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Theoretical investigation of SANS from elastomeric networks with topological constraints

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Summary

This paper presents a theoretical investigation of SANS from labeled chains in polymer networks which are characterized by the topology of tube-like deformation dependent configurational constraints. The deformation dependence of the constraints is assumed to relax and to be determined by a microscopic deformation law. The results lead to the conclusion that the change of the radius of gyration of a network chain may be much less than the deformation of the macroscopic sample. It is pointed out that network defects favour the effect of constraint release.

Introduction

Small-angle neutron-scattering (SANS) on partially deuterated networks allows a direct measurement of polymer chain deformation (stretching or swelling). This makes SANS a unique tool for assessing the validity of theoretical models of polymer networks.
For uniaxially stretched networks (deformation $\lambda_x = \lambda_y = \lambda^{-1/2}$, $\lambda_z = \lambda$), the molecular deformations are characterized by the radii of gyration $R_{g\parallel}$ and $R_{g\perp}$ parallel and perpendicular to the stretching direction, respectively. Within the framework of phantom network theory the molecular deformation of a stretched elastic phantom chain has been calculated for three cases:
(a) Free-fluctuating phantom network (1):

$$\frac{R_{g\parallel}}{R_{gi}} = \left(\frac{f+2+(f-2)\cdot\lambda^2}{2f} \right)^{1/2} \qquad (1)$$

where R_{gi} is the radius of gyration for unstretched isotropic network chains, and f the functionality.

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(b) Affine junction displacement (2):

$$\frac{R_{g\parallel}}{R_{gi}} = \left(\frac{\lambda^2+1}{2}\right)^{1/2} \qquad (2)$$

(c) Affine deformation:

$$\frac{R_{g\parallel}}{R_{gi}} = \lambda \qquad (3)$$

This model assumes that the deformation of each configuration of the chains is affine in the macroscopic deformation.
Most of the scattering experiments which were performed on uniaxially stretched end-linked siloxane networks showed much smaller molecular deformations than would be predicted even from Eq. (1) (3-5). Therefore, the following conclusions could be drawn (6,7):
(a) The concept of network unfolding and junction rearrangement (8) seems to provide a qualitative explanation for the small chain extension. Obviously, the degree of network unfolding depends on network preparation, degree of sample deformation and quantity of solvent in the network.
(b) The scattering on randomly crosslinked networks built up from long primary chains is different from that on end-linked networks. The former shows much greater sensivity to network deformation and much less sensivity to network functionality. The latter seem to be very sensitive to incomplete crosslinking which influences the elastic properties of a network substantially.
In the following section we present calculations of SANS from labeled chains in polymer networks which are characterized by the topology of crosslinking (T_c) and of tube-like deformation dependent configurational constraints (T_t). The deformation dependence of T_t will be described by a microscopic deformation law.

Theory

The network model is characterized by the following assumptions (9-11):
(a) The configurations of the chains are described by space curves $\underline{R}(s)$, s being the arc length of the chain.
(b) The mean configuration $\underline{R}'(s)$ obeys the random walk behaviour:

$$p(\underline{R}'(s)) \sim \exp\left(-\frac{3}{2l}\int_0^{L_c} ds\,(d\underline{R}'(s)/ds)^2\right) \qquad (4)$$

$L_c = N_c l$ is the contour length of a network chain. N_c denotes the number of statistical segments with length l. The statistical weight for a configuration $\underline{R}(s)$ of a chain with a mean configuration (tube axis) $\underline{R}'(s)$ is given by (14)

$$p(\underline{R}(s)|\underline{R}'(s)) \sim \exp\left(- \int_0^{L_c} \left(\frac{3}{2l}(d\underline{R}(s)/ds)^2 + \right.\right.$$
$$\left.\left. + \sum_{\substack{j= \\ x,y,z}} \frac{1}{d_j^4} (R_j(s) - R_j'(s))^2 \right) ds \right) \qquad (5)$$

The strength of the constraints is determined in this model by the prefactors of $(R_j(s) - R_j'(s))^2$. It is assumed that for the undeformed isotropic system the constraining potential is independent of the direction of the constrained chain and diagonal in the principal axis system of the deformation tensor of external deformation. The d_j are the square roots of the mean square deviations of the chains from the tube axis,

$$d_j = \left\langle (R_j(s) - R_j'(s))^2 \right\rangle^{1/2} \qquad (6)$$

(c) The deformation dependence of d_j follows the power law

$$d_j = d_o \lambda_j^n \qquad (j = x,y,z) \qquad (7)$$

with $-1 \leq n \leq +1$. Eq.(7) was obtained by phenomenological considerations and could be derived in the frame of a mean field theory of topological constraints (10-13,18). The exponent $n = a \cdot b$ is the product of two contributions. a describes the constraining mechanism ($-1 \leq a \leq +1$) of network strands and b characterizes the effect of relaxed microscopic deformation,

$$\alpha_j \equiv \lambda_j^b \qquad (0 \leq b \leq 1) \quad .$$

b depends on the amount of solvent, sol fraction, network defects and on the crosslinking density (11). a contains contributions both due to packing effects and pure entanglement effects. In the case of moderately crosslinked networks made by randomly crosslinking of long primary chains the value $a=+1/2$ and $0 \leq b \leq 1$ was derived (11-13). Highly crosslinked networks with small topological constraining effects give $a=-1/4$ and $b \approx 1$ (10-12). The picture of trapped pure entanglements yields $a=-1$ and $b \approx 1$ (11), whereas $a=+1$ and $b=1$ leads to the non-constitutive

Mooney-Rivlin equation of stress-strain behaviour.
It has to be noted that Ullman (19) introduced the concept of microscopic network chain deformation through a harmonic "memory" potential incorporated in the statistical weight of the configuration $\underline{R}(s)$. This potential tends to return the chains to the configurations which they had before deformation.
The scattering function,

$$S(\underline{k}, \underline{\underline{\lambda}}) = \left\langle S_T(\underline{k}, \underline{\underline{\lambda}}) \right\rangle_T$$

($\underline{k}$ - scattering vector), can be calculated following the replica method of Warner and Edwards (16), i.e. averaging the scattering law S_T of a single network topology over the set of all possible topologies. S_T is given in Eq. (8):

$$S_T(\underline{k}, \underline{\underline{\lambda}}) = N_s^{-2} \sum_{m,m'} \int D(\underline{R}(s),(s_i,s_i')) \; p(\underline{R}(s)|\underline{R}'(s)) \cdot \cdot \exp(i\underline{k} \cdot (\underline{R}(s_m) - \underline{R}(s_m,))) \tag{8}$$

N_s denotes the total segment number. The double-sum runs over the segments of the whole network. We will consider that the mean tube axis configuration $\underline{R}'(s)$ changes according to the microscopic deformation law $\underline{R}'(s) \longrightarrow \underline{\underline{\alpha}} \, \underline{R}'(s)$ (9-11).
Averaging of Eq. (8) leads to the expression

$$S(\underline{k},\underline{\underline{\lambda}}) = \int\int p(\underline{R}'(s)) \; S_T(\underline{k}, \underline{\underline{\lambda}}) \; D(\underline{R}'(s),(s_i,s_i')) \prod_{i=1}^{M} ds_i \; ds_i' \tag{9}$$

The formal representation of S_T as a free energy with the external generalized potential

$$xQ(\underline{k}) = xN_s^{-2} \sum \exp(i\underline{k} \cdot (\underline{R}_m - \underline{R}_m,))$$

is given by the following expressions (16):

$$S_T(\underline{k}, \underline{\underline{\lambda}}) = - \frac{d}{dx} S_T'(x,\underline{k}, \underline{\underline{\lambda}}) \Big|_{x=0} , \tag{10}$$

$$S_T'(x,\underline{k}, \underline{\underline{\lambda}}) = \log \int D(\underline{R}(s),(s_i,s_i')) \exp(- \frac{H}{k_B T} - xQ(\underline{k})) \tag{11}$$

H corresponds to the Hamiltonian of Eq. (5). The expression

$$D(\underline{R}(s),(s_i,s_i')) = D\underline{R}(s) \prod_{i=1}^{M} \delta(\underline{R}(s_i)-\underline{R}(s_i'))$$

denotes the measure of functional integration including the configurational space constraints due to the crosslinks. The similar expression holds for the configuration $\underline{R}'(s)$. M is the total number of chemical crosslinks.
Simulating the action of chemical crosslinks by an additional contribution to the harmonic constraining potential, using the replica trick (15) and transforming the n+1 replica -coordinates (15,16) leads for a=1/2 to the expression

$$S(\underline{k},\underline{\lambda}) = N_s^{-2} \sum_{m,m'} \prod_{j} \exp(z) \qquad (12)$$

with

$$z = \frac{k_j^2 \alpha_j^2}{6} \cdot l \cdot |s_m - s_{m'}| - k_j^2 (1 - \alpha_j^2) \cdot$$

$$\cdot (w_j')^{-2} \frac{1}{2} \cdot (1 - \exp(-\frac{1}{3} w_j' \cdot |s_m - s_{m'}|)) \qquad (13)$$

and

$$w_j'^2 = w_j^2 + 6 \cdot d_j^{-4} (\alpha_j) \quad , \qquad (14)$$

$$w_j = \frac{6M}{NlL} \sqrt{1 + \sqrt{1 + (6 \frac{M}{N} \frac{d_j^2}{lL})^{-2}}} \qquad (15)$$

N is the total number of primary chains, their contour length is L.
In the SANS-case ($q \equiv k^2 l^2 N_c/6 \ll 1$), the limit $d_o \longrightarrow \infty$ leads to the scattering law in stretching direction,

$$S(\underline{k},\underline{\lambda}) \simeq 1 - k_{\parallel}^2 R_{g\parallel}^2 = 1 - \frac{q}{3} (\frac{\lambda^2+3}{4}) \quad , \qquad (16)$$

which is equal to the scattering law of tetrafunctional phantom networks in the free-fluctuation limit. Equation (16) provides Eq. (1) for the case f=4.
The more interesting case of topologically constrained moderately crosslinked networks ($M/N \gtrsim 1$) gives with $lL/d_o^2 \gg M/N$ the expression

$$S(\underline{k}_{\parallel}, \lambda) \approx 1 - \frac{q}{3}\Lambda^2 \qquad (17)$$

with

$$\Lambda^2 = \alpha^2 - 3\sqrt{6}\,\frac{M}{N}\,\frac{d_{\parallel}^2}{lL}\,(1 + \frac{1}{2}\,\frac{M}{N}\,\frac{d_{\parallel}^2}{lL})^{-1}\,(\alpha^2 - 1) \qquad (18)$$

and

$$d_{\parallel} = d_o\,\alpha^{1/2}\,, \quad \alpha \equiv \lambda^b\,.$$

$\lambda \equiv \lambda_{\parallel}$ is the stretch ratio parallel to the principal strain axes.

Discussion

The result

$$R_{g\parallel}/R_{gi} = \Lambda \qquad (19)$$

leads to the conclusion that (in dependence of the value of b) the change of the radius of gyration of a network chain may be much less than the change of the macroscopic sample.
It is to be noted that the network model of restricted junction fluctuation (20,21) does not give such a result (22). It interpolates between the two phantom models (a) and (b) mentioned in the Introduction.
Following the interpretation proposed by Bastide et al. (8), the parameter b correlates for completely crosslinked networks with the ratio of the total number of crosslinks within a Flory-coil (n) to the number of topological neighbours (f). The larger this ratio, the more likely the deformation by knot-rearrangement and desinterpenetration of network chains. Further, network defects favour the constraint release and reduce the amount of b. As no theory is available, we proposed the relations $b \approx (n/f)^{-1}$ in the case of completely crosslinked networks and $b \sim T_e^{1/2}$ in the case of networks with defects (11). T_e is the trapping factor (17) with the limiting values zero at the gel point and unity for perfect networks without dangling ends.
The comparison of Eq. (19) with experimental scattering data (3-5) obtained on end-linked PDMS networks yields values of b much smaller than one (11). The theory of Ref. 11 predicts that for $b \ll 1$ the topological constraints are nearly independent on deformation as they have relaxed and

therefore, the elastic properties of the networks are nearly phantom-like. Further, it may be said that network defects favour constraint release, and the amount of defects depends on the completeness of crosslinking reaction (24). So, it can be concluded that the values of b close to zero obtained from the scattering experiments indicate that the PDMS networks were not perfect networks. In this way, the small changes of the radius of gyration may be explained. Also some other explanations are possible, e.g. in Ref. 23 the observed change of the scattering pattern has been discussed in connection with the assumption of an imperfect miscibility of the hydrogenated and deuterated polymers.

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