Correlations among Chains along a Cross-Linked Path in a Phantom Network and Their Characterization by SANS

A. Kloczkowski* and J. E. Mark

Department of Chemistry and the Polymer Research Center, University of Cincinnati, Cincinnati, Ohio 45221

B. Erman

Polymer Research Center, Bogazici University, Bebek 80815, Istanbul, Turkey

Received February 9, 1990; Revised Manuscript Received January 21, 1992

ABSTRACT: The form factor for small-angle neutron scattering from an ensemble of labeled paths in a phantom network is calculated. Instead of the assumption that the labeled path is freely-jointed (i.e., instantaneous end-to-end vectors for various subchains along the path in the undeformed state are uncorrelated), we use the more rigorous result for an ensemble of labeled paths according to which it is the mean values of the end-to-end vectors for various subchains between cross-links along the path in the undeformed state that are uncorrelated. This non-freely-jointed behavior of labeled cross-linked paths increases the maxima on the Kratky plots significantly in comparison with the freely-jointed labeled path model. For sufficiently long paths there is possibly a maximum in the Kratky plot for the neutron scattering from undeformed, unswollen phantom networks.

Introduction

Small-angle neutron scattering (SANS)[1–5] is a modern experimental technique enabling the study of the structure and dynamics of polymer chains in networks in both the undeformed and the deformed states at the molecular level. To study chains using neutron scattering, labeled (deuterated) chains are incorporated into the normal, nondeuterated network. The scattering form factor depends strongly on the number of cross-links along a deuterated path as evidenced by recent experimental data.[1–5] The simplest useful representation of a network is the phantom network model,[6,7] which neglects excluded volume constraints and entanglement effects but allows fluctuations of junctions and chains around their mean positions. The problem of small-angle neutron scattering from end-linked chains (with no other cross-links along the path) in a phantom Gaussian network with treelike topology was first studied by Pearson.[8] The first evaluation of neutron scattering from labeled chains cross-linked into a network was given by Warner and Edwards[9] for tetrafunctional networks using the replica model. The scattering from a labeled path with a specified number of cross-links in a phantom Gaussian network of arbitrary functionality and with the topology of the symmetrically grown tree was studied by Ullman.[10] He, however, used the simplifying assumption that different chain vectors along the path are uncorrelated in both the undeformed and the deformed states. Recently, the calculations of Ullman have been improved[11,12] by removing the assumption that different chain vectors of the path are uncorrelated in the deformed state. However, in the undeformed state, the assumption was made that the different chain vectors are uncorrelated; i.e., the path is freely-jointed. This assumption is expressed by the equation

$$\langle r_{ij}^{\,2}\rangle_0 = \eta\langle r^2\rangle_0 \qquad (1)$$

where $\mathbf{r}_{ij}$ is the vector between points i and j on the path, $\mathbf{r}$ is the end-to-end vector for a chain between two consecutive cross-links along the path, and η is the ratio of the contour length between i and j to that of a chain between two consecutive cross-links. In eq 1 and in all the following equations, angular brackets denote ensemble averages and the subscript zero identifies the undeformed state. All authors[9–13] studying the problem of SANS from labeled paths have used this assumption. For two instantaneous vectors $\mathbf{r}_{m,m+1}$ and $\mathbf{r}_{n,n+1}$ joining junctions m with $m + 1$ and n with $n + 1$ along a path, this assumption implies

$$\langle \mathbf{r}_{m,m+1}\cdot\mathbf{r}_{n,n+1}\rangle_0 = 0 \qquad m \neq n \qquad (2)$$

In the present study, we replace this assumption by

$$\langle \bar{\mathbf{r}}_{m,m+1}\cdot\bar{\mathbf{r}}_{n,n+1}\rangle_0 = 0 \qquad m \neq n \qquad (3)$$

where the overbar denotes time averaging. We feel that eq 3 is more plausible for cross-linked paths in a phantom network. This statement rests on the postulate that in the undeformed state the distribution of the mean end-to-end vectors in the ensemble is isotropic. From the statistical-mechanical point of view the cross-linked system differs significantly from the un-cross-linked one. Equation 2 was originally derived for free chains where ensemble and time averages are the same. For the cross-linked system we have to distinguish between time and ensemble averaging, and the symmetry of the ensemble requires that eq 3 rather than eq 2 be satisfied.

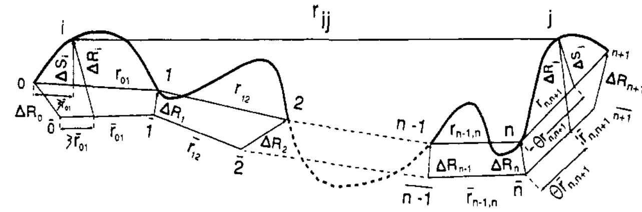

Figure 1. Instantaneous configuration of a cross-linked chain with two points i and j separated by n cross-links.

Correlations among Chains in a Cross-Linked Path

Let us consider a cross-linked path as shown in Figure 1. Points $\bar{0}$, $\bar{1}$, ..., $\bar{n}$, $\overline{n+1}$ represent mean positions of junctions, and points 0, 1, ..., n, $n + 1$ their instantaneous positions along the path. The fluctuations of junctions from their mean positions are $\Delta\mathbf{R}_\nu$ ($\nu = 0, 1, ..., n + 1$). The mean (time-averaged) end-to-end vectors between consecutive junctions are $\bar{\mathbf{r}}_{\nu,\nu+1}$ ($\nu = 0, 1, ..., n$), while $\mathbf{r}_{\nu,\nu+1}$ are end-to-end vectors at a given instant. The distance between two arbitrary points i and j on the path separated by n junctions is $\mathbf{r}_{ij}$. The fractional distances of points i and j from the nearest junctions on their left are ζ and θ, respectively. Vectors $\zeta\bar{\mathbf{r}}_{01}$ and $\theta\bar{\mathbf{r}}_{n,n+1}$ show the mean positions of points i and j for fixed $\Delta\mathbf{R}_\nu$ ($\nu = 0, 1, ..., n + 1$), and $\Delta\mathbf{S}_i$ and $\Delta\mathbf{S}_j$ are fluctuations of points i and j from these positions. From Figure 1 it follows that

$$\Delta\mathbf{R}_i = (1-\zeta)\Delta\mathbf{R}_0 + \zeta\Delta\mathbf{R}_1 + \Delta\mathbf{S}_i$$

and

$$\Delta\mathbf{R}_j = (1-\theta)\Delta\mathbf{R}_n + \theta\Delta\mathbf{R}_{n+1} + \Delta\mathbf{S}_j \tag{4}$$

The analysis proceeds by multiplying $\Delta\mathbf{R}_i$ by $\Delta\mathbf{R}_j$, ensemble averaging, using the result that fluctuations $\Delta\mathbf{S}_i$ and $\Delta\mathbf{S}_j$ are uncorrelated with fluctuations of the junctions and that $\langle\Delta\mathbf{S}_i\cdot\Delta\mathbf{S}_j\rangle_0 = 0$ for points i and j belonging to different chains (separated by one or more cross-links), and using the known formula for correlations of fluctuations of junctions along the path[10,12,14]

$$\langle\Delta\mathbf{R}_\nu\cdot\Delta\mathbf{R}_\mu\rangle_0 = \frac{1}{\phi(\phi-2)(\phi-1)^{|\nu-\mu|-1}}\langle r^2\rangle_0 \tag{5}$$

(in which cross-links along the path are labeled by consecutive natural numbers $0 \le \nu, \mu \le n + 1$). This leads to the expression for the fluctuations of the $\mathbf{r}_{ij}$ vector[12,14]

$$\langle(\Delta\mathbf{r}_{ij})^2\rangle_0 = \langle(\Delta\mathbf{R}_j - \Delta\mathbf{R}_i)^2\rangle_0 = \left\{\frac{2(\phi-1)}{\phi(\phi-2)}[1-(\phi-1)^{-n}] + \left(1-\frac{2}{\phi}\right)[\zeta(1-\zeta) + \theta(1-\theta) - (\zeta+\theta-2\zeta\theta)/(\phi-1)^n] + (\eta - n)/(\phi-1)^n\right\}\langle r^2\rangle_0 \tag{6}$$

where ϕ denotes the network functionality. Equation 6 is an exact result for a phantom Gaussian network and does not depend on the assumptions given by eq 2 or 3. From Figure 1 it follows that

$$\mathbf{r}_{ij} = (1-\zeta)\bar{\mathbf{r}}_{01} + \sum_{\nu=1}^{n-1}\bar{\mathbf{r}}_{\nu,\nu+1} + \theta\bar{\mathbf{r}}_{n,n+1} + \Delta\mathbf{R}_j - \Delta\mathbf{R}_i \tag{7}$$

when point i is on the left of point j on the path and is separated by at least one cross-link. If point i is on the right side of point j and is separated by at least one junction, then ζ and θ in eq 7 have to be interchanged. Squaring, ensemble averaging eq 7, and applying our postulate (eq 3), one obtains

$$\langle r_{ij}^2\rangle_0 = [(1-\zeta)^2 + \theta^2 + n - 1]\left(1-\frac{2}{\phi}\right)\langle r^2\rangle_0 + \langle(\Delta r_{ij})^2\rangle_0 \tag{8}$$

In the strained state, the mean vectors transform affinely, the fluctuations are assumed to be strain independent,[6,7] and the x component of $\mathbf{r}_{ij}$ may be written

$$\langle x_{ij}^2\rangle = \lambda_x^2\langle\bar{x}_{ij}^2\rangle_0 + \langle(\Delta x_{ij})^2\rangle \tag{9}$$

with

$$\langle\bar{x}_{ij}^2\rangle_0 = [(1-\zeta)^2 + \theta^2 + n - 1]\left(1-\frac{2}{\phi}\right)\langle r^2\rangle_0/3 \tag{10a}$$

if point i is on the left of j and is separated by junction(s)

$$\langle\bar{x}_{ij}^2\rangle_0 = [(1-\theta)^2 + \zeta^2 + n - 1]\left(1-\frac{2}{\phi}\right)\langle r^2\rangle_0/3 \tag{10b}$$

if point i is on the right of j and is separated by junction(s), and

$$\langle\bar{x}_{ij}^2\rangle_0 = (\zeta-\theta)^2\left(1-\frac{2}{\phi}\right)\langle r^2\rangle_0/3 \tag{10c}$$

if i and j are on the same chain. Equations 9 and 10 may be used to calculate the scattering form factor.

The Scattering Form Factor

The expression for the form factor $S_\parallel(q)$ in the direction parallel to stretch (the x direction) is

$$S_\parallel(q) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp\left[-\frac{1}{2}q_x\langle x_{ij}^2\rangle\right] \tag{11}$$

where q_x is the magnitude of the scattering vector in the x direction and N is the total number of scattering centers along the path. The assumption of the freely-jointed behavior of the path given by eq 2 leads to[11]

$$S_\parallel(q) = \frac{1}{n_c^2}\sum_{n_i=1}^{n_c}\sum_{n_j=1}^{n_c}\int_0^1 d\theta\int_0^1 d\zeta\,\exp\Bigg[-\nu\Bigg[\lambda_\parallel^2|n_j+\theta-n_i-\zeta| + (1-\lambda_\parallel^2)\Bigg\{\frac{2(\phi-1)}{\phi(\phi-2)}(1-(\phi-1)^{-|n_j-n_i|}) + \left(1-\frac{2}{\phi}\right)[\zeta(1-\zeta) + \theta(1-\theta) - (\zeta+\theta-2\zeta\theta)/(\phi-1)^{|n_j-n_i|}] + \frac{|n_j+\theta-n_i-\zeta| - |n_j-n_i|}{(\phi-1)^{|n_j-n_i|}}\Bigg\}\Bigg]\Bigg] \tag{12}$$

where $\nu = q^2\langle r^2\rangle_0/6$, $\lambda_\parallel$ is the component of the deformation gradient tensor in the direction parallel to the direction of stretch, and n_c is the number of chains along the path. For simplicity, dangling chains have been neglected in eq 12, which may easily be incorporated into the scattering form factor as has been done by Ullman.[10] For scattering perpendicular to the direction of stretch, $\lambda_\parallel$ is replaced by $\lambda_\perp = 1/\lambda_\parallel^{1/2}$. The scattering form factor has been calculated[11] for varying lengths of the labeled path in the network. A characteristic feature of cross-linked paths is the maximum in the Kratky plot of $q^2S(q)$ vs q for perpendicular scattering. The more cross-linked the path and the larger the deformation, the more distinct is the maximum. For end-linked labeled chains there is no maximum at all in the Kratky plot. These basic results obtained for a simple phantom network model agree qualitatively with SANS experimental data.[1-5]

In the present work we apply eq 3 instead of eq 2 for the calculation of $S(q)$. The scattering form factor from the cross-linked path calculated with this assumption is

$$S_\parallel(q) = \frac{1}{n_c^2}\sum_{n_i=1}^{n_c}\sum_{n_j=1}^{n_c}\int_0^1 d\theta\int_0^1 d\zeta\,\exp\Bigg[-\nu\Bigg[\lambda_\parallel^2\left(1-\frac{2}{\phi}\right)\{|n_i-n_j| + \theta^2 + \zeta^2 - 2[\zeta\theta\delta_{n_in_j} + \zeta H(n_j-n_i) + \theta H(n_i-n_j)]\} + \frac{2(\phi-1)}{\phi(\phi-2)}(1-(\phi-1)^{-|n_j-n_i|}) + \frac{\phi-2}{\phi}\Bigg[\zeta(1-\zeta) + \theta(1-\theta) - \frac{\zeta+\theta-2\zeta\theta}{(\phi-1)^{|n_j-n_i|}}\Bigg] + \frac{|n_j+\theta-n_i-\zeta| - |n_j-n_i|}{(\phi-1)^{|n_j-n_i|}}\Bigg]\Bigg] \tag{13}$$

where $\delta_{n_in_j}$ is the Kronecker delta and $H(n_j-n_i)$ is the step function defined by

$$H(n_j-n_i) = 1 \quad \text{if } n_j > n_i$$
$$= 0 \quad \text{if } n_j \le n_i \tag{14}$$

Results of representative calculations based on eq 13 can now be given and compared with our previously

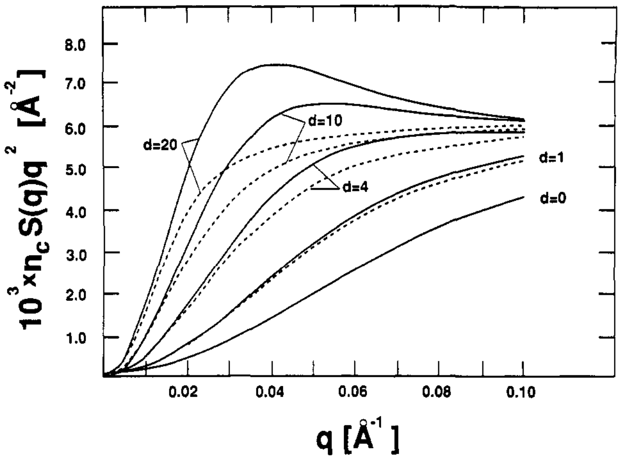

Figure 2. Kratky plots for unswollen, undeformed (λ = 1) networks. The number of cross-links along the path changes from d = 0 (single chain) to d = 20. Solid lines correspond to form factors calculated from eq 13, and dashed lines to form factors calculated from eq 12.

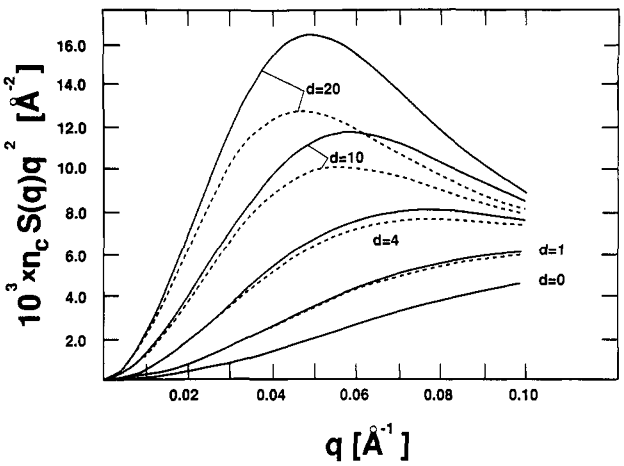

Figure 3. Kratky plots for unswollen, deformed networks ($\alpha_{\perp}$ = 0.5) for scattering perpendicular to the direction of stretch.

obtained results[11] for freely-jointed labeled paths based on eq 12. The results are presented in the form of Kratky plots of $n_c q^2 S(q)$ vs q. There is a difference between the Kratky plots presented here and those presented previously, when values of $q^2 S(q)$ are plotted.[11] Here we multiply each form factor by the number of chains along the path n_c. This rescaling of form factors enables the comparison of Kratky plots for polymers with the same total molecular weight of deuterated chains. The calculations have been performed for tetrafunctional networks (ϕ = 4) with $\langle r^2 \rangle_0$ = 2000 Å^2.

Figure 2 shows Kratky plots for the undeformed (λ = 1), unswollen networks with varying length of the path from single chain (n_c = 1) with no cross-links along the path to path consisting of n_c = 21 chains (and $d = n_c - 1$ = 20 cross-links). Full lines correspond to results obtained by using eq 13 while dashed lines correspond to results obtained using eq 12. For a single chain without cross-links (an end-linked chain), the equations give the same result. With increasing numbers of cross-links along the path, the difference between the curves increases rapidly. The scattering form factor calculated from eq 13 based on the assumption given by eq 3 is always greater than the form factor calculated using eq 2. The most striking result is the maximum on the Kratky plots for sufficiently long non-freely-jointed paths. The more cross-links along the path, the more pronounced the maximum. None of the previous theories[9–12] based on eq 2 predicted a maximum in the Kratky plot for an undeformed, unswollen network.

Figure 3 shows Kratky plots for deformed, unswollen networks with regard to perpendicular scattering ($\alpha_{\perp}$ = 0.5). The effect of using eq 3 is significant, especially for paths with many cross-links. The maxima on the Kratky plots calculated from eq 13 (full lines) are much larger than those obtained previously (dashed lines). For a labeled path with a small enough number of cross-links ($d < 4$), neither model gives a maximum. With increasing number of cross-links along the path, however, the maxima on the Kratky plots become more pronounced and the difference between the plots for the present and the previous models increases rapidly.

For scattering parallel to the direction of stretch the difference between form factors obtained from eq 21 (full lines) and from eq 19 (dashed lines) is very small, and in neither case is there a maximum on the Kratky plot, irrespective of the number of cross-links along the path.

Although the Kratky plots presented in this paper have been calculated for the specific value $\langle r^2 \rangle_0$ = 2000 Å^2 of the unperturbed mean-square end-to-end vector for chains between cross-links, the basic results are independent of $\langle r^2 \rangle_0$ (changing $\langle r^2 \rangle_0$ affects only the q scale of the Kratky plots).

Discussion

The present study is based on the assumption that the ensemble distribution of *mean* vectors between junctions along a path in an undeformed phantom Gaussian network is isotropic. Calculations of the scattering form factor based on this assumption show significant differences from those obtained previously by various authors. All previous studies made the less-plausible assumption that the *instantaneous* vectors between junctions along a path in an undeformed phantom network are uncorrelated. The difference between the two approaches increases with increasing number of cross-links along the path and with elongation upon stretching. The most striking result of the theory based on eq 3 is the prediction of the maxima on Kratky plots for the small-angle neutron scattering from undeformed, unswollen networks. None of the theories based on eq 2 lead to this result.

Almost no experimental data show a maximum for scattering from labeled paths in undeformed, unswollen networks. In a few cases (e.g., Figure 2 in ref 1 for scattering from a Friedel–Crafts rubber), a very small maximum (within experimental error) is observed. It should be stressed, however, that our calculations have been performed for the phantom model of the polymer network. Real networks are not phantom and the phantom network theory generally encounters serious problems in the explanation of experimental data. The experimental maxima on Kratky plots are too low and too broad to be successfully described by phantom network theories based on eq 2. Our treatment based on eq 3 leads to even greater discrepancies with experiment. This suggests that entanglements and steric effects in real networks could be very important and contribute significantly to the scattering properties of networks. It should be noted that for real networks with relatively short chains between cross-links, the ensemble average given by eq 3 will not equate to zero. This is due to the fact that steric effects (i.e., volume exclusion) will tend to prevent overlapping of two neighboring chain vectors. A successful theory of polymer networks has to account for all these effects.

We hope that our work will help test the validity of existing molecular theories of rubber elasticity and encourage new experimental studies.

Acknowledgment. It is a pleasure to acknowledge the financial support provided J.E.M. by the National Science Foundation through Grant DMR 89-18002 (Polymers Program, Division of Materials Research).

References and Notes

(1) Boué, F.; Bastide, J.; Buzier, M.; Collette, C.; Lapp, A.; Herz, J. *Prog. Colloid Polym. Sci.* **1987**, *75*, 152.
(2) Picot, C. *Prog. Colloid Polym. Sci.* **1987**, *75*, 83.
(3) Boué, F.; Farnoux, B.; Bastide, J.; Lapp, A.; Herz, J.; Picot, C. *Europhys. Lett.* **1986**, *1*, 637.
(4) Bastide, J.; Herz, J.; Boué, F. *J. Phys. (Paris)* **1985**, *46*, 1967.
(5) Boué, F. *Adv. Polym. Sci.* **1987**, *82*, 1.
(6) James, H. M. *J. Chem. Phys.* **1947**, *15*, 651.
(7) James, H. M.; Guth, E. *J. Chem. Phys.* **1947**, *15*, 669.
(8) Pearson, D. S. *Macromolecules* **1977**, *10*, 696.
(9) Warner, M.; Edwards, S. F. *J. Phys. A: Math. Gen.* **1978**, *11*, 1649.
(10) Ullman, R. *Macromolecules* **1982**, *15*, 1395.
(11) Kloczkowski, A.; Mark, J. E.; Erman, B. *Macromolecules* **1989**, *22*, 4502.
(12) Higgs, P. G.; Ball, R. C. *J. Phys. Fr.* **1988**, *79*, 1785.
(13) Vilgis, T.; Boué, F. *Polymer* **1986**, *27*, 1154.
(14) Kloczkowski, A.; Mark, J. E.; Erman, B. *Macromolecules* **1989**, *22*, 1423.
(15) Erman, B.; Kloczkowski, A.; Mark, J. E. *Macromolecules* **1989**, *22*, 1432.

Registry No. Neutron, 12586-31-1.