Modified Gaussian Model for Rubber Elasticity. 3. Hard-Tube Model

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ABSTRACT: A modified Gaussian, three-hard-tube model for rubber elasticity is developed. The approximate free energy of a modified Gaussian model for a freely jointed chain confined to a hard rectangular tube is calculated. This free energy is then used in a three-tube model for rubber elasticity that incorporates both the effects of finite-chain extensibility and interchain entanglements in an approximate way. The theory is compared to experimental data from the literature for both uniaxial and biaxial deformation.

Introduction

In the first two papers in this series[1,2] we introduced two variants of a mathematically simple model for rubber elasticity that incorporates the effects of the finite extensibility and stiffness of the polymer chain. In this paper we will apply the modified Gaussian model for the freely jointed chain presented in part 1 to the problem of the entanglement constraints on a chain in a rubbery polymeric solid. The entanglement constraints will be incorporated by confining the polymer chain to a tube. This approach to the entanglement constraints was introduced by Edwards[3] and has been used in rubber elasticity theories by Gaylord[4,5] and Marrucci.[6] In this paper we will follow the approach used by Gaylord in a recent paper[5] and confine the chain within a hard square tube. As the macroscopic system is deformed in a constant-volume process the tube deforms affinely in length while maintaining a square cross section and a constant volume.

The major difference between this paper and the recent work of Gaylord is that we will use modified Gaussian statistics for the polymer chain. This has two effects, both of which appear in the high-extension region. The first is that the modified Gaussian chain has finite extensibility and therefore shows a sharp upturn in the stress-strain curve at high extensions. The second is that a chain of finite length had less "lateral wiggling" as the chain is stretched, and therefore the confining tube has a smaller effect on the free energy at large extensions.

The theory is developed in two parts. First we use the formalism of Gaylord and Lohse[7] to calculate the free energy of a modified Gaussian chain confined within a hard rectangular tube. The chain free energy can be calculated exactly in terms of an infinite series. The exact free energy can then be represented by an approximate closed-form expression. Second, the approximate confined-chain free energy can be incorporated into a simple three-hard-tube model for a network. The network free energy is a simple closed-form expression which includes both finite-chain extensibility and entanglement constraints in an approximate way. This free energy is then used to derive stress-strain equations for two experimental situations, uniaxial extension and biaxial extension. The resulting equations are then compared to experimental data taken from the literature.

Free Energy of a Confined Modified Gaussian Chain

In part 1 we calculated the entropy of the modified Gaussian model of a freely jointed chain with contour length L. This entropy corresponds to a distribution function given by the simple expression

$$W = W_0(1 - (R/L)^2)^{3N/2} \tag{1}$$

where R is the magnitude of the end-to-end vector of the chain and N is the number of rigid links of length l. W_0 is the normalization constant given by

$$W_0 = \frac{\Gamma\left(\frac{3N}{2} + \frac{5}{2}\right)}{2\pi L^3 \Gamma(3/2)\Gamma\left(\frac{3N}{2} + 1\right)} \tag{2}$$

where $\Gamma(x)$ is the usual Γ function. Since the chain has a finite length, W is nonzero only in the range

$$0 \le R/L \le 1 \tag{3}$$

At all other values of R/L, the function $W(R/L)$ vanishes.

Gaylord and Lohse[7] have used the method of images to calculate the general form of the distribution function for a polymer chain with ends fixed at (x_A, y_A, x_B) and (x_B, y_B, z_B) confined to a rectangular box defined by the planes $x = 0$, $x = a$, $y = 0$, $y = b$. The confined-chain distribution, W_c, is given in terms of the free-chain distribution function, W, by the following expression:

$$W_c = \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \{W(x_A - x_B - 2la, y_A - y_B - 2mb, z_A - z_B) - W(x_A + x_B - 2la, y_A - y_B - 2mb, z_A - z_B) - W(x_A - x_B - 2la, y_A + y_B - 2mb, z_A - z_B) + W(x_A + x_B - 2la, y_A + y_B - 2mb, z_A - z_B)\} \tag{4}$$

Therefore, the general expression for the distribution function of the confined modified Gaussian chain will be

$$W_c = W_0 \sum_{l=-\infty}^{\infty}{}' \sum_{m=-\infty}^{\infty}{}' \left\{\left[1 - \left(\frac{x_A - x_B - 2la}{L}\right)^2 - \left(\frac{y_A - y_B - 2mb}{L}\right)^2 - \left(\frac{z_A - z_B}{L}\right)^2\right]^{3N/2} - \left[1 - \left(\frac{x_A + x_B - 2la}{L}\right)^2 - \left(\frac{y_A - y_B - 2mb}{L}\right)^2 - \left(\frac{z_A - z_B}{L}\right)^2\right]^{3N/2} - \left[1 - \left(\frac{x_A - x_B - 2la}{L}\right)^2 - \left(\frac{y_A + y_B - 2mb}{L}\right)^2 - \left(\frac{z_A - z_B}{L}\right)^2\right]^{3N/2} + \right.$$

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$$\left[1-\left(\frac{x_A+x_B-2la}{L}\right)^2-\left(\frac{y_A+y_B-2mb}{L}\right)^2-\left(\frac{z_A-z_B}{L}\right)^2\right]^{3N/2}\Bigg\} \quad (5)$$

The prime on the sums indicates that the only terms included are those in which $W \neq 0$. We introduce the reduced variables defined by

$$\begin{gathered} x_A' \equiv x_A/L,\ x_A' \equiv x_B/L,\ y_A' \equiv y_A/L,\ y_B' \equiv y_B/L \\ z_A' \equiv z_A/L,\ z_B' \equiv z_B'/L,\ a' \equiv a/L,\ b' \equiv b/L \end{gathered} \quad (6)$$

To separate out the effects of the tube from the free-chain distribution we factor out the z component of the distribution and obtain

$$\begin{aligned} W_c = W_0\,[1-(z_A'-z_B')^2]^{3N/2}\sum_{l=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} \Bigg\{ & \left[1-\frac{(x_A'-x_B'-2la')^2+(y_A'-y_B'-2mb')^2}{1-(z_A'-z_B')^2}\right]^{3N/2} - \\ & \left[1-\frac{(x_A'+x_B'-2la')^2+(y_A'-y_B'-2mb')^2}{1-(z_A'-z_B')^2}\right]^{3N/2} - \\ & \left[1-\frac{(x_A'-x_B'-2la')^2+(y_A'+y_B'-2mb')^2}{1-(z_A'-z_B')^2}\right]^{3N/2} + \\ & \left[1-\frac{(x_A'+x_B'-2la')^2+(y_A'+y_B'-2mb')^2}{1-(z_A'-z_B')^2}\right]^{3N/2}\Bigg\} \end{aligned} \quad (7)$$

Equation 7 is of the form of a free-chain distribution in the z direction times a confinement term. In contrast to the Gaussian case considered by Gaylord the confinement term here depends on the relative extension of the chain.

Equation 7 is an exact expression for the confined-chain distribution, but, because of the infinite series, it is not very useful for practical calculations. A useful approximate expression can be obtained by first approximating each of the binomials in the confinement energy by exponentials, that is

$$(1-x)^{3N/2} \simeq \exp(-3Nx/2) \quad (8)$$

Using eq 8 in eq 7 we obtain

$$\begin{aligned} W_c = {} & W_0[1-(z_A'-z_B')^2]^{3N/2}\sum_{l=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\Bigg\{\exp\left[-\frac{3N}{2}\times\frac{(x_A'-x_B'-2la')^2+(y_A'-y_B'-2mb')^2}{1-(z_A'-z_B')^2}\right] - \\ & \exp\left[-\frac{3N}{2}\,\frac{(x_A'+x_B'-2la')^2+(y_A'-y_B'-2mb')^2}{1-(z_A'-z_B')}\right] - \\ & \exp\left[-\frac{3N}{2}\,\frac{(x_A'-x_B'-2la')+(y_A'+y_B'-2mb')^2}{1-(z_A'-z_B')}\right] + \\ & \exp\left[-\frac{3N}{2}\,\frac{(x_A'+x_B'-2la')+(y_A'+y_B'-2mb')^2}{1-(z_A'-z_B')^2}\right]\Bigg\} \end{aligned} \quad (9)$$

The double sum can be written in a Fourier series of the form

$$\begin{aligned} W_c = {} & W_0[1-(z_A'-z_B')^2]^{3N/2}\times \\ & \left\{\frac{2}{a'}\sum_{l=0}^{\infty}\sin\left(\frac{\pi l x_A'}{a'}\right)\sin\left(\frac{\pi l x_B'}{a'}\right)\exp\left(-\frac{l^2\pi^2}{4\beta a'^2}\right)\right\}\times \\ & \left\{\frac{2}{b'}\sum_{m=0}^{\infty}\sin\left(\frac{\pi m y_A'}{b'}\right)\sin\left(\frac{\pi m y_B'}{b'}\right)\exp\left(-\frac{m^2\pi^2}{4\beta b'^2}\right)\right\} \end{aligned} \quad (10)$$

where

$$\beta = 3N/\{2[1-(z_A'-z_B')^2]\} \quad (11)$$

To apply eq 10 to the theory of rubber elasticity we consider the special case where the chain ends are fixed at the center of a retangular tube. We therefore assume that the chain ends are placed at $(a/2, b/2, z_A)$ and $(a/2, b/2, z_B)$. Equation 10 reduced to

$$\begin{aligned} W_c = {} & W_0\frac{8\pi kT}{3N}(1-r'^2)^{3N/2+1}\left(\frac{1}{a'b'}\right)\times \\ & \sum_{l=1}^{\infty}\exp\left(\frac{-(2l-1)^2\pi^2}{4\beta a'^2}\right)\sum_{m=1}^{\infty}\exp\left(\frac{-(2m-1)^2\pi^2}{4\beta b'^2}\right) \end{aligned} \quad (12)$$

where

$$r' = (z_A'-z_B') \quad (13)$$

The two infinite series will be dominated by their first terms, so we approximate eq 12 by

$$\begin{aligned} W_c = {} & S_0\left(\frac{8\pi kT}{3N}\right)\times \\ & (1-r'^2)^{(3N/2kT)+1}\left(\frac{1}{a'b'}\right)\exp\left(\frac{-\pi^2}{4\beta a^2}\right)\exp\left(\frac{-\pi^2}{4\beta b^2}\right) \end{aligned} \quad (14)$$

The confined-chain free energy is then computed as

$$A_c = -kT\ln W_c \quad (15)$$

Hence

$$\begin{aligned} A_c = {} & -\left(\frac{3N}{2}+1\right)kT\ln(1-r'^2) + kT\ln(a'b') + \\ & \frac{\pi^2(kT)}{6Na'^2}(1-r'^2) + \frac{\pi^2(kT)}{6Nb'^2}(1-r'^2) + \text{constant} \end{aligned} \quad (16)$$

There are three types of terms in eq 16. The first term is essentially the free energy of an unconfined chain. The second term involves the cross-sectional area of the tube and in a network model will lead to a contribution proportional to the logarithm of the volume. This term will vanish in a constant-volume process. The third and fourth terms are similar to the tube confinement energy derived by Gaylord.[4] The major difference is the multiplicative factor $(1 - r'^2)$, which couples the confinement energy to the chain extension. The confinement contribution varies from its Gaussian value at low extensions to zero at high extensions. This is physically reasonable. The effect of the tube depends on the magnitude of the excursions of the chain perpendicular to the direction of the extension. At low extensions the finite-length modified Gaussian chain will behave similarly to the Gaussian chain since most of the chain will be available for lateral excursions. As the finite-length chain is stretched there is less and less excess contour length available for excursions in the perpendicular directions, and so the effect of the tube constraint must decrease. The Gaussian chain, on the other hand, is effectively infinite, and so the tube constraint is

Table I
Parameters Obtained in Regression Analysis

parameter	uniaxial	biaxial
F	0.501	0.328
τ	1.277	0.212
N	79.9	53.5

felt equally at all extensions.

Constant-Volume Tube Model

Equation 16 represents the free energy of a single modified Gaussian chain confined in a hard rectangular tube. In this section it will be applied to the three-hard-tube model for a network used by Gaylord. The three-tube model is a simple but satisfactory way to represent the network, and it leads without further approximation to simple closed-form expression for the network free energy.

There are two important contributions to the chain free energy in eq 16. The first is the free-chain free energy A_{fc} which is of the form

$$A_{fc} = -F \ln (1 - r'^2) \qquad (17)$$

where we have replaced the numerical constants in eq 16 by an adjustable parameter F. For a square tube with edges of length a tube confinement free energy A_τ is of the form

$$A_\tau = \tau (1 - r'^2)/a'^2 \qquad (18)$$

where we have again replaced the numerical constants in eq 16 by an adjustable parameter τ. The remaining term in eq 16 will vanish in any constant-volume process, so it will not be considered in this paper. It may by important for the analysis of swelling measurements, however. The Gaussian hard-tube model has been applied to the swelling problem by Gaylord.[8]

In the three-hard-tube model a single chain confined to a hard square tube is placed along each of the three coordinate axes. The total network free energy is then written

$$A_{net} = -F [\ln (1 - x'^2) + \ln (1 - y'^2) + \ln (1 - z'^2)] + \tau[(1 - x'^2)/a'^2 + (1 - y'^2)/b'^2 + (1 - z'^2)/c'^2] \qquad (19)$$

where x', y', and z' are the reduced extensions of the three chains and a', b', and c' are the tube dimensions perpendicular to the x, y, and z axes, respectively. The length of the tube is assumed to be equal to the end-to-end distance of the chain.

The chains and the tube lengths are assumed to deform affinely with the macroscopic deformation. In the undeformed state each chain is assumed to have its equilibrium end-to-end separation. The cross section of the tube is assumed to remain square, and the area is assumed to change so as to keep the tube volume constant. If the extension ratios along the three axes are given by λ_1, λ_2, and λ_3, then these assumptions give the following values for the relative extensions and the tube cross sections:

$$\begin{gathered} x' = \lambda_1 N^{-1/2},\ y' = \lambda_2 N^{-1/2},\ z' = \lambda_3 N^{-1/2} \\ a' = \lambda_1^{-1/2},\ b' = \lambda_2^{-1/2},\ c' = \lambda_3^{-1/2} \end{gathered} \qquad (20)$$

The network free energy can then be written

$$A_{net} = -F \ln [1 - N^{-1}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) + N^{-2}(\lambda_1^2\lambda_2^2 + \lambda_1^2\lambda_3^2 + \lambda_2^2\lambda_3^2) + N^{-3}(\lambda_1^2\lambda_2^2\lambda_3^2)] + [\lambda_1(1 - \lambda_1^2/N) + \lambda_2(1 - \lambda_2^2/N) + \lambda_3(1 - \lambda_3^2/N)] \qquad (21)$$

We will consider two experimental situations. The first is uniaxial deformation at constant volume. In this case we write

$$\lambda_1 = \lambda \qquad \lambda_2 = \lambda_3 = \lambda^{-1/2} \qquad (22)$$

The network free energy is then

$$A_{net} = -F \ln [1 - N^{-1}(\lambda_2 + 2\lambda^{-1}) + N^{-2}(2\lambda + \lambda^{-2}) - N^{-3}] + \tau[\lambda(1 - \lambda^2/N) + 2\lambda^{-1/2}(1 - (N\lambda)^{-1})] \qquad (23)$$

and the stress–strain relation is given by

$$f = \frac{\partial A_{net}}{\partial \lambda} = F[(\lambda - \lambda^{-2}) + N^{-1}(1 - \lambda^{-3})][1 - N^{-1}(\lambda^2 + 2\lambda^{-1}) + N^{-2}(2\lambda + \lambda^{-2}) - N^{-3}] + \tau[(1 - \lambda^{-3/2}) - 3N^{-1}(\lambda^2 - \lambda^{-5/2})] \qquad (24)$$

The second case is that of biaxial extension at constant volume. In this case λ_1 and λ_2 are independent and λ_3 is given by

$$\lambda_3 = (\lambda_1\lambda_2)^{-1} \qquad (25)$$

For this situation the newtork free energy becomes

$$A_{net} = -F \ln [1 - N^{-1}(\lambda_1^2 + \lambda_2^2 + (\lambda_1\lambda_2)^{-2}) + N^{-2}(\lambda_1^2\lambda_2^2 + \lambda_1^2 + \lambda_2^2) - N^{-3}] + \tau[\lambda_1(1 - \lambda_1^2/N) + \lambda_2(1 - \lambda_2^2/N) + (\lambda_1\lambda_2)^{-1}(1 - (\lambda_1\lambda_2)^{-2}N^{-1})] \qquad (26)$$

The experimental data that are ordinarily reported are the differences in the principle stresses. The principal stresses are defined by

$$t_i = \lambda_i f_i = \lambda_i(\partial A_{net}/\partial\lambda_i) \qquad i = 1, 2, 3 \qquad (27)$$

The two principle stress differences can easily be computed from eq 27. They are

$$t_1 - t_2 = F[(\lambda_1^2 - \lambda_2^2) - N^{-1}(\lambda_2^2 - \lambda_1^2)] \times [1 - N^{-1}(\lambda_1^2 + \lambda_2^2) + (\lambda_1\lambda_2)^{-2} + N^{-2}(\lambda_1^2\lambda_2^2 + \lambda_1^2 + \lambda_2^2) - N^{-3}]^{-1} + \tau[(\lambda_1 - \lambda_2) - 3N^{-1}(\lambda_1^3 - \lambda_2^3)] \qquad (28)$$

$$t_3 - t_2 = -t_2 = -F[(\lambda_2^2 - \lambda_3^2) - N^{-1}(\lambda_3^2 - \lambda_2^2)] \times [1 - N^{-1}(\lambda_2^2 + \lambda_3^2 + (\lambda_2\lambda_3)^{-2}) + N^{-2}(\lambda_2^2\lambda_3^2 + \lambda_3^2) - N^{-3}]^{-1} + \tau[(\lambda_2 - \lambda_3) - 3N^{-1}(\lambda_2^3 - \lambda_3^3)] \qquad (29)$$

Equations 24, 28, and 29 can be fit to experimental data. There are three adjustable parameters: the coefficients F and τ, which give the relative contributions of the free-chain and tube-free energies, respectively, and N, which is the number of rigid links in the freely jointed chain. N is a rough measure of the chain stiffness. As $N \to \infty$ the Gaussian result is obtained. At $N = 1$ the chain is a rigid rod.

Comparison with Experiment

As a test of the theory we have fit eq 24 and 28 to experimental data taken from the literature. For the uniaxial extension–compression case we have taken the data of Pak and Flory[9] for PDMS chemically cross-linked with 3% dicumyl peroxide. For biaxial extension we have used the data of Vangerko and Treloar[10] for natural rubber cured with 5% sulfur. The fits have been done by using an unweighted regression procedure. Because the equations are nonlinear in the parameters, no correlation coefficients are reported.

If Figure 1 are shown the Pak–Flory data for the reduced force $f^* = f(\lambda - \lambda^{-2})^{-1}$ plotted against the inverse extension λ^{-1}. The solid line is the best fit of eq 24. The three parameters obtained in the fit are listed in Table I. Qualitatively, eq 24 fits the data as well as both the Gaussian tube model of Gaylord[5] and the Flory[11] con-

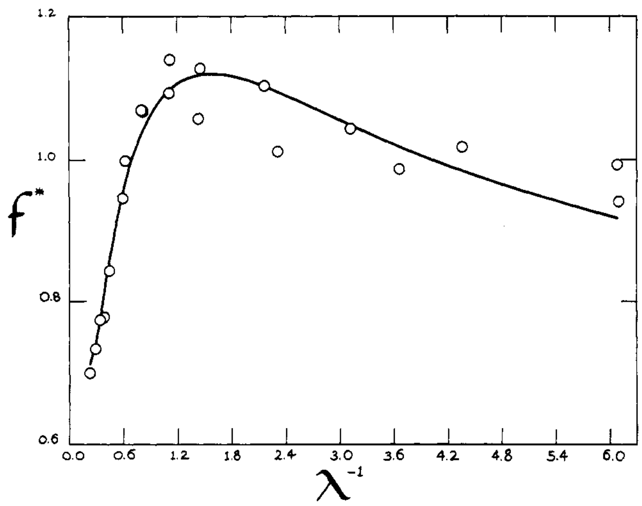

Figure 1. Plot of the reduced force $f^* = f(\lambda - \lambda^{-2})^{-1}$ vs. inverse extension, λ^{-1}, in uniaxial extension–compression. The units of f^* are force × length^{-2}. The experimental points weretaken from ref 8. The solid line is the best fit of eq 24 to the experimental points.

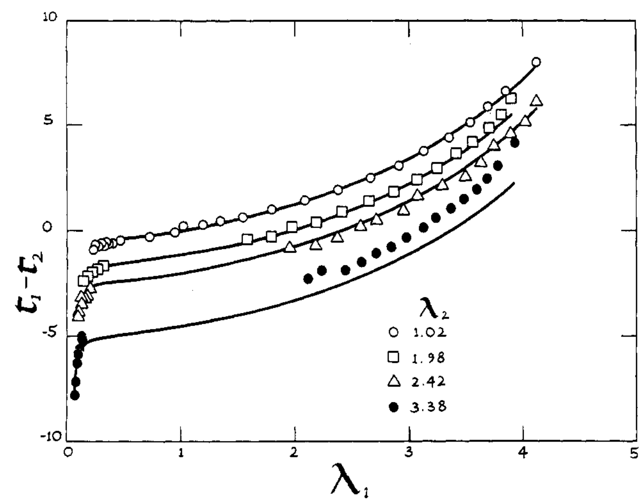

Figure 2. Plot of the difference in principle stresses, $t_1 - t_2$, vs. extension in the λ_1 direction for biaxial extension. The units of $t_1 - t_2$ are force × length^{-2}. Data are shown for four values of λ_2. The experimental points are taken from ref 9. The solid lines are the best fit of eq 28 to the experimental points.

strained-junction model as seen in the paper of Gottlieb and Gaylord.[12]

Figure 2 shows the data of Vangerko and Treloar for biaxial extension of natural rubber. The difference in the principle stresses $t_1 - t_2$ is plotted vs. λ_1 for various values of λ_2. The solid lines are the best fits of eq 28 to the data. The fitting parameters are also given in Table I. The fits are qualitatively very good except at the largest value of λ_2. Treloar[13] has fit the constrained-junction theory of Flory[11] to the same experimental data, although in a very different way. This makes direct comparison more difficult. The conclusion of Treloar's analysis, however, is that the Flory theory fails in the high-extension region, probably because of the neglect of non-Gaussian or strain-induced-crystallization effects. The present theory fits the data quite well over the entire range of extensions, including the high-strain region where the Gaussian theory is inadequate.

The parameters obtained in the two fits of experimental data are reasonable. In particular the values obtained for N, the number of rigid links in the model chain, are quite sensible. A more stringent test of the theory would be to independently fit uniaxial and biaxial data for the same sample to see if the parameters are the same for both fits. As far as we know such data do not exist.

Conclusions

The theory presented in this paper is both conceptually and mathematically simple, yet it incorporates two important effects, entanglements and finite-chain extensibility. Clearly, the three-tube model is an oversimplification of the complicated interactions in a real network. It does, however, provide closed-form mathematical expressions for the network free energy. The fits to two different kinds of experimental data are qualitatively very good.

In addition we have derived an approximate expression for a non-Gaussian chain confined in a hard tube. This expression may be useful in analyzing a variety of confined-chain situations.

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References and Notes

(1) Kovac, J. *Macromolecules* **1978**, *11*, 362.
(2) Kovac, J.; Crabb, C. C. *Macromolecules* **1982**, *15*, 537.
(3) Edwards, S. F. *Proc. Phys. Soc.* **1967**, *92*, 9.
(4) Gaylord, R. J. *Polym. Eng. Sci.* **1979**, *19*, 263.
(5) Gaylord, R. J. *Polym. Bull. (Berlin)* **1982**, *8*, 325.
(6) Marrucci, G. *Macromolecules* **1981**, *14*, 434.
(7) Gaylord, R. J.; Lohse, D. J. *J. Chem. Phys.* **1976**, *65*, 2779.
(8) Gaylord, R. J. *Polym. Bull. (Berlin)* **1983**, *9*, 181.
(9) Pak; H.; Flory, P. J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *17*, 1845.
(10) Vangerko, H.; Treloar, L. R. G. *J. Phys. D*: **1978**, *11*, 1969.
(11) (a) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720. (b) Erman, B.; Flory, P. J. *J. Chem. Phys.* **1978**, *68*, 5363. (c) Flory, P. J.; Erman, B. *Macromolecules* **1982**, *15*, 800.
(12) Gottlieb, M.; Gaylord, R. J. *Polymer* **1983**, *24*, 1644.
(13) Treloar, L. R. G. *Br. Polym. J.* **1982**, *14*, 121.