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Analysis of Small Angle Neutron Scattering Data on Poly(dimethylsiloxane) Network Unfolding

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Introduction

Small angle neutron scattering (SANS) allows us to probe chain conformations of temporary and permanent macromolecular networks unambiguously. Progress in this field has been reviewed by Boué,[1] Picot,[2], and Boué et al.[3] Analysis of SANS data of rubber networks reveals that large macroscopic deformations resulting from swelling or deswelling of networks do not result in equivalent microscopic chain deformations at the level of the mesh size. A similar loss of affineness is observed for rubber samples stretched uniaxially in the bulk state. This behavior cannot be interpreted in the context of classical affine or phantom network models. The loss of affineness seems to proceed according to topological chain rearrangements, which result in an unfolding of the network that is not described by classical network theories.

Boué et al.[3] proposed an affine rotation mechanism without chain stretching, when discussing SANS measurements of Beltzung et al.[4] on uniaxially elongated poly(dimethylsiloxane) (PDMS) networks with labeled elementary chains. This approach, which is akin to the Doi–Edwards tube model[5] employed to describe polymer melt rheology, gave much better predictions than the classical network theories for the radius of gyration measured parallel and perpendicular to the direction of elongation.

However, the calculations of Boué et al.[3] were approximate: a network average of a ratio was replaced by a ratio of network averages. It is the purpose of this paper to give the exact radius of gyration result for the affine rotation model. Further, predictions of the radii of gyration in uniaxial elongation are presented for a molecular stress function model,[6,7] which allows an accurate description of the mechanical behavior of rubber. Comparison is made with the SANS data of Beltzung et al.[4] on uniaxially elongated PDMS rubber cross-linked in bulk with elementary chains of molar mass M_n = 10000. This particular network was chosen from the set of PDMS networks investigated by Beltzung et al. with M_n ranging from 3000 to 25000 cross-linked at polymer concentrations between 0.6 and 1.0, because (a) M_n = 10000 is above the entanglement molar mass of PDMS, (b) cross-linking was done in the bulk, and (c) elongations up to a stretch of nearly 2 are reported. According to the molecular stress function model,[7] networks with properties (a) and (b) show an especially simple strain behavior, which corresponds to the strain behavior of the un-cross-linked parent polymer.

Radius of Gyration in Anisotropic Neutron Scattering

In the Guinier range, i.e. for $qR_g \ll 1$, the form functions parallel ($S_\parallel$) and perpendicular ($S_\perp$) to the direction of elongation are given by[3]

$$S_k(q) = N^2\left(1 - \frac{1}{3}q^2R_{gk}^2\right) \tag{1}$$

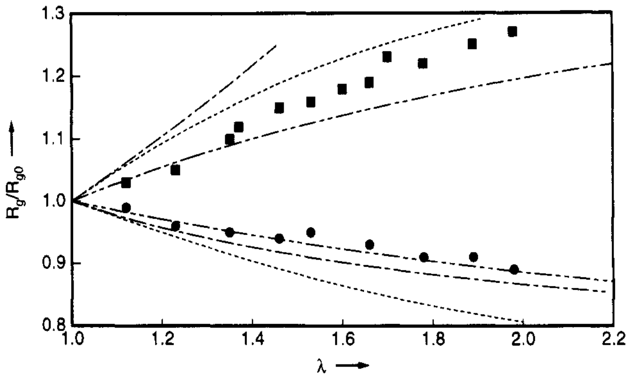

Figure 1. Relative radius of gyration R_g/R_{g0} for labeled elementary chains as a function of elongational stretch λ [(■) parallel and (●) perpendicular to the direction of stretch] from Beltzung et al.[4] on PDMS rubber cross-linked in bulk with M_n = 10000. Curves are predictions of the following models: (— — —) junction affine, eqs 7 and 8; (- - -) affine rotation, approximation of Boué et al.,[3] eqs 12 and 13; (— — — —) affine rotation, exact result, eqs 18 and 19.

k denotes ∥ or ⊥ respectively, q is the value of the wave vector, and N is the number of elementary chains. The anisotropic radii of gyration relevant to scattering, $R_{g\parallel}$ and $R_{g\perp}$, are given by

$$R_{gk}^2 = R_{g0}^2\left(\frac{1}{2} + \frac{3}{2}\frac{\langle R_k^2\rangle}{\mathbf{R}_0^2}\right) \tag{2}$$

R_{g0} is the isotropic radius of gyration, and $\mathbf{R}_0$ is the isotropic end-to-end vector of the elementary chain. R_k is the projection of the deformed end-to-end vector $\mathbf{R}$ in the direction parallel ($R_\parallel$) and perpendicular ($R_\perp$) to the direction of elongation, and ⟨...⟩ denotes a network average over all elementary chains.

With respect to the deformation of $\mathbf{R}$, we neglect junction fluctuations and restrict attention to the following three cases:

(1) Junction Affine Model. For the classical junction affine model, the end-to-end vector $\mathbf{R}$ is assumed to deform affinely with the macroscopic deformation, i.e.

$$\mathbf{R} = R_0\mathbf{u}' \tag{3}$$

with

$$\mathbf{u}' = \boldsymbol{F}^{-1}\cdot\mathbf{u} \tag{4}$$

$\mathbf{u}'$ is a deformed unit vector $\mathbf{u}$, and $\boldsymbol{F}^{-1}$ is the deformation gradient transforming the isotropic into the anisotropic state. Thus eq 2 is reduced to

$$\frac{R_{gk}^2}{R_{g0}^2} = \frac{1}{2} + \frac{3}{2}\langle u_k'^2\rangle \tag{5}$$

For uniaxial elongation with stretch ratio λ, $\boldsymbol{F}^{-1}$ is given by

$$\boldsymbol{F}^{-1} = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \lambda^{-1/2} & 0 \\ 0 & 0 & \lambda^{-1/2} \end{pmatrix} \tag{6}$$

which leads immediately to

$$\frac{R_{g\parallel}^2}{R_{g0}^2} = \frac{1 + \lambda^2}{2} \tag{7}$$

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and

$$\frac{R_{g\perp}^2}{R_{g0}^2} = \frac{1+\lambda}{2\lambda} \tag{8}$$

Both ratios are plotted in Figure 1.

(2) Affine Rotation Model. Assuming affine rotation with no stretch, the end-to-end vector $\mathbf{R}$ is given by

$$\mathbf{R} = R_0\frac{\mathbf{u}'}{u'} \tag{9}$$

where $u' = |\mathbf{u}'|$ is the value of $\mathbf{u}'$. This leads to the following expression for the radius of gyration:

$$\frac{R_{gk}^2}{R_{g0}^2} = \frac{1}{2} + \frac{3}{2}\left\langle\frac{u_k'^2}{u'^2}\right\rangle \tag{10}$$

Boué et al.[3] approximated the network average by

$$\left\langle\frac{u_k'^2}{u'^2}\right\rangle \approx \frac{\langle u_k'^2\rangle}{\langle u'^2\rangle} = 3\frac{\langle u_k'^2\rangle}{\lambda^2 + 2/\lambda} \tag{11}$$

which leads to the following results for the radii of gyration, also plotted in Figure 1:

$$\frac{R_{g\parallel}^2}{R_{g0}^2} = \frac{2\lambda^2 + \lambda^{-1}}{\lambda^2 + 2\lambda^{-1}} \tag{12}$$

and

$$\frac{R_{g\perp}^2}{R_{g0}^2} = \frac{\lambda^2 + 5\lambda^{-1}}{2\lambda^2 + 4\lambda^{-1}} \tag{13}$$

The exact expressions for the averages are

$$\left\langle\frac{u_\parallel'^2}{u'^2}\right\rangle = \int_0^{\pi/2}\frac{\lambda^3\cos^2\theta\sin\theta}{\lambda^3\cos^2\theta + \sin^2\theta}\,d\theta \tag{14}$$

and

$$\left\langle\frac{u_\perp'^2}{u'^2}\right\rangle = \frac{1}{2}\int_0^{\pi/2}\frac{\sin^3\theta}{\lambda^3\cos^2\theta + \sin^2\theta}\,d\theta \tag{15}$$

The integrals can be solved in closed form, and the results are

$$\left\langle\frac{u_\parallel'^2}{u'^2}\right\rangle = \frac{\lambda^3}{\lambda^3-1}\left[1 - \frac{\arctan\sqrt{\lambda^3-1}}{\sqrt{\lambda^3-1}}\right] \tag{16}$$

and

$$\left\langle\frac{u_\perp'^2}{u'^2}\right\rangle = \frac{1}{2}\frac{\lambda^3}{\lambda^3-1}\left[\frac{\arctan\sqrt{\lambda^3-1}}{\sqrt{\lambda^3-1}} - \frac{1}{\lambda^3}\right] \tag{17}$$

which lead to the following exact expressions for the radii of gyration, also plotted in Figure 1:

$$\frac{R_{g\parallel}^2}{R_{g0}^2} = \frac{1}{2} + \frac{3}{2}\left(\frac{\lambda^3}{\lambda^3-1}\right)\left[1 - \frac{\arctan\sqrt{\lambda^3-1}}{\sqrt{\lambda^3-1}}\right] \tag{18}$$

and

$$\frac{R_{g\perp}^2}{R_{g0}^2} = \frac{1}{2} + \frac{3}{4}\left(\frac{\lambda^3}{\lambda^3-1}\right)\left[\frac{\arctan\sqrt{\lambda^3-1}}{\sqrt{\lambda^3-1}} - \frac{1}{\lambda^3}\right] \tag{19}$$

For the affine rotation model with no stretch, the following identities hold:

$$\left\langle\frac{u_\parallel'^2}{u'^2}\right\rangle + 2\left\langle\frac{u_\perp'^2}{u'^2}\right\rangle = 1 \tag{20}$$

and therefore

$$R_{g\parallel}^2 + 2R_{g\perp}^2 = 3\,R_{g0}^2 \tag{21}$$

(3) Molecular Stress Function Model. Recently, in an effort to derive a nonlinear strain measure, which describes the mechanical behavior of polymer melts and rubbers accurately, we have introduced a molecular stress function model.[6,7] This is based on the following three assumptions.

(a) Real molecular chains (as distinct from classical phantom chains) cannot pass through each other. Following Doi and Edwards,[5] we model this uncrossability condition by the tube concept: The mesh of constraints caused by surrounding chains confines the molecular chain laterally to a tubelike region of diameter a.

(b) By analyzing the strain data for polymer melts and rubbers, we found that the tension in the molecular chains increases and the tube diameter decreases with increasing deformation.[6,7] As the tube diameter represents the mean stress field of the surrounding chains and its effect on the network strand considered, we make the assumption that the tube diameter a is a function of the average macroscopic stretch, $\langle u'\rangle$. The deformed end-to-end vector of an elementary chain follows then as

$$\mathbf{R} = R_0 f\frac{\mathbf{u}'}{u'} \tag{22}$$

where the molecular stress function f, which represents the relative tension in the chain, is equal to the relative inverse tube diameter $a_0/a(\langle u'\rangle)$. a_0 is the tube diameter in the isotropic state.

(c) Up to moderate strains, e.g. up to a stretch ratio of ca. 2 in uniaxial elongation, the molecular stress function f is found to be *universal* for linear and branched polymer melts as well as for rubber networks with elementary chains of molar mass equal or above the entanglement molar mass of the un-cross-linked parent polymer,[6,7]

$$f^2 = \langle u'\rangle \tag{23}$$

Equation 23 follows directly from the assumption that the total tube volume of all network strands remains invariant with respect to deformation.[8] f^2 being linear in the average stretch $\langle u'\rangle$, we refer to it as the linear molecular stress function theory. From eqs 2, 22, and 23 follows immediately

$$\frac{R_{gk}^2}{R_{g0}} = \frac{1}{2} + \frac{3}{2}\langle u'\rangle\left\langle\frac{u_k'^2}{u'^2}\right\rangle \tag{24}$$

with $\langle u'\rangle$ given by

$$\langle u'\rangle = \frac{1}{2}\lambda\left[1 + \frac{\sinh^{-1}\sqrt{\lambda^3-1}}{\sqrt{\lambda^3}\sqrt{\lambda^3-1}}\right] \tag{25}$$

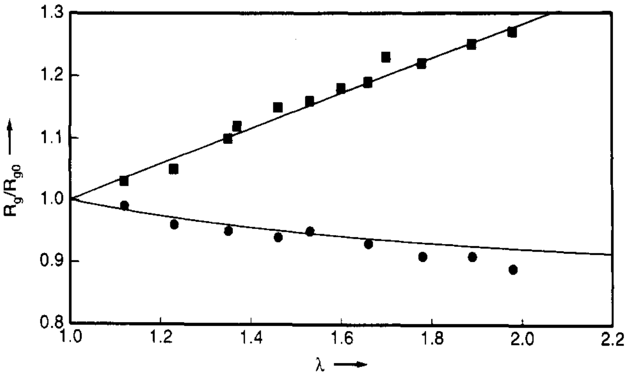

Figure 2. Relative radius of gyration R_g/R_{g0} for labeled elementary chains as a function of elongation stretch λ [(■) parallel and (●) perpendicular to the direction of stretch] from Beltzung et al.[4] on PDMS rubber cross-linked in bulk with $M_n = 10000$. Curves are predictions of the linear molecular stress function theory, eq 24.

and $\langle u'_k{}^2/u'^2\rangle$ given by eqs 16 and 17. Equation 24 is plotted in Figure 2.

Discussion

Figure 1 compares the data of Beltzung et al.[4] with the predictions of the junction affine and the affine rotation model. As is well-known, the junction affine model overpredicts the anisotropy of SANS scattering. The elementary chains are less extended in the direction of elongation than expected from the assumption of affine deformation. The affine rotation model in the approximation of Boué et al., eqs 12 and 13, shows better agreement with the data in the parallel direction; however, deviations in the perpendicular direction increase. The exact affine rotation model, eqs 18 and 19, underpredicts the radius of gyration in the parallel direction, while it approaches the data in the perpendicular direction from below.

Within experimental scatter, the linear molecular stress function model, eq 24, gives quantitative agreement with the experimental data of Beltzung et al. (Figure 2). This is the more remarkable, as this model provides an accurate description of mechanical stress in uniaxial elongation and compression of rubber.[6,7] Unfortunately, Beltzung et al. do not report the Mooney stress of their PDMS. Xu and Mark[9] investigated the strain dependence of end-linked PDMS samples with somewhat higher molar masses of the elementary chains ($M_n = 13000$ and 21000) in uniaxial elongation and compression. Their data together with the data of Pak and Flory on randomly cross-linked PDMS,[10] and of Rivlin and Saunders on natural rubber,[11] are plotted in Figure 3 as normalized Mooney stress $h = \sigma_M/G_\infty$ versus 1/λ, where σ_M is the Mooney stress and G_∞ is the small-strain equilibrium modulus. Note that within experimental scatter all six rubber networks considered show the same strain dependence $h(\lambda)$ if normalized by G_∞. h is equivalent to the well-known damping function in polymer melt rheology[12] and is proportional to the difference of the second moments of the end-to-end vector projections $R_\|$ and $R_\perp$,

$$h = \frac{g}{R_0^2}[\langle R_\|^2\rangle - \langle R_\perp^2\rangle]/(\lambda^2 - 1/\lambda) \qquad (26)$$

g is a normalization constant assuring accordance with linear elasticity.

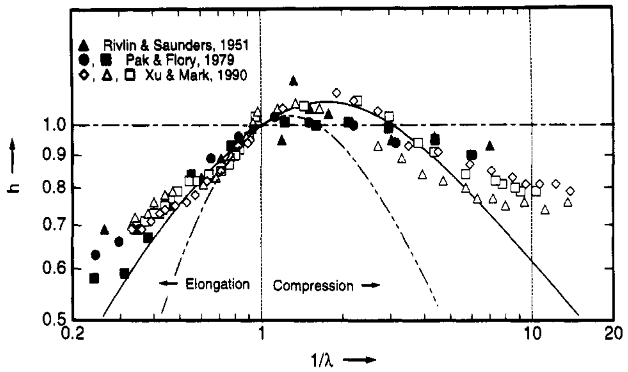

Figure 3. Normalized Mooney stress h as a function of inverse elongational stretch ratio 1/λ. Data (symbols) are for several rubber networks. Curves are predictions of the following models: (— — —) junction affine, eq 27; (– – – –) affine rotation, eq 28; (—) linear molecular stress function theory, eq 29.

For the affine junction model, eq 26 reduces to

$$h = 3[\langle u'^2_\|\rangle - \langle u'^2_\perp\rangle]/(\lambda^2 - 1/\lambda) \equiv 1 \qquad (27)$$

The corresponding relation for the affine rotation model is

$$h = 5\left[\left\langle\frac{u'^2_\|}{u'^2}\right\rangle - \left\langle\frac{u'^2_\perp}{u'^2}\right\rangle\right]/(\lambda^2 - 1/\lambda) \qquad (28)$$

where the network averages (for $\lambda \leq 1$) are given by eqs 16 and 17. Multiplying eq 28 by $\langle u'\rangle$ from eq 25 results in the normalized Mooney stress for the linear molecular stress function theory,

$$h = 5\langle u'\rangle\left[\left\langle\frac{u'^2_\|}{u'^2}\right\rangle - \left\langle\frac{u'^2_\perp}{u'^2}\right\rangle\right]/(\lambda^2 - 1/\lambda) \qquad (29)$$

Predictions of eqs 27–29 are compared with experimental data in Figure 3. It is obvious from Figure 3 that in uniaxial elongation ($1/\lambda \leq 1$) the junction affine model overpredicts the mechanical stress, while the affine rotation model predicts stress values too low at higher stretches.

Agreement of data and predictions in elongation and compression is obtained for the linear molecular stress model up to strains of ca. λ = 2 in elongation and ca. λ = 0.2 in compression. Deviations at higher strains are due to the finite extensibility of the networks, which can be accounted for by a Langevin-type function approach.[7]

Conclusions

SANS data and mechanical measurements demonstrate that network deformation is nonaffine on the mesh level. Network unfolding proceeds by an affine rotation of elementary chains, combined with a nonaffine stretch. This chain stretching, which is less than expected from the macroscopic deformation, is caused by an increased restriction of lateral motion of the chains due to the deformation of surrounding chains. In the tube model, this corresponds to the constant tube volume assumption.[8] The resulting linear molecular stress function theory describes both the radius of gyration measured by SANS and the strain dependence of the mechanical stress. We have thus succeeded in demonstrating the consistency of SANS and mechanical measurements for at least one PDMS network. Further work is needed to extend these results to networks cross-linked in solution and to networks with elementary chains of molar mass below the entanglement molar mass of the un-cross-linked parent polymer.

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References and Notes

(1) Boué, F. *Adv. Polym. Sci.* **1987**, *82*, 47.
(2) Picot, C. *Prog. Colloid Polym. Sci.* **1987**, *75*, 83.
(3) Boué, R.; Bastide, J.; Buzier, M.; Collette, C.; Lapp, A.; Herz, J. *Prog. Colloid Polym. Sci.* **1987**, *75*, 152.
(4) Beltzung, M.; Picot, C.; Herz, J. *Macromolecules* **1984**, *17*, 663.
(5) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1818.
(6) Wagner, M. H.; Schaeffer, J. *J. Rheol.* **1993**, *37*, 643.
(7) Wagner, M. H. *J. Rheol.* **1994**, *38*, 655.
(8) Wagner, M. H.; Schaeffer, J. *J. Rheol.* **1992**, *36*, 1.
(9) Xu, P.; Mark, J. E. *Rubber Chem. Technol.* **1990**, *63*, 276.
(10) Pak, H.; Flory, P. J. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1845.
(11) Rivlin, R. S.; Saunders, D. W. *Philos. Trans. R. Soc. London* **1951**, *A243*, 251.
(12) Wagner, M. H. *Makromol. Chem., Macromol. Symp.* **1993**, *68*, 95.