-

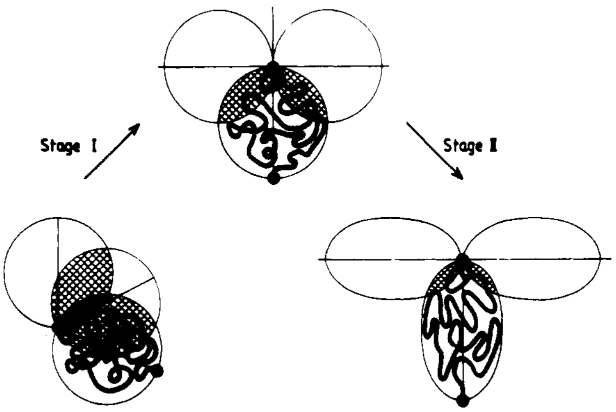

Figure 2. Schematic representation of the isotropic swelling of a cross-linked network. During stage I the chains disintersperse; in stage II the separated chains elongate with the addition of solvent. Within the volume circumscribed by a given chain (circles or ellipses) there are many segments from neighboring chains (not illustrated).

tions are further separated by the swelling dilation. If this view were correct, one would anticipate an increase in the local (intrachain) anisotropy on swelling the network. However, this anisotropy could only be interrogated on the scale of the volume pervaded by a single cross-linked chain (or that pervaded by a subchain trapped between physical constraints) as the network remains isotropic on a macroscopic scale. Increased (local) segmental anisotropy would mean, in an NMR sense, larger residual nuclear interactions. This has in fact been observed by Cohen-Addad et al.;[7] residual proton dipolar interactions increase at high degrees of network swelling. We emphasize this counterintuitive point: addition of solvent into polymer chains generally increases chain mobility (plasticization) and concomitantly facilitates the motional averaging of the relevant nuclear interactions. This is exactly the situation that obtains in a concentrated polymer solution when it is diluted. However, due to the constraints imposed by the junctions (or trapped entanglements), dilution of the network eventually stretches out the chains (subchains) along their respective end-to-end vectors and the increase in segmental mobility on swelling the network is accompanied by a corresponding increase in the anisotropy of the segmental reorientational motion. In other words, the *efficacy* of the motional average deteriorates with increasing isotropic dilation. Building on this conceptual background with Cohen-Addad's NMR observations on isotropically swollen networks and our own NMR studies in uniaxially deformed networks, we are encouraged to consider whether or not the formalism introduced before to explain the network response to mechanical deformations might be translated to the case of isotropic dilation. We propose such a translation below and examine its implications with respect to the predicted behavior of the dilation modulus.

Free Energy. As a starting point for a thermodynamic analysis of a network undergoing isotropic dilation, we recall the classical free energy of a swollen network based on the assumption of additivity of the elastic and mixing contributions. In the framework of the lattice model, the free energy per site of one elementary network chain is[8]

$$F(\varphi,T)/kT = (1-\varphi)\log(1-\varphi) + \varphi(1-\varphi)\chi_0 + \frac{\varphi}{2N}[3r^2 - x\log r] \quad (4)$$

The first two terms have the same meaning as previously (eq 1). The third term is the Wall–Flory elastic energy[15] which opposes network extension and compression; the ill-defined coefficient x assumes a variety of values in the literature ($0 < x < 6$).[16] We set $x = 1$ throughout. In such a single-chain description it is assumed that the behavior is characteristic of disinterspersed chains (stage II). This implies that the φ-dependence of r^2 (the ratio R^2/R_0^2 defined following eq 1) is given by the so-called packing condition: $r^2(\varphi) \cong \varphi^{-2/3}$.

Dilation increases the chain dimensions which in turn increases the (local) chain segment ordering. We posit segment–segment orientational correlations (direct interactions between topologically remote pairs and, to a more limited extent, via solvent interactions) within the extended chain similar to those correlations described in the mechanically deformed network. By analogy with the procedures used in the preceding section, we propose to describe these correlations in terms of an orientational potential experienced by the segments within the hypothetical volume pervaded by each chain (see Figure 2). This local potential is assumed to have quadrupolar symmetry in the direction R; its magnitude is characterized by an order parameter, $s = \langle P_2(\cos\theta)\rangle$, where θ is the angle between the segment symmetry axis and R. This gives a potential with its strength coupled to chain elongation along R. The consequences of such orientational correlations transform eq 4 into the following expression for the free energy:

$$F(\varphi,T)/kT = (1-\varphi)\log(1-\varphi) + \varphi(1-\varphi)\chi(s) + \varphi A\frac{s^2}{2} + \frac{\varphi}{2N}[3r^2 - \log r - 3Ur^2 s] \quad (5)$$

In eq 5, the segment–solvent interaction is described by an effective interaction parameter, $\chi(s) = \chi_0 + \chi_1 s^2/2$, where χ_1 is a correction to χ_0 arising from short-range orientational couplings between interacting species: chain segments and solvent molecules (see Appendix). The first of the two terms linear in φ is quadratic in s and represents the self-energy of one segment in the orientational potential. The second is the entropic elasticity modified by the coupling of segment orientation to chain elongation on swelling. As previously illustrated, this coupling term Ur^2s is designed to decrease the configurational entropy ($U > 0$), the decrement becoming more significant with increased swelling. The coupling coefficient U is independent of φ to first order but may be temperature-dependent.

Reduced Dilation Modulus. In this section we follow the prescription of previous workers in this field[17-19] and use the assumption of additivity of the free energy of mixing and the elastic free energy.[20] In our description including orientational correlations, for a given degree of swelling, the elastic free energy per site, F_{el}, is given by

$$F_{\mathrm{el}}/kT = \varphi(1-\varphi)\chi_1\frac{s^2}{2} + \varphi A\frac{s^2}{2} + \frac{\varphi}{2N}[3r^2 - \log r - 3Ur^2 s] \quad (6)$$

It follows that the φ-dependence of the elastic contribution to the chemical potential of the solvent ($kT\log(a_{1,\mathrm{c}}/a_{1,\mathrm{u}})$, where $a_{1,\mathrm{c}}$ is the solvent activity in the network and $a_{1,\mathrm{u}}$ that in a comparable solution of un-cross-linked chains) is given by[18]

$$\mu_{\mathrm{el}} = -\varphi^2\left[\frac{\partial}{\partial\varphi}\left(\frac{F_{\mathrm{el}}}{\varphi}\right)\right]_T \quad (7)$$

Written in this form it is clear that μ_{el} is related to the contribution of the elastic free energy to the osmotic pressure (i.e., μ_{el} is related to the differential osmotic pressure between cross-linked and un-cross-linked sys-

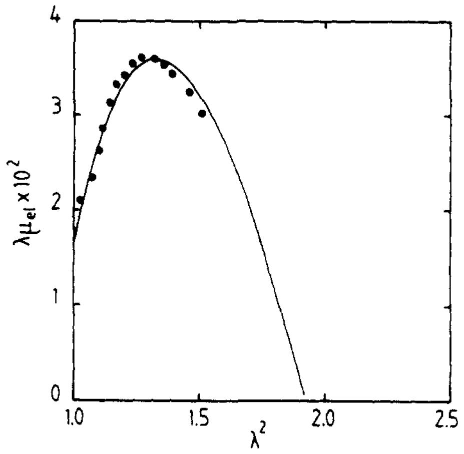

Figure 3. Plot of the reduced dilation modulus $\lambda\mu_{el}$ versus λ^2. The experimental data are from measurements on PDMS networks swollen with benzene (see ref 21, Figure 5). The solid line is calculated with eq 11 for $N = 50$, $A = 0.5$, $U = 5$, and $\chi_1 = 0.082$.

tems). Before taking the appropriate derivatives of F_{el}, we must first insert the equilibrium value of the local segment order parameter $\bar{s}$ obtained by minimizing the free energy at constant φ and T:

$$\bar{s} = \frac{3}{2N} \frac{U}{[A + (1 - \varphi)\chi_1]} r^2 \tag{8}$$

Now F_{el} may be expressed as a function of $r(\varphi)$ only

$$F_{el}/kT = \frac{3\varphi}{2N}\left[r^2 - \frac{1}{3} \log r - \frac{3}{4N} \frac{U^2}{A + (1 - \varphi)\chi_1} r^4 \right] \tag{9}$$

where $r(\varphi) = b\varphi^{-1/3}$ with $b = N^{1/3}aR_0^{-1}$. From eq 9 we find

$$\frac{\mu_{el}}{kT} = \varphi^{1/3}\frac{b^2}{N}\left[1 - \frac{1}{6b^2}\varphi^{2/3} - \frac{3b^2}{2N}U^2\left(\frac{\varphi^{-2/3}}{A + (1 - \varphi)\chi_1} - {}^3\!/_4 \frac{\varphi^{1/3}\chi_1}{\{A + (1 - \varphi)\chi_1\}^2} \right) \right] \tag{10}$$

In order to facilitate comparisons with the literature,[2] we show the reduced dilation modulus, $\lambda\mu_{el}$, expressed as a function of the extension ratio $\lambda = \varphi^{-1/3}$:

$$\lambda\mu_{el} = \frac{kTb^2}{N}\left[1 - \frac{\lambda^{-2}}{6b^2} - \frac{3b^2}{2N}U^2 \frac{\lambda^2}{A + (1 - \lambda^{-3})\chi_1} + {}^9\!/_8 b^2 \frac{U^2}{N} \frac{\lambda^{-1}\chi_1}{\{A + (1 - \lambda^{-3})\chi_1\}^2} \right] \tag{11}$$

$\lambda\mu_{el}$ satisfies the second experimental criterion used by Gottlieb and Gaylord: A plot of $\lambda\mu_{el}$ versus λ^2 exhibits a maximum. This may be easily appreciated with simplifying approximations in eq 11. For example, if the last term is negligible and in term three, $\lambda^{-3} \ll 1$, then

$$\lambda^2_{max} = {}^1\!/_3 \left[\frac{N(A + \chi_1)}{U^2} \right]^{1/2} \frac{1}{b^2} \tag{12}$$

Moreover, we see that the maximum exhibited by the reduced dilation modulus is solvent-dependent via χ_1. In Figure 3 we contrast the full expression (eq 11) for the reduced dilation modulus with experimental observations[21] and find the agreement between theory and experiment very satisfactory for the parameter set: $N = 50$, $U = 5$, $A = 0.5$, and $\chi_1 = 0.082$.

IV. Discussion

A quantitative molecular interpretation of rubber elasticity has been sought by researchers for quite some time.[20] The inclusion of various molecular-based interactions among network chains in the ideal entropic model dates from the incorporation of excluded volume considerations suggested by DiMarzio 25 years ago.[22] It would appear from the results reported here that the incorporation of even more subtle aspects of chain behavior is required. When orientational correlations are introduced into the classical model of rubber elasticity, new insights into this long-standing problem emerge. Our focus is on orientational correlations between segments on neighboring chains, including correlations between "remote" segment pairs within the same chain. This mean field treatment of proposed orientational correlations is to be distinguished from the purely intramacromolecular correlations among nearest-neighbor chain segments dictated by dihedral angle energetics.[23]

The inclusion of orientational correlations in the modeling yields stress–strain relationships that exhibit the key features of corresponding experimental observations: The calculated stress–strain curve shows a maximum for $\lambda^{-1} > 1$ ($\lambda_{max}^{-1} \cong 1.5$). Figure 1 does show that our expression for the stress diverges as $\lambda \to \infty$, but the high strain regime exceeds the range of validity of the correction terms; these were derived by assuming $\lambda \leq 2$. Since there are now several models that reproduce stress–strain observations,[1] we do not further pursue this necessary but insufficient test of theories of rubber elasticity. It would, however, be very instructive to measure the nominal stress $[f^*(\lambda)]$ and the order parameter $S(\lambda)$ in the same sample to determine if the same set of coupling constants (E and A) describe both kinds of data.

Gottlieb and Gaylord emphasize that a crucial test of models is their ability to reproduce the observed maximum in the dilation modulus versus λ^2 plot.[2] Very few of the existing models can even qualitatively satisfy this criterion. We find that incorporating orientational correlations into the single-chain model of isotropic swelling yields a semiquantitative description of this maximum. The maximum arises from a competition between the first two terms of eq 11, i.e., the classical Wall–Flory contribution,[18] with those terms corresponding to the effects of correlations that we are discussing. Moreover, our description gives some physical insights into one of the more prominent features of this maximum, namely, its dependence (both its position and magnitude) on the nature of the solvent.[24] This dependence is suggested to originate in a correction χ_1 to the interaction parameter χ_0 stemming from segment–solvent correlations analogous to those we found in uniaxially deformed networks.[25] At the single-chain level, we anticipate such correlations in isotropically swollen networks to be comparable to those observed with NMR in uniaxially deformed rubbers at comparable λ values.[3] (Note that in isotropically dilated samples, rapid solvent self-diffusion among network chains (extended between an isotropic constellation of junctions) averages the solvent tensorial nuclear interactions to zero, preventing a simple assessment of the magnitude of segment–solvent correlations in isotropic networks with the NMR technique.[13]) Additionally, our explanation of the source of the solvent-dependent maximum in the dilation modulus would appear to remove one current objection to the Flory–Rehner assumption of additivity of the elastic and the mixing contributions to the network free energy.[21,26]

Finally, it should be observed that in both parts of this paper the results have been derived with a single order parameter[27] S (or s) to describe the induced ordering of the chain segments or the solvent molecules. This is a crude approximation and may be improved by including a segment and a solvent order parameter which are coupled together.

V. Concluding Remarks

We have proposed a phenomenological description of rubber elasticity that includes in an elementary way the effects of orientational couplings between chain segments (and swelling agents). Our description provides access to the λ-dependence of the reduced force *and* the dilation modulus and easily accommodates the main features of the corresponding data for PDMS networks. Unfortunately this description only yields a conceptual rather than a molecular interpretation of chain orientation on stretching or swelling. In other words, we do not know the exact nature of the molecular interactions which underlie the coupling constants of interest, A, E (or U), and χ_1. Nevertheless, previous NMR investigations of network chains and swelling agents support the kinds of orientational correlations invoked herein.

Acknowledgment. During the course of this work we received encouragement and helpful discussions from P.-G. de Gennes, F. Brochard, J. F. Joanny, and S. Candau. This work was supported by U.S.–France cooperative research grants: CNRS 040.002 and NSF INT-8213113.

Appendix: Energetic Considerations in the Presence of Orientational Correlations

A system exhibiting short-range orientational correlations among interacting species (chain segments and solvent molecules) requires a modification to the usual interaction parameters χ_{ij}. The various interactions (segment–segment, solvent–solvent, and segment–solvent) are dependent on the orientational order S (defined in the text). In the framework of the lattice model, an expansion to second order (preserving the invariance of the energy[28]) yields the following expression for the energy per site:[8]

$$\frac{E}{kT} = \frac{\varphi^2}{2}(\chi_{cc} + \chi'_{cc}S^2) + \varphi(1-\varphi)(\chi_{cm} + \chi'_{cm}S^2) + \frac{(1-\varphi)^2}{2}(\chi_{mm} + \chi'_{mm}S^2) \quad (13)$$

where χ'_{im} are the second-order corrections to χ_{ij} (i and j = c and m for chain segment and solvent molecule, respectively). The Flory interaction parameter, χ_0,[20] a combination of the χ_{ij}, is introduced by rewriting this expression as follows:

$$\frac{E}{kT} = \varphi\frac{AS^2}{2} + (1-\varphi)\frac{BS^2}{2} + \varphi(1-\varphi)[\chi_0 + \chi_1 S^2] + \varphi\frac{\chi_{cc} - \chi_{mm}}{2} + \frac{\chi_{mm}}{2} \quad (14)$$

In eq 14, $A = \chi'_{cc}$, $B = \chi'_{mm}$, and $\chi_1 = (\chi'_{mc} - (\chi'_{cc} + \chi'_{mm})/2)$. As the last two terms are commonly subsumed into the reference state of the interaction energy, we drop them from the expression of the free energy in the text.

It is difficult to gauge the relative magnitudes of the χ'_{ij} values. In order to simplify our derivation of stress–strain behavior, we make the coarse assumption that $A = B$ and that the contribution χ_1 is negligible.[3] This leads to the following contribution to the free energy F, where we show the contributions from the segment and solvent separately (eq 1 in the text follows directly):

$$\frac{E}{kT} = \varphi\frac{AS^2}{2} + (1-\varphi)\frac{AS^2}{2} + \varphi(1-\varphi)\chi_0 \quad (15)$$

In the case of isotropic swelling, on the other hand, it seems plausible to assume χ'_{mm} is negligible compared to χ'_{mc} and χ'_{cc}. The internal energy (eq 5 in the text) has the following form:

$$\frac{E}{kT} = \varphi\frac{As^2}{2} + \varphi(1-\varphi)\left[\chi_0 + \chi_1\frac{s^2}{2}\right] \quad (16)$$

where $\chi_1 = 2\chi'_{cm} - \chi'_{cc}$ and s is the segment order parameter within one chain.

References and Notes

(1) Gottlieb, M.; Gaylord, R. *Polymer* **1983**, *24*, 1644.
(2) Gottlieb, M.; Gaylord, R. *Macromolecules* **1984**, *17*, 2024.
(3) Deloche, B.; Samulski, E. T. *Macromolecules* **1981**, *14*, 575.
(4) de Gennes, P.-G. *C.R. Seances Acad. Sci., Ser. B* **1975**, *281*, 101.
(5) Deloche, B.; Dubault, A.; Herz, J.; Lapp, A. *Europhys. Lett.* **1986**, *1*, 629. Sotta, P.; Deloche, B.; Herz, J.; Lapp, A.; Durand, R.; Ravadeux, J. C. *Macromolecules* **1987**, *20*, 2769.
(6) Toriumi, H.; Deloche, B.; Herz, J.; Samulski, E. T. *Macromolecules* **1985**, *18*, 305.
(7) Cohen-Addad, J. P.; Domard, M.; Lorentz, G.; Herz, J. *J. Phys. (Les Ulis, Fr.)* **1984**, *45*, 575.
(8) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979.
(9) Tanaka, T.; Allen, G. *Macromolecules* **1977**, *10*, 426.
(10) Jarry, J. P.; Monnerie, L. *Macromolecules* **1979**, *12*, 316.
(11) Dubault, A.; Deloche, B.; Herz, J. *Polymer* **1984**, *25*, 1405.
(12) Pak, H.; Flory, P. J. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1845.
(13) Samulski, E. T. *Polymer* **1985**, *26*, 177.
(14) Bastide, J.; Picot, C.; Candau, S. *J. Macromol. Sci., Phys.* **1981**, *B19*, 13.
(15) Wall, F. T.; Flory, P. J. *J. Chem. Phys.* **1951**, *19*, 1435.
(16) Allen, G.; Egerton, P.; Walsh, D. J. *Eur. Polym. J.* **1979**, *15*, 98. A comprehensive discussion of the meaning of the logarithmic term is given in: Deam, R. T. Ph.D. Dissertation, Cambridge University, 1976.
(17) Gee, G.; Herbert, J. B. M.; Roberts, R. C. *Polymer* **1965**, *6*, 541.
(18) Yen, L. Y.; Eichinger, B. E. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 121.
(19) Brotzman, R. W.; Eichinger, B. E. *Macromolecules* **1981**, *14*, 1445.
(20) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
(21) Brotzman, R. W.; Eichinger, B. E. *Macromolecules* **1982**, *15*, 531.
(22) DiMarzio, E. A. *J. Chem. Phys.* **1962**, *36*, 1563.
(23) Flory, P. J. *Statistical Mechanics of Chain Molecules*, Wiley: New York, 1969.
(24) Brotzman, R. W.; Eichinger, B. E. *Macromolecules* **1983**, *16*, 1131.
(25) This correction of χ_0 is unrelated to that based on chemical distinctions between segments and junctions proposed previously by Brotzman and Eichinger[21] to rationalize the solvent-dependent maximum in the dilation modulus. See also: Iechinger, B. E. E.; Neuburger, N. A. In *Biological and Synthetic Polymer Networks*; Kramer, O., Ed.; Elsevier Applied Science: London and New York, 1988; Chapter 28.
(26) Flory, P. J. *Macromolecules* **1979**, *12*, 119.
(27) For the case where χ_1 may be neglected, the expression of the order parameter s in eq 8 exhibits the same form of that derived by Cohen-Addad et al. However, our enhancement factor $U(T)/A(T)$ should not be identified with the factor $\beta(T)$ introduced by these authors to account for the internal constraints found in real chains (as opposed to Gaussian chains). See: Cohen-Addad, J. P.; Domard, M.; Herz, J. *J. Chem. Phys.* **1982**, *76*, 2744. Reference 23, Chapter 9.
(28) Brochard, F. *C.R. Seances Acad. Sci., Ser. B* **1979**, *289*, 229.