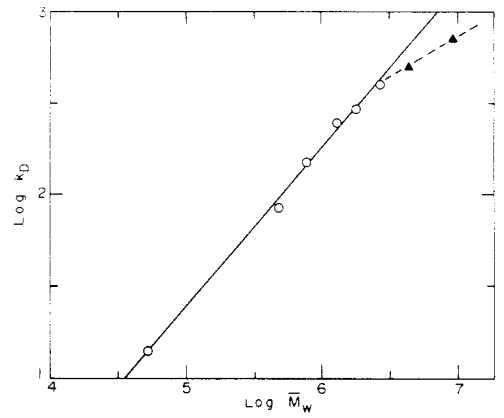

Figure 2. log–log plot of the effective interaction coefficient $k_{D,eff}$ of PS measured at 40 °C in THF as a function of the weight average molar mass ($\bar{M}_w$ in g/mol; $k_{D,eff}$ in mL/g; symbol ▲ and dashed line: for explanation see text).

with the highest molar masses (PS7 and PS9), the condition $qR_h < 0.4$–0.5 was not fulfilled (see Table I). The corresponding $k_{D,eff}$ values in Figure 2 are labeled with ▲ and are connected by a dashed line. The exponent υ in the relationship $k_D \propto (\bar{M}_w)^{\upsilon}$ has a value of $\upsilon = 0.86$ if $qR_h < 0.4$ (solid line) and $\upsilon = 0.49$ for the two samples PS7 and PS9 (dashed line). This difference in the slopes clearly corresponds to the influence of the chain internal movements on the effective interaction coefficient for PS7 and PS9. A similar deviation toward smaller values of the exponent υ at high molar masses was reported by Tsunashima[9] in a thorough analysis of PCS results for PS in good solvents. A careful reanalysis of the data reported in ref 9 and, in particular, those of ref 11 and 12 shows that the four data points for k_D in ref 9, for which $\bar{M}_w > 5 \times 10^6$, are based on measurements where the magnitude of qR_h was close to or higher than 0.4. Correspondingly, the first-order correction factor of the concentration dependence discussed by Tsunashima[9] et al. represents at high molar masses $k_{D,eff}$ rather than $k_{D,0}$ values. This recognition led us to the conclusion that the previously published apparent decrease in the value of the exponent υ is associated with a contribution of the chain-internal dynamics to the measured time autocorrelation function at high molar masses rather than with an intrinsic effect.

Finally it is worthwhile to note that the use of synthetic polymers as model systems at high molar masses ($M \gtrsim 10^7$ g/mol) is affected by a serious problem arising from the polydispersity of the MMD function. Even if the relative polydispersity ratio $\bar{M}_w/\bar{M}_n$ is kept constant while the whole function is shifted toward higher M values, the absolute width of the distribution is increasing. This means that the influence of the polymer molecules at the high M tail of the distribution becomes more important in samples with similar polydispersity index but with high M. A possible way out of this dilemma might be the use of biopolymers as model systems[13] with strictly monodisperse MMD. Only a further decrease in the scattering angle to lower values, a significant improvement in the accuracy of polydispersity analyses of the measured ACF, and the use of monodisperse model polymers will allow one to obtain reliable information about the scaling of k_D and D_t with M of high molar mass polymers from PCS measurements.

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Neutron Scattering from Elastomeric Networks. 2. An Alternative Phantom Network Model

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Introduction

In our recent paper[1] an alternative treatment of fluctuations $\langle(\Delta r_{ij})^2\rangle$ of the distance $\mathbf{r}_{ij}$ between two points i and j on a chain has been proposed. In the classical theory of rubber elasticity[2,3] it is assumed that points on a chain are equivalent to bifunctional junctions. This assumption leads directly to the strain independence of fluctuations of these points, similar to the strain independence of fluctuations of multifunctional junctions in the network. The neutron scattering from a labeled, end-linked chain with the assumption of the strain independence of fluctuations has been studied by Pearson.[4] Recently we have generalized this result to the case of neutron scattering from a labeled, cross-linked path in a network[5] without the additional assumption[6] that different chains along the path are randomly oriented.

Theory

If only the multifunctional junctions ($\phi > 2$) are retained in the configurational function in the James–Guth theory[2,3] there would be no information on the behavior of points

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along the chain. In the undeformed state the mean-square distance $\langle r_{ij}^2\rangle_0$ between points i and j on the chain is proportional to the fractional distance η (the ratio of the contour length of the chain between points i and j to the total length of the chain)

$$\langle r_{ij}^2\rangle_0 = \eta\langle r^2\rangle_0 \tag{1}$$

where $\langle r^2\rangle_0$ is the mean-square end-to-end distance for the undeformed chain and $\langle\ \rangle$ denotes ensemble averaging. Equation 1 is always satisfied if the whole chain and each of its subchains with points i and j at its ends may be treated as freely jointed chains. We might assume[1] that a relation similar to the eq 1 is satisfied also in the deformed state

$$\langle r_{ij}^2\rangle = \eta\langle r^2\rangle \tag{2}$$

i.e., that

$$\langle r_{ij}^2\rangle/\langle r_{ij}^2\rangle_0 = \langle r^2\rangle/\langle r^2\rangle_0 \tag{3}$$

This means that the mean-square distance between points i and j is always the same fraction of the mean-square end-to-end vector in the undeformed as well as in the stretched state. This assumption should not be too inaccurate especially at lower deformations. The assumption of the strain independence of fluctuations[4] $\langle(\Delta r_{ij})^2\rangle$ leads to the equation[1,6]

$$\langle r_{ij}^2\rangle = \eta(1-\eta)\langle r^2\rangle_0 + \eta^2\langle r^2\rangle \tag{4}$$

instead of eq 2. The fluctuations $\langle(\Delta r_{ij})^2\rangle_0$ of the distance between points i and j relevant to the undeformed state are

$$\langle(\Delta r_{ij})^2\rangle_0 = \eta(1-\eta)\langle\bar{r}^2\rangle_0 + \eta\langle(\Delta r)^2\rangle_0 \tag{5}$$

(here $\bar{r}_0$ is the mean end-to-end vector in the undeformed state and $\langle(\Delta r)^2\rangle_0$ its fluctuations). Equation 2 is equivalent[1] to the assumption that a similar equation might be written for the deformed state:

$$\langle(\Delta r_{ij})^2\rangle = \eta(1-\eta)\langle\bar{r}^2\rangle + \eta\langle(\Delta r)^2\rangle \tag{6}$$

where $\bar{r}$ is the mean end-to-end vector in the deformed state and $\langle(\Delta r)^2\rangle$ its fluctuations. $\bar{r}_0$ and $\bar{r}$ denote time averages for the end-to-end vector for a single chain in undeformed and stretched states, respectively, and $\langle\bar{r}^2\rangle_0$ and $\langle\bar{r}^2\rangle$ are ensemble averages of $\bar{r}_0^2$ and $\bar{r}^2$.

The fluctuations of the end-to-end distance are always strain independent

$$\langle(\Delta r)^2\rangle = \langle(\Delta r)^2\rangle_0 \tag{7}$$

and the mean vectors transform affinely with strain

$$\bar{\mathbf{r}} = \boldsymbol{\lambda}\bar{\mathbf{r}}_0 \tag{8}$$

with $\boldsymbol{\lambda}$ the deformation gradient tensor. Rewriting eq 6 for the x component only and using eq 7 and 8 and the known result for ϕ-functional networks

$$\langle(\Delta r)^2\rangle_0 = \frac{2}{\phi}\langle r^2\rangle_0 \tag{9}$$

we obtain

$$\langle(\Delta x_{ij})^2\rangle = \eta\left[\lambda_x^2(1-\eta)\left(1-\frac{2}{\phi}\right)+\frac{2}{\phi}\right]\langle r^2\rangle_0/3 \tag{10}$$

Here λ_x is the x-component of the diagonalized deformation gradient tensor $\boldsymbol{\lambda}$, which is the ratio of the final length to the reference length. The fluctuations of the distance between points i and j of the chain are strain dependent, although the fluctuations of the distance between junctions are strain independent. Because of this the scattering form factor

$$S(\mathbf{q}) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle\exp(i\mathbf{q}\cdot\mathbf{r}_{ij})\rangle \tag{11}$$

for the deformed network will be different from the result obtained by Pearson.[4] Here $\mathbf{q}$ is the scattering vector and N the number of scattering centers of the chain. It might be useful to compare the results of both assumptions with each other and with experiment. For Gaussian chains eq 11 might be written[4-6] in terms of Cartesian components of the scattering vector q_x, q_y, q_z as

$$S(\mathbf{q}) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp\left[-\frac{1}{2}(q_x^2\langle x_{ij}^2\rangle + q_y^2\langle y_{ij}^2\rangle + q_z^2\langle z_{ij}^2\rangle)\right] \tag{12}$$

By replacement of the double sum over the scattering centers (monomers) of the chain by integrals, the scattering form factor for the scattering parallel to the direction of extension becomes[4]

$$S_\parallel(q) = 2\int_0^1 d\eta\,(1-\eta)\exp\left\{-\nu\eta\left[1-\eta(1-\lambda_\parallel^2)\left(1-\frac{2}{\phi}\right)\right]\right\} \tag{13}$$

with

$$\nu = q^2\langle r^2\rangle_0/6 \tag{14}$$

if the assumption of strain independence of fluctuations (eq 4) is used. This result has been obtained by Pearson.[4] From an alternative assumption (eq 2 or equivalently eq 6) there follows

$$S_\parallel(q) = 2\int_0^1 d\eta\,(1-\eta)\exp\left\{-\nu\eta\left[\lambda_\parallel^2+\frac{2}{\phi}(1-\lambda_\parallel^2)\right]\right\} = \frac{2}{x^2}(e^{-x}+x-1) \tag{15}$$

where

$$x = \nu\left[\lambda_\parallel^2+\frac{2}{\phi}(1-\lambda_\parallel^2)\right] \tag{16}$$

i.e., the well-known formula for scattering from Gaussian coils with the parameter x depending on deformation. For scattering $S_\perp(q)$ perpendicular to the direction of extension, $\lambda_\parallel$ has to be replaced by $\lambda_\perp = 1/\lambda_\parallel^{1/2}$ or generally for any $\boldsymbol{\lambda}$ and any $\mathbf{q}$ by vector $\boldsymbol{\lambda}^*$

$$\boldsymbol{\lambda}^* = \boldsymbol{\lambda}\mathbf{q}/q \tag{17}$$

As the strain goes to zero both eq 13 and 15 have the same limiting form

$$\lim_{\lambda\to 1} S(q) = \frac{2}{\nu^2}(e^{-\nu}+\nu-1) \tag{18}$$

corresponding to the scattering from an unperturbed Gaussian coil.[7] In the long-wavelength limit ($\nu \to 0$), eq 13 gives

$$S(q) \approx 1-\frac{\nu}{3}\left[\lambda^2\left(\frac{1}{2}-\frac{1}{\phi}\right)+\frac{1}{2}+\frac{1}{\phi}\right] \tag{19}$$

while eq 15 gives

$$S(q) \approx 1-\frac{x}{3} = 1-\frac{\nu}{3}\left[\lambda^2\left(1-\frac{2}{\phi}\right)+\frac{2}{\phi}\right] \tag{20}$$

In the limit $\nu \to \infty$ eq 13 gives

$$S(q) = \frac{2}{\nu}\left\{1-\frac{1}{\nu}\left[\lambda^2\frac{2(\phi-2)}{\phi}+\frac{4-\phi}{\phi}\right]\right\} \tag{21}$$

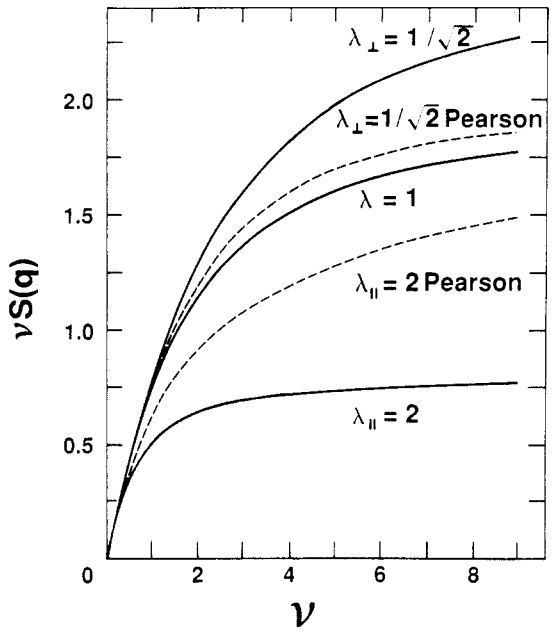

Figure 1. Kratky plot of $\nu S(q)$ versus ν for an unstretched chain ($\lambda = 1$) and for elongation $\lambda = 2$, for scattering parallel (below) and perpendicular (above) to the deformation calculated by Pearson's model (dotted lines) and the alternative phantom network model (solid lines).

while eq 15 gives

$$S(q) = \frac{2}{x^2}(x-1) = 2\left\{1 - \frac{1}{\nu\left[\lambda^2 + \frac{2}{\phi}(1-\lambda^2)\right]}\right\} \Big/ \nu\left[\lambda^2 + \frac{2}{\phi}(1-\lambda^2)\right] \quad (22)$$

Figure 1 shows the Kratky plots of $\nu S(q) = q^2 S(q)\langle r^2\rangle_0/6$ versus ν for the undeformed chain ($\lambda = 1$) and for the stretched chain ($\lambda = 2$) for a network with functionality $\phi = 4$. The dotted lines correspond to the scattering parallel ($\lambda_\parallel = 2$) or perpendicular ($\lambda_\perp = 1/2^{1/2}$) to the principal axis of deformation calculated by using eq 13, i.e., Pearson's[4] assumption of the strain independence of fluctuations. The solid lines correspond to the Kratky plots for the stretched chain calculated by using eq 15, based on the assumption that fluctuations of points along the chain are strain dependent. There is a significant difference between the scattering form factors calculated by using these two different equations. The scattering form factor $S_\parallel(q)$ obtained from eq 13 is larger than $S_\parallel(q)$ calculated from eq 15. For scattering perpendicular to the principal axis of deformation the reverse relationship is satisfied and $S_\perp(q)$ calculated from eq 13 is smaller than $S_\perp(q)$ calculated from eq 15. As λ increases, the difference between scattering form factors calculated from these two equations also increases. In the limit $\lambda \to 1$ both equations give the same solution.

Comparison with Experiment

Recent progress in experimental techniques enables direct study of the small-angle neutron scattering from a single chain. The single labeled (deuterated) chain is end linked into the nondeuterated network. The scattering form factor for such a chain in the unstrained and strained states has been measured recently by Boué et al.[8,9] The experiment has been performed for relatively small elongation, specifically $\lambda = 1.3$. Figure 2 shows the comparison of Kratky plots calculated from eq 13 (dotted lines) and from eq 15 (full lines) with experimental data.[8,9] The lines below the Kratky plot for the undeformed Gaussian chain ($\lambda = 1$) correspond to scattering parallel, and above to scattering perpendicular, to the deformation. Calculations were performed for a chain with radius of gyration $R_g = ((1/6)\langle r^2\rangle_0)^{1/2} = 42$ Å, without correction for polydispersity. It seems the proposed alternative phantom network model (eq 15) better describes scattering perpendicular to the deformation than does Pearson's model (eq 13). For scattering parallel to the deformation, eq 13 overestimates the scattering factor while eq 15 underestimates it for larger q. Experiments performed for larger elongations could supply more conclusive data. Thus, the alternative phantom network model presented in this note might be a useful guide for the interpretation of future experimental data.

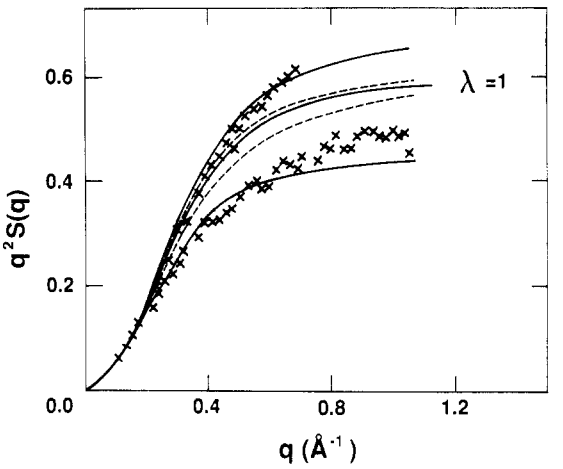

Figure 2. Comparison of form factors calculated from Pearson's model (dotted lines) and from the alternative phantom network model (solid lines) with experimental data by Boué et al.[8,9] for a chain with a radius of gyration $R_g = 42$ Å and elongation $\lambda = 1.3$.

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