As noted earlier, for the KP chain with $\kappa_0 = \rho = 0$, the parameter λ^{-1} is equal to the Kuhn length A_K. (This condition is satisfied approximately by PM and POM chains.) In this case, λ^{-1} is just twice the persistence length of the KP type.[8] For the helical wormlike chain, the component of the persistence vector in the direction of the initial unit tangent vector $\mathbf{u}_0$ in the limit $t \to \infty$ is equal to one-half of A_K (not of λ^{-1}) and has the meaning of the persistence length, but it also has the nonvanishing components in the directions perpendicular to $\mathbf{u}_0$.[14] Thus, we recommend to use the Kuhn length rather than the persistence length. For the same kind of chains, e.g., PMMA chains, differing in tacticity, A_K is theoretically proportional to C_∞, but is not necessarily proportional to λ^{-1}. The fact that the former proportionality does not strictly hold in Table I arises from the slight differences in the determined M_L. The breakdown of the latter proportionality indicates that although the Kuhn length or the persistence length is a measure of chain stiffness for the KP chain, this criterion is in general not appropriate. Thus, we propose that the parameter λ^{-1} should be adopted as an absolute measure of chain stiffness for all types of real chains, considering its physical meaning. Then, for example, s-PMMA chains may be regarded as more stiff than i-PMMA and also PS chains, though A_K (or C_∞) of the former is smaller than those of the latter. This is also a consequence of the hypothesis.

Concluding Remarks

From the practical point of view in part, we initiated the study of the helical wormlike chain that can mimic the conformational behavior of real chains or rotational isomeric state models. From the analysis made so far, it is however clear that our model can provide interesting information about chain configurations on the bond length or somewhat longer scales, which is therefore different in quality from that obtained from the rotational isomeric state model alone. We believe that the former has significance more than a convenient replacement of the latter. Although the model parameters have been determined so far from a comparison with rotational isomeric state models with respect to the computed moments, this must also be done from an analysis of experimental data on, for instance, steady-state transport coefficients. Evaluation of them will be carried out in another series of papers. The statistical-mechanical problems, which remain, will be studied in the SMHWC series. The dynamical problems are also interesting in relation to the kinetic rigidity of the chain, but it can be shown that adoption of the helical wormlike chain, as it is, leads to a nonlinear equation of motion, as in the case of the KP chain of fixed length.[34,35] For the study of such problems, some device will therefore be necessary.

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Scattered Intensity from a Chain in a Rubber Network

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ABSTRACT: A scattering law, $S(\mathbf{q})$, is derived for a chain in a rubber network in which the chains interact only at the cross-links, i.e., a "phantom" rubber network. The result is compared to a scattering law previously derived by Jannink and co-workers for a network chain whose units move affinely with the applied strain. The scattered intensity for the two cases has a significantly different dependence on $|\mathbf{q}|$ where $\mathbf{q}$ is the scattering vector defined as the difference between the incident and scattered wave vectors. For example, the new expression for $S(\mathbf{q})$ indicates that the radius of gyration of a chain in a phantom rubber network changes less rapidly with the applied strain than an affinely deformed chain. This prediction is consistent with recent neutron scattering results on rubber networks.

Neutron scattering has proven to be a useful method for investigating the static and dynamic properties of polymers. One of the important applications has been the determination of the shape of polymer molecules in concentrated systems by measuring the scattering from labeled chains. This method, of course, could be used to study rubber networks. Recently, Jannink et al.[1] derived the scattering law $S(\mathbf{q})$ for a polymer chain in a stretched network. In their analysis it was assumed

that each unit of the chain transformed affinely as the material was strained. Although the validity of this assumption for real rubber networks is not known,[2] James[3] and Deam and Edwards[4] have shown that the deformation of "phantom chain" networks, i.e., networks composed of volumeless chains that interact only at the cross-links, has a nonaffine component. In what follows we derive the scattering law for a chain in a phantom rubber network. Because of the nonaffine nature of the deformation our results are significantly different than those of Jannink.

The Phantom Rubber Network

The model for a phantom rubber network is not an entirely realistic one. The potentials which appear in the configuration integral are strictly attractive and hence in the absence of any external forces the *average* position of each element would lie at the same point in space. To make the model more realistic additional constraints must be imposed. In the method of James it is assumed that the network is connected to a set of fixed points which lie on the bounding surface of the material. These points preserve the volume of the network and on deformation move affinely with the dimensions of the sample. In the method of Deam and Edwards the additional constraint is imposed by assuming that the density is constant throughout the network. In both cases the conclusions are the same: (1) the elements of the network have well-defined average positions ($\bar{\mathbf{R}}_i$), (2) these average positions are transformed affinely when the network is strained, (3) the fluctuations of an element about its average position ($\Delta\mathbf{R}_i = \mathbf{R}_i - \bar{\mathbf{R}}_i$) are independent of the applied strain. These statements can be put in a more mathematical form.[2] Let $\bar{\mathbf{r}}_{ij}{}^0 = \bar{\mathbf{R}}_j{}^0 - \bar{\mathbf{R}}_i{}^0$ be the average distance between two elements of the network in the undeformed state. Upon deformation the new average separation is

$$\bar{\mathbf{r}}_{ij} = \lambda\bar{\mathbf{r}}_{ij}{}^0 \tag{1}$$

where λ, the deformation gradient tensor, maps a homogeneous affine transformation.[5] The instantaneous separation in the strained state will now be the sum of the average separation plus the fluctuation

$$\mathbf{r}_{ij} = \bar{\mathbf{r}}_{ij} + \Delta\mathbf{r}_{ij} \tag{2}$$

where $\Delta\mathbf{r}_{ij} = \Delta\mathbf{R}_i - \Delta\mathbf{R}_j$. Clearly if $\Delta\mathbf{r}_{ij}$ is independent of the applied strain, the vector $\mathbf{r}_{ij}$ does not transform affinely.

Recently, Flory[2] has given a method for deriving the distribution function for the vectors connecting the ends of a chain in a phantom rubber network. We now develop his method in more detail by generalizing it to include the vectors which connect any pair of units in a chain.

The free chains which are used to form a rubber network are normally of sufficient length so that the distribution function of end-to-end vectors is Gaussian.

$$W(\mathbf{r}) = (\gamma/\pi)^{3/2}\exp(-\gamma r^2) \tag{3}$$

$$\gamma = (3/2)/\langle r^2\rangle_0 \tag{3a}$$

where $\langle r^2\rangle_0$ is the mean-square length of the vector connecting the ends of the chain. When these chains are united together to form a rubber network, it is expected that this distribution function will not be altered.[2,6] Therefore

$$\Omega^0(\mathbf{r}) = W(\mathbf{r}) \tag{4}$$

where $\Omega^0(\mathbf{r})$ is the fraction of chains in the undeformed network which have an end-to-end vector equal to $\mathbf{r}$. James has shown that if $W(\mathbf{r})$ is a Gaussian function, then the fluctuations in the average distance between chain ends is also Gaussian

$$\Psi(\Delta\mathbf{r}) = (\psi/\pi)^{3/2}\exp(-\psi(\Delta r)^2) \tag{5}$$

$$\psi = (3/2)/\langle(\Delta r)^2\rangle \tag{5a}$$

where $\Delta\mathbf{r} = \mathbf{r} - \bar{\mathbf{r}}$. Let $X(\bar{\mathbf{r}})$ be the distribution function for the mean vectors connecting the chain ends in the network. Then Ω^0 will be given by the convolution of X^0 and Ψ^0,[2]

$$\Omega^0(\mathbf{r}) = \int X^0(\bar{\mathbf{r}})\Psi^0(\Delta\mathbf{r})\,d\bar{\mathbf{r}} \tag{6}$$

By application of the convolution theorem for Fourier transforms,[7] it can be shown that $X^0(\bar{\mathbf{r}})$ is also a Gaussian function

$$X^0(\bar{\mathbf{r}}) = (\chi/\pi)^{3/2}\exp(-\chi\bar{r}^2) \tag{7}$$

$$\chi = (3/2)/\langle\bar{r}^2\rangle = \psi\gamma/(\psi - \gamma) \tag{7a}$$

or equivalently

$$\langle r^2\rangle = \langle\bar{r}^2\rangle + \langle(\Delta r)^2\rangle$$

The distribution function for the chain vectors in the strained state is obtained similarly

$$\Omega(\mathbf{r}) = \int X(\bar{\mathbf{r}})\Psi(\Delta\mathbf{r})\,d\bar{\mathbf{r}} \tag{8}$$

As pointed out above, the magnitude of the fluctuations, $\langle(\Delta r)^2\rangle$, is independent of the applied strain, hence the function $\Psi(\Delta\mathbf{r})$ is the same as $\Psi^0(\Delta\mathbf{r})$. However, the mean chain vectors are altered affinely and hence the function $X(\bar{\mathbf{r}})$ is different from $X^0(\bar{\mathbf{r}})$. We have from eq 1 that

$$\bar{\mathbf{r}} = \lambda\bar{\mathbf{r}}^0 \tag{1}$$

hence

$$X(\bar{\mathbf{r}}) = X^0(\lambda^{-1}\bar{\mathbf{r}})/|\lambda| \tag{9}$$

Dividing by the determinant of λ, $|\lambda|$, which is equal to the ratio of the volume in the strained state to the volume in the undeformed state, i.e., V/V^0, normalizes $X(\bar{\mathbf{r}})$. By substituting eq 9 into eq 8 and carrying out the indicated integration we obtain

$$\Omega(\mathbf{r}) = (\chi/\pi)^{3/2}\exp(-\chi\mathbf{r}^{\mathrm{T}}\mathbf{B}^{-1}\mathbf{r})/|\mathbf{B}|^{1/2} \tag{10}$$

$$\mathbf{B} = (\chi/\psi)\mathbf{E} + \lambda\lambda^{\mathrm{T}} \tag{10a}$$

where $\mathbf{E}$ is the 3×3 identity tensor.

To use eq 10 we must determine the magnitude of the fluctuations, $\langle(\Delta r)^2\rangle = (3/2)/\psi$. This is done in Appendix A. For networks that are composed of chains all of the same length and connected together at tetrafunctional junctions we find

$$\psi = 2\gamma \tag{11}$$

or

$$\langle(\Delta r)^2\rangle = \langle r^2\rangle_0/2 \tag{11a}$$

a result given earlier by Flory.[2] Obviously the fluctuations are quite large being equal to ½ the mean-square end-to-end distance of an undeformed chain.

Equation 11 is an expression for the magnitude of the fluctuations for the vector connecting the ends of a chain. If this result is generalized so that it applies to the vector connecting the ith and jth units of the chain, we find (see Appendix A)

$$1/\psi_{ij} = (2/3)\langle(\Delta r_{ij}{}^2)\rangle = (\eta - \eta^2/2)/\gamma \tag{12}$$

where $\eta = (|i - j|/n)$ and n is the number of units in the chain. Equation 7a can now be used to calculate the mean-square value of $\bar{\mathbf{r}}_{ij}$

$$1/\chi_{ij} = (2/3)\langle\bar{r}_{ij}{}^2\rangle = \eta^2/2\gamma \tag{13}$$

The essential feature of eq 12 and 13 is that $\langle(\Delta r_{ij}^2)\rangle$ and $\langle \bar{r}_{ij}^2\rangle$ are quadratic functions of $|i-j|$ whereas $\langle r_{ij}^2\rangle_0$ is linear in $|i-j|$. This quadratic dependence leads to an expression for the scattering from a stretched chain which is different from that found for an unperturbed chain. It should also be noted that it was assumed in the derivation of these equations that $\Omega(\mathbf{r}_{ij})$ is a Gaussian function. This of course will not be the case for small $|i-j|$. However, we are interested in deriving a scattering law which is valid for small and intermediate scattering angles. In this region the departure of $\Omega(\mathbf{r}_{ij})$ from the Gaussian form will not be important.[8]

The Scattering Law

The scattering law for an individual polymer chain is just the Fourier transform of the intra-chain pair correlation function.[9] Hence

$$S(\mathbf{q}) = n^{-2}\sum_{i,j=1}^{n}\int e^{i\mathbf{q}\cdot\mathbf{r}_{ij}}\Omega(\mathbf{r}_{ij})\,d\mathbf{r}_{ij} \tag{14}$$

where the scattering vector $\mathbf{q}$ is the difference between the incident and scattered wave vectors, $\mathbf{k}_0$ and $\mathbf{k}$. It has a magnitude $q = (2\pi/\lambda')\sin\theta/2$ where λ' is the neutron wavelength and θ is the angle between $\mathbf{k}_0$ and $\mathbf{k}$. If we substitute eq 10 into eq 14 and complete the transformation we have

$$S(\mathbf{q}) = n^{-2}\sum_{i,j=1}^{n}\exp(-\mathbf{q}^{\mathrm{T}}\mathbf{B}\mathbf{q}/4\chi) \tag{15}$$

It is convenient now to specialize to the case of a tensile deformation with the scattering vector either parallel or perpendicular to the principal strain axis. For the first case

$$S(\mathbf{q}_\parallel) = n^{-2}\sum_{i,j=1}^{n}\exp[-q_\parallel^2(\lambda_\parallel^2/\chi_{ij} + 1/\psi_{ij})/4] \tag{16}$$

where $\lambda_\parallel$ is the stretch ratio and $\mathbf{q}_\parallel$ is the scattering vector parallel to the principal strain axis. The double sum is of the form

$$\sum_{i,j}^{n} f(|i-j|)$$

and hence can be transformed to

$$2\sum_{m=0}^{n-1}(n-m)f(m)$$

where $m = |i-j|$. Using this relationship and then converting to an integral we have

$$S(\mathbf{q}_\parallel) = 2n^{-2}\int_0^n (n-m) \times \exp(-(\nu/2)\{(m^2/n^2)(\lambda_\parallel^2-1) + 2(m/n)\})\,dm \tag{17}$$

where $\nu = q^2\langle r^2\rangle_0/6$. After integration, the scattering law is

$$S(\mathbf{q}_\parallel) = 2\left(\frac{2}{\nu\alpha}\right)^{1/2}\left(\frac{\alpha+1}{\alpha}\right)\left\{F_1\left(\frac{\nu}{2\alpha}\right)^{1/2} - \exp[-\nu(\alpha+2)/2]F_1\left(\left(\frac{\nu}{2\alpha}\right)^{1/2}(\alpha+1)\right)\right\} + \frac{2}{\nu\alpha}\{\exp[-\nu(\alpha+2)/2] - 1\} \tag{18}$$

where $\alpha = \lambda_\parallel^2 - 1$ and

$$F_1(x) = e^{x^2}\int_x^\infty e^{-t^2}\,dt = \frac{\pi^{1/2}}{2}e^{x^2}\operatorname{erfc} x \tag{19}$$

For the second case, the stretch ratio perpendicular to the principal strain axis will be less than one. The scattering law is then

$$S(\mathbf{q}_\perp) = 2\left(\frac{2}{\nu\beta}\right)^{1/2}\left(\frac{\beta-1}{\beta}\right) \times \left\{\exp[-\nu(2-\beta)/2]F_2\left(\left(\frac{\nu}{2\beta}\right)^{1/2}(1-\beta)\right) - F_2\left(\frac{\nu}{2\beta}\right)^{1/2}\right\} - \frac{2}{\nu\beta}\{\exp[-\nu(2-\beta)/2] - 1\} \tag{20}$$

where $\beta = 1 - \lambda_\perp^2$ and

$$F_2(x) = e^{-x^2}\int_0^x e^{t^2}\,dt \tag{21}$$

By making use of the series and asymptotic expansions of F_1 and F_2, it can be shown that $S(\mathbf{q})$ has the following limiting forms. As the strain goes to zero

$$\lim_{\lambda\to 1} S(\mathbf{q}) = (2/\nu^2)(e^{-\nu} - 1 + \nu) \tag{22}$$

which is the well-known formula for scattering from an unperturbed Gaussian coil.[10] In the intermediate wavelength (or submolecular) region where $\nu \gg 1$ ($\mathbf{q} = \mathbf{q}_\parallel$ or $\mathbf{q}_\perp$)

$$S(\mathbf{q}) = \frac{2}{\nu}\left(1 - \frac{\lambda^2}{\nu}\right) \tag{23}$$

and in the long wavelength (or small angle) region where $\nu \ll 1$

$$S(\mathbf{q}) = 1 - \frac{\nu}{3}\left(\frac{\lambda^2+3}{4}\right) \tag{24}$$

The scattering law in this region can be written in general as[11]

$$S(\mathbf{q}) = 1 - q^2\langle s^2\rangle_k + 0(q^4) \tag{25}$$

where $\langle s^2\rangle_k$ is the component of the radius of gyration parallel to the scattering vector. Using eq 25 we can rederive eq 24 by using the results obtained in the last section. The mean-square vector connecting the ith and jth unit is

$$\langle r_{ij}^2\rangle = \int r_{ij}^2\Omega(\mathbf{r}_{ij})\,d\mathbf{r}_{ij} = \tfrac{1}{2}\operatorname{tr}\left(\frac{1}{\chi_{ij}}\mathbf{B}\right) = \tfrac{1}{2}\left[\frac{1}{\chi_{ij}}\sum_{k=1}^{3}\lambda_k^2 + \frac{3}{\psi_{ij}}\right] \tag{26}$$

and

$$\langle s^2\rangle = n^{-2}\sum_{i>j}^{n}\langle r_{ij}^2\rangle = \frac{\langle r^2\rangle_0}{18}\left[\frac{\sum_{k=1}^{3}(\lambda_k^2+3)}{4}\right] + 0(1/n) \tag{27}$$

Hence

$$\langle s^2\rangle_k = \frac{\langle r^2\rangle_0}{18}\left(\frac{\lambda_k^2+3}{4}\right) \tag{28}$$

which when substituted into eq 25 gives eq 24.

Discussion

To determine chain dimensions by neutron scattering would require the preparation of rubber networks with a small fraction of deuterated chains in an otherwise protonated matrix (or vice versa). If these networks were prepared without diluents present it is possible that interchain entanglements would restrict the range of fluctuations below that calculated for a phantom rubber network. In fact, if the entanglements were so effective as to reduce the fluctuations to zero, the

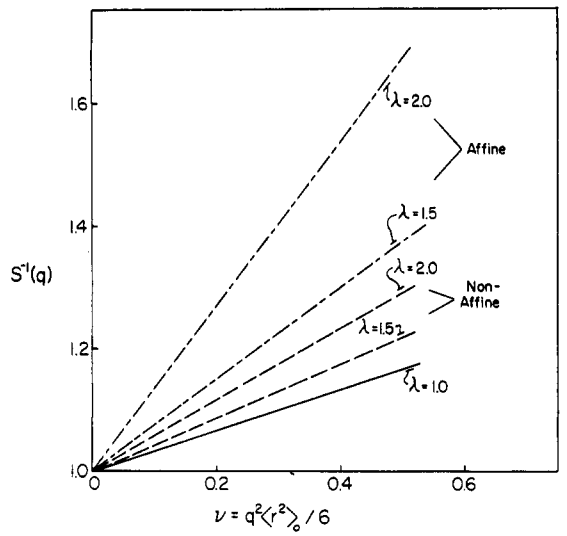

Figure 1. Inverse scattering law, $S^{-1}(\mathbf{q})$, in region where $\nu < 1$. Unperturbed chain (—), phantom rubber network at 50 and 100% strain (- -), affinely deformed network at same degrees of strain (- · -).

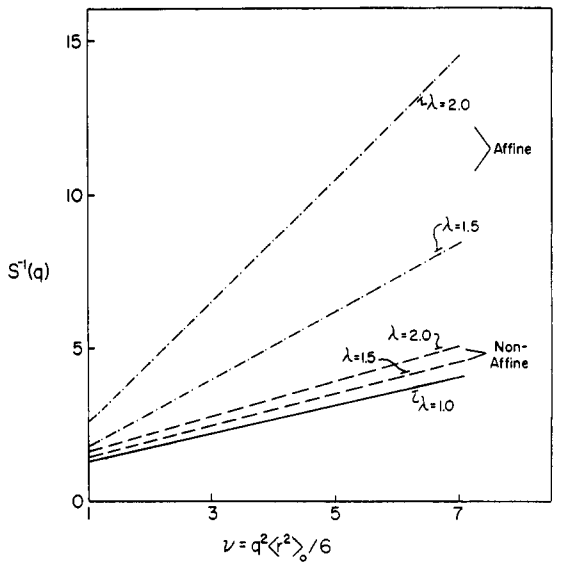

Figure 2. Inverse scattering law, $S^{-1}(\mathbf{q})$, in region where $\nu > 1$. Unperturbed chain (—), phantom rubber network at 50 and 100% strain (- -), affinely deformed network at same degrees of strain (- · -).

function $\Psi(\Delta\mathbf{r}_{ij})$ would become a delta function, $\delta(\mathbf{r}_{ij} - \bar{\mathbf{r}}_{ij})$, and the chain vector distribution would be

$$\Omega(\mathbf{r}_{ij}) = (\gamma_{ij}/\pi)^{3/2} \exp[-\gamma_{ij}\mathbf{r}_{ij}{}^{\mathrm{T}}(\lambda\lambda^{\mathrm{T}})^{-1}\mathbf{r}_{ij}]/|\lambda| \quad (29)$$

$$\gamma_{ij} = (3/2)/\langle r_{ij}{}^2\rangle \quad (29a)$$

Substitution of this expression into eq 13 gives the scattering law previously reported by Jannink et al.[1] for an affine transformation

$$S(\mathbf{q}) = \frac{2}{\nu^2\lambda^4}(e^{-\nu\lambda^2} - 1 + \nu\lambda^2) \quad (30)$$

where $\nu = q^2\langle r^2\rangle_0/6$ and q and λ are both parallel or perpendicular to the principal strain axis.

Neutron scattering data from a real rubber network would presumably lie intermediate to the two extremes given by eq 18 and 30. Such data should be very useful in determining how the shape of a molecule is influenced by the constraints of neighboring molecules and how these constraints change with the applied strain.

In Figure 1 we have plotted the inverse scattering law, $S^{-1}(\mathbf{q})$, vs. ν in the small angle region using eq 18 and 30. It can be seen that the change in $S^{-1}(\mathbf{q})$ with $\mathbf{q}$ is significantly different for the two cases and that if the transformation is nonaffine the radius of gyration of a network chain changes more slowly with the applied strain. Data consistent with this behavior have recently been published by Benoit et al.[12]

The behavior in the submolecular region is even more striking. From eq 23 and 30, we have

$$S^{-1}(\mathbf{q}) = \frac{\nu}{2} + \frac{\lambda^2}{2} \quad (31)$$

for the phantom network model, and

$$S^{-1}(\mathbf{q}) = \frac{\nu\lambda^2}{2} + \frac{1}{2} \quad (32)$$

for the affine model. In the first case the slope of $S^{-1}(\mathbf{q})$ vs. ν is independent of the applied strain but the intercept is not. The opposite behavior is found in the second case. Because of the large difference between the two cases (see Figures 1 and 2), neutron scattering should provide a useful test of the affine deformation assumption.

In the equations given above we have assumed that the rubber network is connected together with tetrafunctional junctions. If the junction functionality were higher the magnitude of the fluctuations would decrease. The relationship between the two is given in Appendix A and the scattering law for a network with any junction functionality is given in Appendix B. As the junction functionality goes to infinity the scattering law does not reduce to the expression obtained by Jannink et al.[1] In their calculation it is assumed that each element of the network moves as if embedded in an affinely deforming continuum. However, in a phantom rubber network with junctions of infinite functionality only the junctions themselves move affinely while the remaining elements of the network are free to fluctuate.

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Appendix A

Fluctuations in Phantom Rubber Networks. In this appendix we make use of the configuration partition function as formulated by James.[3] James' method has recently been reviewed and simplified by Flory[2] and we have adopted the nomenclature used in that article.

The potential energy of a phantom rubber network of Gaussian chains can be written as

$$V/kT = \sum_{k<l} \gamma_{kl}(\mathbf{R}_l - \mathbf{R}_k)^2$$

$$\gamma_{kl} = (3/2)/\langle r_{kl}{}^2\rangle \quad (A1)$$

where the sum is over all pairs kl of junctions and fixed points that are connected by a chain. Equation A1 can be rewritten as the quadratic form

$$V/kT = \mathbf{R}^{\mathrm{T}}\Gamma\mathbf{R} \quad (A2)$$

where $\mathbf{R}$ is the 3μ dimensional column vector composed of the position vectors for each of the μ fixed points and junctions.[13]

The symmetric matrix Γ has elements

$$\gamma_{kl} = (3/2)/\langle r_{kl}{}^2\rangle \qquad (k \neq l) \quad (A3)$$

if k and l are connected; $\gamma_{kl} = 0$ otherwise. The diagonal elements of Γ are

$$\gamma_{kk} = -\sum_{l} \gamma_{kl} = -\sum_{k} \gamma_{kl} \qquad (k \neq l) \quad (A4)$$

Equation A2 can be factored as follows:

$$V/kT = \mathbf{R}_\sigma{}^T\Gamma_\sigma\mathbf{R}_\sigma + 2\mathbf{R}_\tau{}^T\Gamma_{\tau\sigma}\mathbf{R}_\sigma + \mathbf{R}_\tau{}^T\Gamma_\tau\mathbf{R}_\tau \quad \text{(A5)}$$

where $\mathbf{R}_\sigma$ and $\mathbf{R}_\tau$ are the columns of position vectors for the fixed points and free junctions, respectively. The matrix Γ_σ is formed from Γ by striking out the rows and columns corresponding to the free junctions. Likewise Γ_τ is formed by striking rows and columns of the fixed point and $\Gamma_{\tau\sigma}$ by striking rows of fixed points and columns of free junctions.

If the positions of the free junctions are varied to find the minimum of V, we obtain

$$\frac{\partial(V/kT)}{\partial\mathbf{R}_\tau} = 2\Gamma_{\tau\sigma}\mathbf{R}_\sigma + 2\Gamma_\tau\mathbf{R}_\tau \quad \text{(A6)}$$

and hence

$$\bar{\mathbf{R}}_\tau = -\Gamma_\tau{}^{-1}\Gamma_{\tau\sigma}\mathbf{R}_\sigma \quad \text{(A7)}$$

where the $\bar{\mathbf{R}}_\tau$ are the equilibrium or most probable position vectors. Because the probability functions describing the fluctuations of the $\mathbf{R}_\tau$ and $\bar{\mathbf{R}}_\tau$ are Gaussian[2,3] the $\bar{\mathbf{R}}_\tau$ are also the mean positions. Defining $\Delta\mathbf{R}_\tau = \mathbf{R}_\tau - \bar{\mathbf{R}}_\tau$, we can rewrite eq A5

$$V/kT = \mathbf{R}_\sigma{}^T\mathbf{G}_\sigma\mathbf{R}_\sigma + \Delta\mathbf{R}_\tau{}^T\Gamma_\tau\Delta\mathbf{R}_\tau \quad \text{(A8)}$$

where $\mathbf{G}_\sigma = \Gamma_\sigma - \Gamma_{\sigma\tau}\Gamma_\tau{}^{-1}\Gamma_{\tau\sigma}$. Thus the potential energy has been separated into two parts: one depending on the fixed points and the other on the fluctuations of the free junctions about their mean positions.

The configurational partition function can now be written

$$Z = \int \exp(-V/kT)\,d\mathbf{R}$$
$$= \int \exp(-\mathbf{R}_\sigma{}^T\mathbf{G}_\sigma\mathbf{R}_\sigma - \Delta\mathbf{R}_\tau{}^T\Gamma_\tau\Delta\mathbf{R}_\tau)\,d\mathbf{R}_\sigma\,d\Delta\mathbf{R}_\tau \quad \text{(A9)}$$

Using this equation, the average of any function which depends only on the $\Delta\mathbf{R}$ is given by

$$\langle g(\Delta\mathbf{R})\rangle = \frac{\int g(\Delta\mathbf{R})\exp(-\Delta\mathbf{R}_\tau{}^T\Gamma_\tau\Delta\mathbf{R}_\tau)\,d\Delta\mathbf{R}_\tau}{\int \exp(\Delta\mathbf{R}_\tau{}^T\Gamma_\tau\Delta\mathbf{R}_\tau)\,d\Delta\mathbf{R}_\tau} \quad \text{(A10)}$$

For example

$$\langle(\Delta R_i)^2\rangle = \frac{\int(\Delta R_i)^2\exp(-\Delta\mathbf{R}_\tau{}^T\Gamma_\tau\Delta\mathbf{R}_\tau)\,d\Delta\mathbf{R}_\tau}{\int \exp(-\Delta\mathbf{R}_\tau{}^T\Gamma_\tau\Delta\mathbf{R}_\tau)\,d\Delta\mathbf{R}_\tau}$$
$$= {}^3/_2\gamma_{ii}{}^{-1} \quad \text{(A11)}$$

where $\gamma_{ii}{}^{-1}$ is the ii element of $\Gamma_\tau{}^{-1}$. Similarly

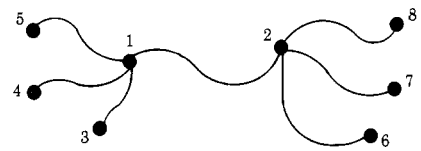
$$\langle\Delta\mathbf{R}_i\cdot\Delta\mathbf{R}_j\rangle = {}^3/_2\gamma_{ij}{}^{-1} \quad \text{(A12)}$$

and

$$\langle(\Delta r_{ij})^2\rangle = \langle(\Delta\mathbf{R}_i - \Delta\mathbf{R}_j)\cdot(\Delta\mathbf{R}_i - \Delta\mathbf{R}_j)\rangle$$
$$= {}^3/_2(\gamma_{ii}{}^{-1} + \gamma_{jj}{}^{-1} - 2\gamma_{ij}{}^{-1}) \quad \text{(A13)}$$

The evaluation of eq A11–A13 requires a knowledge of the network structure as embodied in Γ_τ. In his paper, James[3] assumed a simple network model having the connectivity of a cubic lattice. It is highly doubtful that a random cross-linking process will lead to a structure with such a regular pattern. Because of the large spatial domain pervaded by high molecular weight polymers, intermolecular contacts are more frequent than intramolecular contacts for polymers in an undiluted state. Hence after cross-linking the local connectivity of the network should be similar to that of a tree. As shown by Flory[2] this type of connectivity simplifies the calculation of the fluctuations. Our method is similar to his, but it is more easily generalized to calculate the fluctuations of any elements of the network.

For simplicity we assume that all chains in the network have the same length. In this case the parameters $\gamma_{kl} = ({}^3/_2)/\langle r_{kl}{}^2\rangle$ which appear in Γ_τ can be set equal to a constant, γ. Now consider a portion of the network having the connectivity shown in the sketch and located remotely from the surface of the sample.



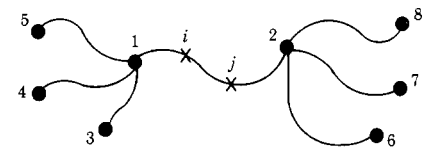
If we temporarily fix the outer junctions of the tree at their mean positions ($\Delta\mathbf{R} = 0$), we can calculate the fluctuations of the inner free junctions by inverting Γ_τ. This process can then be repeated by releasing these junctions and fixing those in the next higher tier. In general we find for the junctions labeled 1 and 2

$$\begin{vmatrix}\langle(\Delta R_1)^2\rangle & \langle\Delta R_1\Delta R_2\rangle\\ \langle\Delta R_1\Delta R_2\rangle & \langle(\Delta R_2)^2\rangle\end{vmatrix}$$
$$= \frac{3}{2\gamma}\left[\begin{vmatrix}4 & -1\\ -1 & 4\end{vmatrix} - \frac{1}{\mu_J}\begin{vmatrix}\mu_J-2 & 0\\ 0 & \mu_J-2\end{vmatrix}\right]^{-1} \quad \text{(A14)}$$

where μ_J is the number of free junctions in the tree.[14] The second term in the brackets rapidly converges to the 2×2 identity matrix, and hence

$$\begin{vmatrix}\langle(\Delta R_1)^2\rangle & \langle\Delta R_1\Delta R_2\rangle\\ \langle\Delta R_1\Delta R_2\rangle & \langle(\Delta R_2)^2\rangle\end{vmatrix} = \frac{3}{2\gamma}\begin{vmatrix}\frac{3}{8} & \frac{1}{8}\\ \frac{1}{8} & \frac{3}{8}\end{vmatrix} \quad \text{(A15)}$$

Substitution of these results into eq A13 gives eq 11a. The treatment given above can easily be extended to calculate the fluctuations corresponding to any two elements, ij, such as shown in the following sketch.



For this case we find

$$\begin{vmatrix}\langle(\Delta R_i)^2\rangle & \langle\Delta R_i\Delta R_j\rangle\\ \langle\Delta R_i\Delta R_j\rangle & \langle(\Delta R_j)^2\rangle\end{vmatrix}$$
$$= \frac{3}{2\gamma}\begin{vmatrix}\frac{3}{8}+\frac{\zeta(1-\zeta)}{2} & \frac{3}{8}+\frac{2\zeta\theta-\eta}{4}\\ \frac{3}{8}+\frac{2\zeta\theta-\eta}{4} & \frac{3}{8}+\frac{\theta(1-\theta)}{2}\end{vmatrix} \quad \text{(A16)}$$

where $\zeta = i/n$, $\theta = j/n$, and $\eta = |i-j|/n$. Equations A16 and A13 can be combined to give eq 12. Finally, if the entire treatment is generalized to networks of any functionality, f, the right-hand side of eq A16 becomes

$$\frac{3}{2\gamma}\begin{vmatrix}\frac{(f-1)}{f(f-2)}+\frac{\zeta(1-\zeta)}{f/(f-2)} & \frac{(f-1)}{f(f-2)}+\frac{(f-2)\zeta\theta-\eta}{f}\\ \frac{(f-1)}{f(f-2)}+\frac{(f-2)\zeta\theta-\eta}{f} & \frac{(f-1)}{f(f-2)}+\frac{\theta(1-\theta)}{f/(f-2)}\end{vmatrix} \quad \text{(A17)}$$

and eq A13 becomes

$$\langle(\Delta r_{ij})^2\rangle = ({}^3/_2\gamma)[\eta - \eta^2(f-2)/f] \quad \text{(A18)}$$

In the above derivation, we have assumed that the connectivity of the network resembles a tree. Large scale loops, which are surely present in a rubber network, will alter this pattern. However, the convergence of the fluctuations to a constant value is rapid, and hence only the local connectivity near a junction need be treelike. As an example of the quick con-

vergence, $\langle(\Delta r)^2\rangle$ for a two-tiered tetrafunctional tree is 0.340, for a three-tiered tree it is 0.363, and for an infinite tree it is 0.375.

Appendix B

If the results given in Appendix A are substituted into eq 12, the scattering law for f functional networks with strands of equal length is obtained

$$S(\mathbf{q}_\parallel) = \frac{1}{(\nu\alpha\xi)^{1/2}}\left(\frac{2\alpha\xi+1}{\alpha\xi}\right)\left\{F_1\left(\frac{\nu}{4\alpha\xi}\right)^{1/2} - \exp[-\nu(\alpha\xi+1)]F_1\left(\left(\frac{\nu}{4\alpha\xi}\right)^{1/2}(2\alpha\xi+1)\right)\right\} + \frac{1}{\nu\alpha\xi}\{\exp[-\nu(\alpha\xi+1)]-1\} \quad \text{(B1)}$$

where $\zeta = (f-2)/f$ and $\mathbf{q}$ is the scattering vector parallel to the principal strain axis. The other symbols are defined after eq 16. A similar expression is found when $\mathbf{q}$ is perpendicular to the strain axis.

$$S(\mathbf{q}_\perp) = \frac{1}{(\nu\beta\xi)^{1/2}}\left(\frac{2\beta\xi-1}{\beta\xi}\right) \times \left\{\exp[-\nu(1-\beta\xi)]F_2\left(\left(\frac{\nu}{4\beta\xi}\right)^{1/2}(1-2\beta\xi)\right) - F_2\left(\frac{\nu}{4\beta\xi}\right)^{1/2}\right\} - \frac{1}{\nu\beta\xi}\{\exp[-\nu(1-\beta\xi)]-1\} \quad \text{(B2)}$$

References and Notes

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(13) The matrix Γ as defined in eq A3 has dimensions $\mu \times \mu$. To conform with $\mathbf{R}$ it should be expanded to $3\mu \times 3\mu$ by direct multiplication with the 3×3 identity matrix. Furthermore Γ will not be positive definite unless one of the fixed points is chosen as an internal coordinate. When this is done the dimensionality of $\mathbf{R}$ is reduced to $3(\mu-1)$ and Γ to $(\mu-1)\times(\mu-1)$. See B. E. Eichinger, *Macromolecules*, **4**, 496 (1972).
(14) The number of free junctions in a symmetric tree built up from a central strand is $\mu_J = 2[(f-1)^t - 1]/(f-2)$ where f is the functionality of the junctions and t is the number of tiers in the tree.

Interactions between Poly(L-lysine) and Chondroitin 6-Sulfate. Quasi-Elastic Light Scattering Studies

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ABSTRACT: Quasi-elastic laser light scattering studies have shown that large multimolecular aggregates are formed on mixing dilute aqueous solutions of poly(L-lysine) and chondroitin 6-sulfate. For the two components in equimolar residue proportions at a total concentration of 0.178 mg/mL, the aggregates have hydrodynamic radii of 1200 Å. Circular dichroism spectroscopy indicates that the polypeptide conformation changes from a coil to the α-helix on cooling the solution. This change can be reversed by increasing the temperature; the midpoint for the transition is 47 °C. Throughout these changes the size of the aggregates remains approximately constant, and thus the conformational transition detected by circular dichroism occurs within the aggregates, which otherwise remain intact. In addition, changes in ratio of the two components, pH, and ionic strength, affect the size of the aggregates.

Our studies of the interactions between oppositely charged polyelectrolytes originate from interest in the structure and composition of the extensive extracellular regions of connective tissue. These regions consist primarily of protein fibers surrounded by a hydrated matrix, comprised mainly of proteoglycans; the latter are branched macromolecules consisting of a protein core to which numerous polyanionic glycosaminoglycan chains are covalently attached as side chains. It has been suggested that an electrostatic attraction occurs between positively charged lysine and arginine residues of collagen and the negatively charged glycosaminoglycans.[1] Previous work in this laboratory has investigated the interactions in model systems comprised of individual glycosaminoglycans (GAGs) and poly(L-lysine) (PLL) or poly(L-arginine) (PLA) in dilute aqueous solution.[2-6] Circular dichroism (CD) spectroscopy indicates that a conformational change is induced in the polypeptides in the presence of the polysaccharides. Maximum interaction between the polypeptides and the seven common GAGs, as judged by the maximum change in ellipticity at 222 nm (reflecting α-helix content), occurs at amino acid:disaccharide ratios characteristic of each system. In addition, the α-helix-directing effects break down as the temperature is increased; each system exhibits a "melting effect", with a characteristic melting temperature, above which the polypeptide reverts to a nonhelical form.

A conformational change for the polypeptide is almost all that can be determined from the CD spectra, and we learn little else about the molecular nature of the interaction. However, some of the CD spectra show scattering distortions indicative of large aggregates in the interacting mixtures, which in extreme cases are visibly turbid. We have used laser homodyne light scattering to investigate the dimension of the aggregates in the interacting mixtures. Initially we have concentrated on the interactions between poly(L-lysine) and chondroitin 6-sulfate. The polysaccharide approximates to an alternating copolymer of β(1,4)-linked D-glucuronic acid and β(1,3)-linked 2-deoxy-2-acetoamido-D-galactosamine 6-sulfate, as shown below.