Segmental Orientation in Stretched Gaussian Networks

Robert Ullman*

Centre de Recherches sur les Macromolécules, 67083 Strasbourg Cedex, France.
Received April 25, 1978

ABSTRACT: Segmental orientation functions have been calculated for stretched Gaussian networks. The results are obtained in terms of a single reduced variable which, itself, is a function of the degree of orientation, the number of segments in the chain, and the number of segments which move cooperatively in the orientation process. It is pointed out that the chain length found in an experiment might be less than anticipated, because entanglements act as effective junction points. This point of view provides a basis for an estimate of the number of entanglements per polymer chain.

A cross-linked rubber may be substantially oriented by stretching, and the macroscopic orientation is reflected in the anisotropy of the segments of the molecular chains of which the rubber is composed. The measurement of anisotropy on a molecular scale can be achieved by light scattering, fluorescence, studies of birefringence, and analysis of NMR line shape.

In this paper, attention is directed to segmental orientation of polymer chains in a deformed network. The model is based on Gaussian statistics taking into account constraints which are imposed on the chains by the network and in the stretching process. The calculations lead to determination of the moments $\langle \cos^{2n} \theta \rangle$, where the angle brackets refer to an ensemble average. θ is the angle between the stretching direction and a vector connecting two specified chain segments. The results are obtained in closed form.

While the model is designed for the analysis of a cross-linked rubber, it is, to some extent, applicable to a polymer which is not chemically cross-linked, in which chain entanglements serve as effective points of reticulation. The relationship between the results for a real network and those found for oriented entangled polymer molecules in a material devoid of chemical cross-links will be discussed later.

The Model and the Calculation

Consider one chain connecting two cross-link points in an infinite polymer network. There are N statistical segments in a chain, each of length b. For simplicity, it shall be assumed that the network is homogeneous; all chains have the same number of segments. The functionality of the network is f, f being an integer equal to or greater than 3.

We assumed that the junction points deform affinely upon stretching. This hypothesis will be modified later, but the modification is easily incorporated in the model. The segments of the chain between the cross-links obey Gaussian statistics subject to the constraints imposed by the extremities of the chain which are bound to the cross-links. Each chain differs from all the others in that the detailed network topology varies from one place to another. The mean orientation of segments throughout the network is determined by averaging over the ensemble of end-to-end distances throughout the system.

Two chain segments i and j of a Gaussian chain containing N segments of length b are separated by a vector $\mathbf{r}_{ij}$ with probability $W(\mathbf{r}_{ij})$. If the chain ends are free, this probability is given by

$$W(\mathbf{r}_{ij}) = (a_{ij}/\pi)^{3/2} \exp[-a_{ij} r_{ij}^2] \quad (1a)$$

$$a_{ij} = \zeta/|i - j| = \zeta/Nw \quad (1b)$$

$$\zeta = 3/(2b^2) \quad (1c)$$

The reduced variable $w = |i - j|/N$ is convenient for calculation and will be retained throughout. If the chain ends are fixed, the probability that i and j are separated by $\mathbf{r}_{ij}$, if the chain ends are separated by $\mathbf{R}$, is given by

$$W(\mathbf{r}_{ij};\mathbf{R}) = (\alpha/\pi)^{3/2} \exp[(\mathbf{r}_{ij} - w\mathbf{R})^2] \quad (2a)$$

$$\alpha = \zeta/(Nw(1 - w)) \quad (2b)$$

The procedure for obtaining eq 2a is given in the Appendix. Consider a process in which the sample is deformed affinely, such that $\lambda_x = X/X_0$, $\lambda_y = Y/Y_0$, and $\lambda_z = Z/Z_0$, where (X_0,Y_0,Z_0) are the Cartesian coordinates of the end-to-end vector before deformation and (X,Y,Z) are the coordinates after deformation. The probability that the end-to-end vector is given by $\mathbf{R}$ may be written

$$W_\lambda(\mathbf{R}) = W_{\lambda_x}(X) W_{\lambda_y}(Y) W_{\lambda_z}(Z) \quad (3a)$$

$$W_{\lambda_x}(X) = (\zeta/\pi N\lambda_x^2)^{1/2} \exp[-\zeta X^2/(N\lambda_x^2)] \quad (3b)$$

Similar formulas hold for $W_{\lambda_y}(Y)$ and $W_{\lambda_z}(Z)$. The probability that i and j are separated by $\mathbf{r}_{ij}$ averaged over all possible values of $\mathbf{R}$ is given by

$$W_\lambda(\mathbf{r}_{ij}) = \int w(\mathbf{r}_{ij};\mathbf{R}) W_\lambda(\mathbf{R})\, d\mathbf{R} \quad (4)$$

There is no difficulty in carrying out this integration in general, but in order to maintain simplicity, only the special case of uniaxial deformation will be treated. It is assumed that the total volume of the sample is unchanged upon deformation. Therefore $\lambda_z = \lambda$ and $\lambda_x = \lambda_y = \lambda^{-1/2}$. The result of the integration of eq 4 becomes

$$W_{\lambda_x}(x_{ij}) = (a_\perp/\pi)^{1/2} \exp[-a_\perp x_{ij}^2] \quad (5a)$$

$$W_{\lambda_z}(z_{ij}) = (a_\parallel/\pi)^{1/2} \exp[-a_\parallel z_{ij}^2] \quad (5b)$$

$$a_\perp = \zeta/(Nw(1 - w + w\lambda^{-1})) \quad (5c)$$

$$a_\parallel = \zeta/(Nw(1 - w + w\lambda^2)) \quad (5d)$$

Equations 5a and 5b can be used for direct determination of the orientation functions $\langle \cos^{2n} \theta \rangle$.

$$W_\lambda(\mathbf{r}_{ij}) = W_\lambda(x_{ij}) W_\lambda(y_{ij}) W_\lambda(z_{ij}) \quad (6a)$$

$$\langle \cos^{2n} \theta \rangle = \int (\cos^{2n} \theta) W_\lambda(\mathbf{r}_{ij})\, d\mathbf{r}_{ij} \quad (6b)$$

Upon integration over $\mathbf{r}_{ij}$ and the azimuthal angle, one obtains

$$\langle \cos^{2n} \theta \rangle = \frac{1}{2}\left[\frac{f_1}{f_2}\right]^{1/2} \int_0^\pi \frac{\cos^{2n} \theta \sin \theta\, d\theta}{[1 - ([f_1 - f_2]/f_1)^{1/2} \cos^2 \theta]^{3/2}} \quad (7a)$$

* Address correspondence to the author at the Research Staff, Ford Motor Co., Dearborn, Michigan 48121.

0024-9297/78/2211-0987$01.00/0

$$f_1 = w(1 - w + w\lambda^2) \tag{7b}$$

$$f_2 = w(1 - w + w\lambda^{-1}) \tag{7c}$$

By a series of transformations, eq 7a may be reduced to

$$\langle \cos^{2n}\Theta \rangle = (\cos\psi/\sin^{2n+1}\psi) I_n(\psi) \tag{8a}$$

$$\sin\psi = \left[\frac{f_1 - f_2}{f_1}\right]^{1/2} = \frac{w(\lambda^2 - \lambda^{-1})}{1 - w + w\lambda^2} \tag{8b}$$

$$I_n(\psi) = \int_0^{\psi} \frac{\sin^{2n} Z}{\cos^2 Z}\, dZ \tag{8c}$$

$I_n(\psi)$ is an elementary integral and may be calculated by the following recursive system.

$$I_1(\psi) = \tan\psi - \psi \tag{9a}$$

$$I_n(\psi) = \left[\frac{2n-1}{2n-2}\right] I_{n-1}(\psi) - \frac{\sin^{2n-1}\psi}{(2n-2)\cos\psi} \tag{9b}$$

Thus

$$\langle \cos^2\Theta \rangle = \csc^2\psi(1 - \psi\cot\psi) \tag{10a}$$

$$\langle \cos^4\Theta \rangle = \frac{3}{2}\csc^4\psi(1 - \psi\cot\psi) - [\csc^2\psi/2] \tag{10b}$$

$$\langle \cos^6\Theta \rangle = {}^{15}/_{8}\csc^6\psi(1 - \psi\cot\psi) - {}^{5}/_{8}\csc^4\psi - [\csc^2\psi/4] \tag{10c}$$

As ψ approaches zero, $\langle \cos^{2n}\Theta \rangle = 1/(2n+1)$, and as ψ approaches $\pi/2$, $\langle \cos^{2n}\Theta \rangle = 1$. Equations 10a through 10c are consistent with this result. As ψ approaches zero all orientation vanishes, as ψ approaches $\pi/2$, the system is perfectly aligned in the z direction.

A plot of $\langle \cos^2\Theta \rangle$, $\langle \cos^4\Theta \rangle$, and $\langle \cos^6\Theta \rangle$ vs. ψ is shown in Figure 1, together with the normalized ratio of fourth to second moment designated as $R(\psi)$.

$$R(\psi) = \frac{5}{9}\frac{\langle \cos^4\Theta \rangle}{\langle \cos^2\Theta \rangle^2} \tag{11}$$

If the system is isotropic, $R(\psi) = 1$; if the system is perfectly oriented, $R(\psi) = {}^{5}/_{9}$.

The Affine Deformation

The deformation of a macroscopic polymeric sample is accompanied by a deformation of the molecule. The level at which the molecular distortions and the sample distortions are the same is by no means a settled question. It is appropriate at this point to deal with this problem.

The derivation of the previous section is based on the supposition that the junction points of a cross-linked network deform affinely. It was shown by James[1] many years ago that the junction points do not deform affinely; fluctuations in the position of the junction points do occur and these fluctuations are independent of the deformation. Since that time, further work on the problem by Eichinger,[2] Graessley,[3] Deam and Edwards,[4,5] and Flory[6,7] have led to the following picture.

The vector, $\mathbf{R}$, connecting the chain ends in a network can be considered as the sum of an average value $\bar{\mathbf{R}}$ and a fluctuation $\Delta\mathbf{R}$. Since each chain is trapped in a unique network topology, $\bar{\mathbf{R}}$ varies from one molecule to another. $\bar{\mathbf{R}}$ should not be confused with $\langle \mathbf{R} \rangle$, the ensemble average of $\mathbf{R}$, which by symmetry is equal to zero.

We adopt a hypothesis of Flory[6] that $\langle \mathbf{R}_0^2 \rangle$, the mean-square end-to-end distance of a chain in an undeformed network, is equal to its value before cross-linking. We utilize as well the phantom chain result,[1-4] $\langle (\Delta\mathbf{R})^2 \rangle = (2/f)\langle \mathbf{R}_0^2 \rangle$. $\bar{\mathbf{R}}_0$, the mean value of $\mathbf{R}_0$, is assumed to deform affinely.

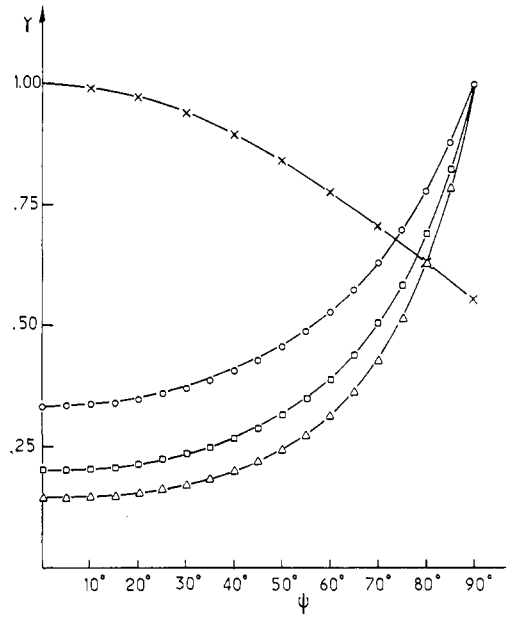

Figure 1. A plot of γ vs. ψ, where γ designates each of the following: ○, $\langle \cos^2\Theta \rangle$; □, $\langle \cos^4\Theta \rangle$; △, $\langle \cos^6\Theta \rangle$; ×, $R(\psi)$.

If λ_i^* is the relative deformation of $\mathbf{R}$ in the ith direction, i.e., $\lambda_x^2 = \langle X^2 \rangle / \langle X_0^2 \rangle$, it is easily shown that

$$\lambda_i^{*2} = \lambda_i^2\left(\frac{f-2}{f}\right) + \frac{2}{f} \tag{12}$$

The macroscopic affine deformation is communicated to the segments through the corresponding displacement of the mean coordinates. The quantities λ_x^*, λ_y^*, and λ_z^* are the nonaffine deformations of the coordinates themselves. The equations of the previous section are applicable by substituting λ_i^* for λ_i throughout. In this way the variable ψ becomes dependent on the network functionality.

When a polymer is not cross-linked, it can be oriented by stretching, provided that the system is not too fluid, that is, the temperature is not much above the glass transition. In that case, the number of chain segments between effective cross-links is a parameter which depends on the number of knots or entanglements between the polymer chain and its neighbors. In fact, the number of segments between knots as determined by a measurement of orientation can be taken as a measure of the extent of this chain entanglement. In these problems, we assume that the affine deformation takes place on a scale measured as the mean number of statistical units between knots.

The calculations on cross-linked networks have been made under the assumption that the chain segments are liquid-like between junctions. This should be reasonably correct for a soft rubber. If the rubber is oriented at a temperature close to the glass transition, this assumption no longer holds. In such a case, the scale of the affine deformation depends on the knots or entanglements. If deformation is carried out very close to the glass transition, the number of entanglements increases, and the applied force does not act on the junction, but throughout the polymer, conceivably at a segmental level.

Results and Discussion

The orientation of segments in a Gaussian polymer network in uniaxial deformation may be presented as a function of a reduced variable ψ, as seen in eq 10a through 10c and in Figure 1. ψ varies between 0 and $\pi/2$; small

Table I
The Moments as Functions of N and λ[a]

λ	N	$\langle\cos^2\Theta\rangle$	$\langle\cos^4\Theta\rangle$	$\langle\cos^6\Theta\rangle$	R
2	20	0.37	0.23	0.17	0.94
	50	0.35	0.21	0.15	0.98
	100	0.34	0.20	0.14	0.99
	200	0.33	0.20	0.14	1.00
	400	0.33	0.20	0.14	1.00
5	20	0.54	0.40	0.33	0.71
	50	0.44	0.30	0.22	0.86
	100	0.39	0.25	0.18	0.92
	200	0.36	0.22	0.16	0.97
	400	0.34	0.21	0.15	0.98

[a] $|i-j|$ is set equal to 5 in all cases. $R = {}^5/_9[\langle\cos^4\Theta\rangle/\langle\cos^2\Theta\rangle^2]$.

ψ corresponds to a small degree of orientation, orientation is perfect at $\psi = \pi/2$. ψ itself depends on three variables: the number of segments in the chain, the extent of deformation, and the number of segments which move as a unit in the process of orientation. The exact dependence is given in eq 8b. ψ increases with deformation, decreases with the distance between chain ends, and increases with the number of segments acting cooperatively. A few numbers are presented in Table I, to indicate the magnitude of the effect.

Roe and Krigbaum[8] carried out calculations on anisotropy in polymer systems a number of years ago. They started from a result of Kuhn and Grün[9] who calculated the most probable distribution of segmental orientation as a function of the distortion of the end-to-end distance. This model is, as explained by Treloar,[10] inherently non-Gaussian and tends to be better than a Gaussian model at chain deformations which are very large ($R^2 > 0.5\ N^2b^2$). At low extensions, there is no advantage for the non-Gaussian model.

The present calculation leads to results in closed form and the results are deceptively simple. If the active element is a single statistical chain element, and the distance between chemical cross-links, N, is known, w equals $1/N$, and there are no free parameters (eq 10a to 10c). In fact, it is never certain that a single statistical unit is the element being oriented, nor are the number of units between chemical cross-links actually the *effective* number of units between junction points. For this reason, w enters as a parameter of the problem. This has its advantages, however, since changes in w with temperatue, for example, could serve as a quantitative measure of the extent of chain entanglement.

It also should be noted that if the experimenter can measure $\langle\cos^2\Theta\rangle$ and $\langle\cos^4\Theta\rangle$, ψ may be determined from Figure 1. From this w can be obtained directly, provided that ψ is in a suitable range.

Summary

1. A Gaussian model of segmental orientation in a stretched polymer has been worked out.

2. Segmental orientation functions, $\langle\cos^{2n}\Theta\rangle$, of all orders are obtained in closed form in terms of a single reduced variable.

3. The use of the analysis for estimation of chain entanglements has been explored.

Appendix

In Figure 2, we exhibit a single polymer chain. Segments i and j are indicated in the figure together with the vector

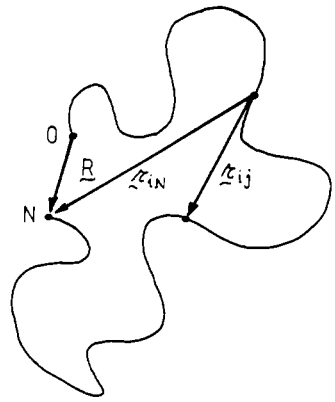

Figure 2. A polymer molecule labeled as indicated in the Appendix.

connecting i and j, $\mathbf{r}_{ij}$. The vectors connecting segment i with the beginning and end of the chain, $\mathbf{r}_{0i}$ and $\mathbf{r}_{iN}$, and the vector connecting the chain ends, $\mathbf{R}$, are also shown.

The probability that i and j are separated by $\mathbf{r}_{ij}$ if i and N are separated by $\mathbf{r}_{iN}$ is given by the bivariate Gaussian

$$W(\mathbf{r}_{ij};\mathbf{r}_{iN}) \sim \exp[-a_{ij}\mathbf{r}_{ij}^2]\exp[-b_{ij}(\mathbf{r}_{iN}-\mathbf{r}_{ij})^2] \quad \text{(A1a)}$$

$$a_{ij} = \zeta/(Nw) \quad \text{(A1b)}$$

$$b_{ij} = \zeta/(N(1-v)) \qquad v = j/N \quad \text{(A1c)}$$

The probability that i and N are separated by $\mathbf{r}_{iN}$ if the chain ends are separated by $\mathbf{R}$ is given by

$$W(\mathbf{r}_{iN};\mathbf{R}) \sim \exp[-a_{iN}r_{iN}^2]\exp[-b_{iN}(\mathbf{R}-\mathbf{r}_{iN})^2] \quad \text{(A2a)}$$

$$a_{iN} = \zeta/(N(1-u)) \quad \text{(A2b)}$$

$$b_{iN} = \zeta/(Nu) \quad \text{(A2c)}$$

The two conditional probabilities are normalized by

$$\int W(\mathbf{r}_{ij};\mathbf{r}_{iN})\,d\mathbf{r}_{ij} = 1 \quad \text{(A3a)}$$

$$\int W(\mathbf{r}_{iN};\mathbf{R})\,d\mathbf{r}_{iN} = 1 \quad \text{(A3b)}$$

The desired function $W(\mathbf{r}_{ij};\mathbf{R})$ is obtained from

$$W(\mathbf{r}_{ij};\mathbf{R}) = \int W(\mathbf{r}_{ij};\mathbf{r}_{iN})W(\mathbf{r}_{iN};\mathbf{R})\,d\mathbf{r}_{iN} \quad \text{(A4)}$$

The result is eq 2a of the text.

Acknowledgment. The author is very grateful to professor G. Weill of the University Louis Pasteur at Strasbourg who brought this problem to his attention. Professor Weill's penetrating judgement provided much guidance throughout the work. Professor L. Monnerie and Drs. G. Jannink and J. P. Jarry were kind enough to show the author unpublished experimental results highly relevant to the present analysis.

References and Notes

(1) H. M. James, *J. Chem. Phys.*, **15**, 651 (1947).
(2) B. Eichinger, *Macromolecules*, **5**, 496 (1972).
(3) W. W. Graessley, *Macromolecules*, **8**, 186 (1975).
(4) W. W. Graessley, *Macromolecules*, **8**, 865 (1975).
(5) R. T. Deam and S. F. Edwards, *Philos. Trans. R. Soc. London*, **280**, 27 (1976).
(6) P. J. Flory, *Proc. R. Soc. London, Ser. A*, **351**, 351 (1976).
(7) P. J. Flory, *J. Chem. Phys.*, **66**, 5720 (1977).
(8) R. J. Roe and W. R. Krigbaum, *J. Appl. Phys.*, **35**, 2215 (1964).
(9) W. Kuhn and F. Grün, *Kolloid-Z.*, **101**, 248 (1942).
(10) L. R. G. Treloar, "The Physics of Rubber Elasticity", 3rd ed, Clarendon Press, Oxford, 1975 Chapter VI.