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Configurational and Viscoelastic Properties of Branched Polymers

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ABSTRACT: We have developed a simple method for calculating the moments of the radius of gyration of branched polymer molecules. It can be applied to any branched molecule which has the shape of a tree, i.e., a molecule free of closed circuits in its structure. In the Rouse theory of viscoelastic behavior various functions such as the viscosity, η_0, and the steady-state recoverable compliance, J_e^0, are directly related to these moments and hence the results we have obtained may prove useful for interpreting rheological data.

Introduction

Recently there has been increased interest in studying the dynamic properties of branched polymers.[1-3] This effort is due in large part to the development of new synthetic techniques for preparing branched polymers with well-characterized structures and narrow molecular weight distributions.[4-6] The dynamic measurements being used to characterize these materials are being made over the entire range of polymer concentrations. Under some conditions such as dilute solutions of branched polymers dissolved in high molecular weight linear polymers,[7] semidilute solutions,[8] and concentrated solutions and melts of low molecular weight,[8] it is expected that the behavior can be described by the Rouse model.[9] If this is the case, use can be made of the relationships which exist for this model between the configurational and viscoelastic properties of a polymer. In what follows we put forth a simple method for calculating the mean-square radius of gyration and higher moments of the radius of gyration of branched polymer molecules. This information is used to derive expressions for the viscosity, η_0, and the steady-state recoverable compliance, J_e^0, two important linear viscoelastic properties.

Rouse Model

In the Rouse model the polymer chain is modeled as a series of N beads, each with friction coefficient ζ_0, connected together by springs with a mean-square extension a^2. The potential energy, V, of the molecule can then be written as[10]

$$V = \frac{3kT}{2a^2}\sum_{i<j}^{N}(\mathbf{r}_i - \mathbf{r}_j)^2 \tag{1}$$

where the sum includes only those pairs of beads that are connected together by a spring. Equation 1 can be rewritten as the quadratic form[10]

$$V = \frac{3kT}{2a^2}\,\mathrm{tr}\,(\mathbf{RKR}') \tag{2}$$

where tr denotes the trace and $\mathbf{R}$ is a $3 \times N$ matrix whose rows contain the x, y, and z components of the N position vectors, $\mathbf{r}_i$. $\mathbf{R}'$ denotes the transpose of $\mathbf{R}$. All off-diagonal elements of the $N \times N$ symmetric matrix $\mathbf{K}$ are zero except when i and j are directly connected by a spring. For this case

$$k_{ij} = -1 \qquad i \neq j \tag{3a}$$

The diagonal elements are

$$k_{ii} = -\sum_{i=1}^{N} k_{ij} = -\sum_{j=1}^{N} k_{ij} \qquad i \neq j \tag{3b}$$

In graph theory the matrix $\mathbf{K}$ is known as the Kirchoff[11] or the admittance[12] matrix and in the polymer physics literature it is called the Zimm matrix.[13]

As has been shown by Eichinger[10] the moments of the radius of gyration can be obtained from the eigenvalues of $\mathbf{K}$. For example

$$\langle S^2\rangle = \frac{a^2}{N}\sum_{i=1}^{N-1}\frac{1}{\tilde{\lambda}_i} \tag{4}$$

$$\langle S^4\rangle - \langle S^2\rangle^2 = \frac{2a^4}{3N^2}\sum_{i=1}^{N-1}\frac{1}{\tilde{\lambda}_i^2} \tag{5}$$

$$\langle S^6\rangle - 3\langle S^4\rangle\langle S^2\rangle + 2\langle S^2\rangle^3 = \frac{8}{9}\,\frac{a^6}{N^3}\sum_{i=1}^{N-1}\frac{1}{\tilde{\lambda}_i^3} \tag{6}$$

The reader is referred to ref 10 for expressions relating the $\tilde{\lambda}_i$ to higher moments of S^2.

The eigenvalues of $\mathbf{K}$ are also related to the relaxation spectrum, $H(\tau)$, of the Rouse model as follows:[13,14]

$$\tau_i = \frac{a^2\zeta_0}{6kT}\,\frac{1}{\tilde{\lambda}_i} \tag{7a}$$

and

$$H(\tau) = \frac{ckT}{N}\sum_{i=1}^{N-1}\delta(\ln\tau - \ln\tau_i) \tag{7b}$$

where c is the concentration of beads per unit volume and $\delta(x)$ is the Dirac delta function.

According to the theory of linear viscoelasticity the zero shear rate viscosity, η_0, is given by $\int_{-\infty}^{\infty}\tau H(\tau)\,\mathrm{d}\ln\tau$.[8] The steady-state recoverable compliance, J_e^0, a measure of the elastic energy stored under steady flow, is

$$J_e^0 = \int_{-\infty}^{\infty}\tau^2 H(\tau)\,\mathrm{d}\ln\tau \Big/ \left[\int_{-\infty}^{\infty}\tau H(\tau)\,\mathrm{d}\ln\tau\right]^2$$

By making use of eq 4, 5, and 7 one can also express these quantities in terms of the moments of the radius of gyration[15]

$$\eta_0 = \frac{c\zeta_0}{6}\langle S^2\rangle \tag{8}$$

$$J_e^0 = \frac{3}{2}\,\frac{N}{ckT}\left[\frac{\langle S^4\rangle - \langle S^2\rangle^2}{\langle S^2\rangle^2}\right] \tag{9}$$

In the following section we develop a method for calculating $\langle S^2\rangle$, $\langle S^4\rangle$, and higher moments for branched molecules.

Kirchoff and Rouse Matrices

As shown above, the elements of the Kirchoff matrix can be easily written down for any linear or branched molecule. $\mathbf{K}$ can also be constructed in a different manner by making use of the incidence matrix of graphy theory, $\mathbf{B}$. For a tree-shaped molecule the incidence matrix is an $N \times (N - 1)$ matrix with N rows for the beads and $N - 1$ columns

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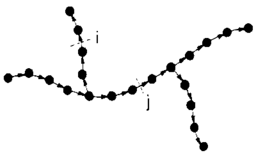

Figure 1. Branched polymer molecule with a direction assigned to each bond. For this example the cuts at bond i and bond j give $N_i = 2$ and $N_j = 10$.

for the bonds which connect them. If each bond in the molecule is assigned a sense or direction (see Figure 1), the elements of **B** will be given by (1) $b_{ij} = -1$ if bond j terminates in bead i and (2) $b_{ij} = 1$ if bond j issues from bead i. Otherwise, (3) $b_{ij} = 0$. The Kirchoff matrix is obtained from **B** by

$$\mathbf{K} = \mathbf{B}\mathbf{B}' \tag{10}$$

The sums of the reciprocal eigenvalues required for calculating $\langle S^2\rangle$ could be obtained by inverting **K** and computing its trace. However, **K** contains one zero eigenvalue and hence does not possess an ordinary inverse. Methods have been developed for calculating $\mathbf{K}^+$, a generalized inverse of **K**, whose trace yields $\langle S^2\rangle$, and these have been applied to certain simple molecules such as linear chains, rings, and stars.[10] However, for more complicated molecules, analytical expressions for the generalized inverse of **K** are difficult to obtain. We have developed an alternate approach based on the matrix formed by the product

$$\mathbf{C} = \mathbf{B}'\mathbf{B} \tag{11}$$

The matrix **C** has been identified as the Rouse matrix.[13,15] It is of order $(N-1) \times (N-1)$ and its nonzero eigenvalues are the same as those of **K**.[10] Because **K** contains only one zero eigenvalue, **C** contains no zero eigenvalues. Furthermore, as is shown in Appendix A, **C** can be readily inverted for any branched molecule regardless of its structure, thereby providing a simple method for calculating the moments of the radius of gyration.

The procedure for expressing the inverse of **C** is as follows. Cut the branched molecule at bond i and bond j (see Figure 1). The cut at bond i divides the molecule into two parts. Let N_i be the number of beads in the part which does not contain bond j and let N_j be defined in the same way for bond j. Then the elements of $\mathbf{C}^{(-1)}$ are given by

$$\begin{aligned} c_{ij}^{(-1)} &= \pm N_i N_j / N \qquad i \neq j \\ c_{ij}^{(-1)} &= N_i(N - N_i)/N \qquad i = j \end{aligned} \tag{12}$$

where the sign is positive if the directions of bond i and bond j are the same and negative if the direction is different. In Appendix A methods are given for labeling a molecule so that the sign of the elements of $\mathbf{C}^{(-1)}$ can be simply determined. However, for calculating the moments of the radius of gyration the sign is not required.

Equation 12 is a particularly useful result. The sums of reciprocal powers of the eigenvalues are easily computed with it by making use of the equation

$$\sum_{i=1}^{N-1} \frac{1}{\lambda_i^{\,n}} = \mathrm{tr}\,\{[\mathbf{C}^{(-1)}]^n\} \tag{13}$$

In the next section we demonstrate the use of eq 12 by calculating some known results for star-shaped molecules. We then derive some new results for comb-shaped and H-shaped branched polymers. Possible extensions to more complicated molecules are also discussed.

Example Calculations

Expressions for calculating $\langle S^2\rangle$ and $\langle S^4\rangle$ can be obtained from eq 4, 5, 12, and 13. We have

$$\langle S^2\rangle = \frac{a^2}{N}\,\mathrm{tr}\,[\mathbf{C}^{(-1)}] \tag{14a}$$

$$\langle S^2\rangle = \frac{a^2}{N}\sum_i c_{ii}^{(-1)} \tag{14b}$$

$$\langle S^2\rangle = \frac{a^2}{N^2}\sum_i N_i(N - N_i) \tag{14c}$$

and

$$\langle S^4\rangle - \langle S^2\rangle^2 = \frac{2a^4}{3N^2}\,\mathrm{tr}\,[(\mathbf{C}^{(-1)})^2] \tag{15a}$$

$$\langle S^4\rangle - \langle S^2\rangle^2 = \frac{2a^4}{3N^2}\sum_i\sum_j [c_{ij}^{(-1)}]^2 \tag{15b}$$

$$\begin{aligned} \langle S^4\rangle - \langle S^2\rangle^2 &= \frac{2a^4}{3N^4}\sum_i\sum_j N_i^2 N_j^2 \qquad i \neq j \\ \langle S^4\rangle - \langle S^2\rangle^2 &= \frac{2a^4}{3N^4}\sum_i\sum_j N_i^2 (N - N_i)^2 \qquad i = j \end{aligned} \tag{15c}$$

Equation 14c is known as Kramers' rule. It has been derived by a number of authors[16-18] and used to calculate the mean-square radius of gyration of linear and various branched molecules.[17-19] Equation 15c is new. It can be thought of as a higher order Kramers' rule for calculating $\langle S^4\rangle$.

Two important parameters for assessing the effects of branching on viscoelastic properties are the ratio of the zero shear rate viscosity of a branched polymer to that of a linear polymer of the same molecular weight, $(\eta_0)_{\mathrm{B}}/(\eta_0)_{\mathrm{L}}$, and the ratio of the steady-state recoverable compliances, $(J_{\mathrm{e}}^0)_{\mathrm{B}}/(J_{\mathrm{e}}^0)_{\mathrm{L}}$.[1]

In the Rouse model the first ratio is given by $\langle S^2\rangle_{\mathrm{B}}/\langle S^2\rangle_{\mathrm{L}}$ and is called g_1

$$g_1 = \langle S^2\rangle_{\mathrm{B}}/\langle S^2\rangle_{\mathrm{L}} \tag{16}$$

The second ratio, $(J_{\mathrm{e}}^0)_{\mathrm{B}}/(J_{\mathrm{e}}^0)_{\mathrm{L}}$, is called g_2, and according to eq 9 is given by

$$g_2 = \left[\frac{\langle S^4\rangle - \langle S^2\rangle^2}{\langle S^2\rangle^2}\right]_{\mathrm{B}} \Bigg/ \left[\frac{\langle S^4\rangle - \langle S^2\rangle^2}{\langle S^2\rangle^2}\right]_{\mathrm{L}} \tag{17}$$

Using eq 14 and 15 and the values of $\langle S^2\rangle$ and $\langle S^4\rangle$ for linear polymers (see Appendix B), we have

$$g_1 = \frac{6}{N^3}\sum_i N_i(N - N_i) \tag{18}$$

and

$$g_2 = \frac{5}{2}\,\frac{\sum_i\sum_j N_i^2 N_j^2}{[\sum_i N_i(N - N_i)]^2} \tag{19}$$

As an example, application of eq 18 and 19 to star-shaped molecules containing f arms of equal length yields the well-known results[20] (see also Appendix B)

$$g_1 = (3f - 2)/f^2 \tag{20}$$

$$g_2 = (15f - 14)/(3f - 2)^2 \tag{21}$$

Comb-shaped polymers can also be treated. Consider, for example, a regular comb containing f side branches of n units (beads) and $f + 1$ backbone segments of m units

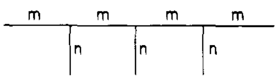

Figure 2. Comb-shaped molecule with m units in the backbone chains and n units in the side chains.

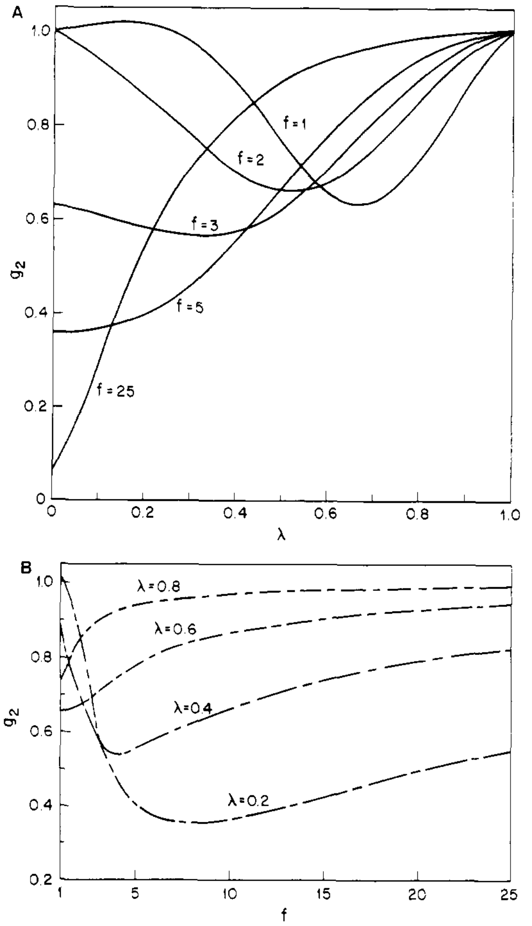

Figure 3. (A) The function g_2 (see eq 17) vs. the fraction of units in the backbone, λ, for various number of branches, f. (B) g_2 vs. the number of branches for various values of λ.

(see Figure 2). Let λ be the fraction of chain units which are in the backbone of the polymer. Then

$$g_1 = \lambda^3 + \left[\frac{2f+1}{f+1}\right]\lambda^2(1-\lambda) + \left[\frac{f+2}{f}\right]\lambda(1-\lambda)^2 + \left[\frac{3f-2}{f^2}\right](1-\lambda)^3 \quad (22)$$

$$g_2 = \left\{\lambda^6 + \left[\frac{4f^3+10f^2+6f-2}{(f+1)^3}\right]\lambda^5(1-\lambda) + \left[\frac{12f^4+24f^3+11f^2-11f-6}{2f(f+1)^3}\right]\lambda^4(1-\lambda)^2 + \left[\frac{4f^4+2f^3+13f^2+7f-6}{f^2(f+1)^2}\right]\lambda^3(1-\lambda)^3 + \left[\frac{2f^4-2f^3+47f^2+23f-10}{2f^3(f+1)}\right]\lambda^2(1-\lambda)^4 + \left[\frac{10f^2+20f-24}{f^4}\right]\lambda(1-\lambda)^5 + \left[\frac{15f-14}{f^4}\right]\times(1-\lambda)^6\right\}\Big/{g_1}^2 \quad (23)$$

The details of the calculations are given in Appendix B.

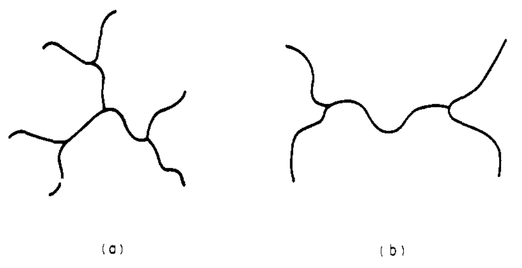

Figure 4. (a) A regular tree-shaped molecule. (b) An H-shaped molecule.

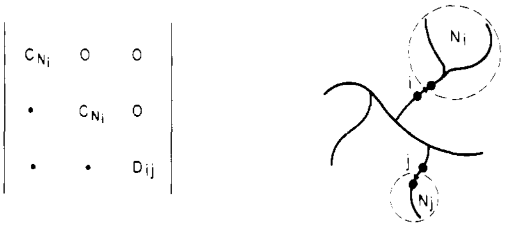

Figure 5. Determinant for calculating the cofactors of **C** and molecule showing i and j units.

In Figure 3 we show g_2 as a function of λ for various values of f, and g_2 as function of f at different λ. Note from eq 23 or Figure 3 that as $\lambda \to 0$, we recover the previous results derived for star molecules with f arms and when $\lambda \to 1$ or $f \to \infty$ at constant λ, we find the limiting value for linear polymers, $g_2 = 1$.

Equation 22 has been derived before,[21] but eq 23 is a new result.[22] It should be useful for interpreting the viscoelastic properties of comb-shaped polymer molecules.[23,24] Other types of branched polymer molecules which are of current interest are the H-shaped molecule and the tree molecule[10] shown in Figure 4. H-shaped molecules are discussed in Appendix B.

Remarks

It is interesting to contrast our approach with the Green's function method developed by Ham.[25] The sums of reciprocal eigenvalues required for calculating $\langle S^2\rangle$ and $\langle S^4\rangle$ can be obtained from the Green's function, $g(x,x')$, as follows:[25,26]

$$\sum 1/\tilde{\lambda}_n = \int g(x,x)\,dx \quad (24)$$

$$\sum 1/\tilde{\lambda}_n^2 = \int\int g^2(x,y)\,dx\,dy \quad (25)$$

Using Ham's nomenclature the Green's function for a branched polymer molecule would be

$$g(x,x') = \pm l_x(L - l_{x'})/L \quad (26)$$

where l_x and $L - l_{x'}$ are the lengths of the polymer segments containing N_i and N_j units as described for eq 12 and L is the total length of the molecule. The sign is determined by the direction given to the segments of the molecule containing x and x' (see Figure 5). Equation 26 generalizes the results presented by Ham so that his method can be applied to any branched molecule.

In most cases the branched polymer samples being studied are not monodisperse but are mixtures of different molecular weights. A particular advantage of the method we have described is that it leads to analytical expressions for the moments. When results are available in this form, Zimm and Stockmayer[17] and Orofino[19] have shown that g_1 can be obtained for such heterogeneous structures as random polycondensates and random comb-shaped polymers. The methods they developed and the equations given above can be applied to these materials to calculate g_2 and higher moments of S^2.

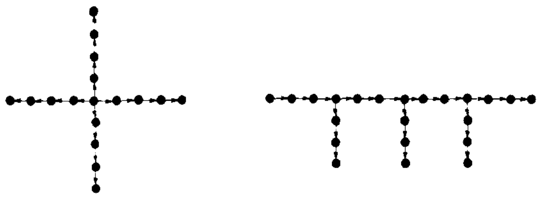

Figure 6. Example of method for labeling stars and combs.

Appendix A

The inversion of the Rouse matrix **C** can be accomplished in the following manner. The elements of $\mathbf{C}^{(-1)}$ are given by

$$c_{ij}^{(-1)} = \mathrm{cof}_{ij}\,(\mathbf{C})/|\mathbf{C}| \quad \text{(A1)}$$

where $\mathrm{cof}_{ij}\,(\mathbf{C})$ is the determinant of the matrix $\mathbf{C}_{ij}$ obtained by striking the ith row and jth column from **C** and then multiplying by $(-1)^{i+j}$. The matrix $\mathbf{C}_{ij}$ is also equal to

$$\mathbf{C}_{ij} = \mathbf{B}'_i\mathbf{B}_j \quad \text{(A2)}$$

where $\mathbf{B}_k$ is the $N \times (N-2)$ matrix obtained by striking the kth column from the incidence matrix, **B**.

By rearranging the rows and columns of $\mathbf{C}_{ij}$, $\mathrm{cof}_{ij}\,(\mathbf{C})$ can be obtained from the determinant of the triangular block matrix shown in Figure 5. $\mathbf{C}_{N_i}$ and $\mathbf{C}_{N_j}$ are the complete Rouse matrices of the two trees obtained by deleting bonds i and j (see Figure 5). The determinant of $\mathbf{D}_{ij}$ times $(-1)^{i+j}$ is ±1, depending on whether the sense of bonds i and j is the same $(+1)$ or different (-1) (in Figure 5 the bonds have an opposite sense and $(-1)^{i+j}|\mathbf{D}_{ij}| = -1$). If bond i is equal to bond j, the matrix in Figure 5 contains only two blocks, $\mathbf{C}_{N_i}$ and $\mathbf{C}_{N-N_i}$.

The determinant of the Rouse matrix for a tree-shaped molecule is equal to the number of beads (vertices) it contains.[27] Therefore $\mathrm{cof}_{ij}\,(\mathbf{C})$ is $\pm|\mathbf{D}_{ij}||\mathbf{C}_{N_i}||\mathbf{C}_{N_j}| = \pm N_iN_j$ and the ijth element of $\mathbf{C}^{(-1)}$ is

$$c_{ij}^{(-1)} = \pm N_iN_j/N \quad \text{(A3)}$$

(see eq 12 above).

For certain applications the sign of $c_{ij}^{(-1)}$ may be important. An easy way to fix the sign is to choose one bead of the molecule as a root and direct all bonds away from it (see Figure 6). For a star molecule with the central bead as the root, $c_{ij}^{(-1)}$ is positive if i and j are on the same branch and negative if i and j are on different branches. For a comb molecule with one end of the backbone as a root, $c_{ij}^{(-1)}$ is positive unless i and j are on different side branches or if i (j) is on a side branch and j (i) is not between i (j) and the root. Simple labeling schemes similar to these can be developed for any branched molecule.

Appendix B

Values of $\langle S^2\rangle$ and $\langle S^4\rangle$ for a linear polymer molecule can be calculated by eq 14 and 15. If the units are numbered consecutively from one end we have

$$\langle S^2\rangle = \frac{a^2}{N^2}\sum_{i=1}^{N-1} i(N-i) = \frac{a^2}{6}\,\frac{(N-1)(N+1)}{N} \cong \frac{Na^2}{6} \quad \text{(B1)}$$

$$\langle S^4\rangle - \langle S^2\rangle^2 = \frac{2a^4}{3N^4}\Big[\sum_{i=1}^{N-1}\sum_{j=1}^{i}(N-i)^2j^2 + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N-1} i^2(N-j)^2\Big] = \frac{a^4}{270}\,\frac{(2N^4+5N^2-7)}{N^2} \cong \frac{N^2a^4}{135} \quad \text{(B2)}$$

and

$$\frac{\langle S^4\rangle - \langle S^2\rangle^2}{\langle S^2\rangle^2} = \frac{2}{15}\,\frac{2N^2+7}{N^2} \cong \frac{4}{15} \quad \text{(B3)}$$

For a star-shaped molecule with f arms and n_j units per arm we find

$$\langle S^2\rangle = \frac{a^2}{N^2}\sum_{j=1}^{f}\sum_{i=1}^{n_j} i(N-i) = \frac{a^2}{N^2}\sum_{j=1}^{f}\left[\frac{n_j(n_j+1)}{2} - \frac{1}{N}\,\frac{n_j(n_j+1)(2n_j+1)}{6}\right] \quad \text{(B4)}$$

If all arms have the same length n and we ignore terms of order unity, we find from eq B1 and B4

$$g_1 = (3f-2)/f^2$$

For $\langle S^4\rangle$ we have

$$\langle S^4\rangle - \langle S^2\rangle^2 = \frac{2a^4}{3N^4}\Big\{\sum_{k=1}^{f}\sum_{i=1}^{n_k}\sum_{j=1}^{i}(N-i)^2j^2 + \sum_{k=1}^{f}\sum_{i=1}^{n_k}\sum_{j=i+1}^{n_k} i^2(N-j)^2 + \sum_{k=1}^{f}\sum_{l=1}^{f}\sum_{i=1}^{n_k}\sum_{j=1}^{n_l}(1-\delta_{kl})i^2j^2\Big\} \quad \text{(B5)}$$

The first two sets of summations are when i and j are on the same arm and the last set is when i and j are on different arms. If all arms have the same length, we find

$$g_2 = (15f-14)/(3f-2)^2$$

For a comb-shaped molecule with m_i bonds in the backbone chains and n_i bonds in the f side chains, we find for $\langle S^2\rangle$

$$\langle S^2\rangle = \frac{a^2}{N^2}\Big\{\sum_{j=1}^{f}\sum_{i=1}^{n_j} i(N-i) + \sum_{j=1}^{f+1}\sum_{i=1}^{m_j}\Big[i + \sum_{k=1}^{j-1}(m_k+n_k)\Big]\Big[N - i - \sum_{k=1}^{j-1}(m_k+n_k)\Big]\Big\} \quad \text{(B6)}$$

If all backbone chains have m bonds, all side chains have n bonds, and λ is the fraction of bonds in the backbone, then $n = N(1-\lambda)/f$ and $m = N\lambda/(f+1)$. Evaluating the sums in eq B6 and then collecting terms in $\lambda^{3-n}(1-\lambda)^n$ for $n = 0 \rightarrow 3$, we get g_1 as given by eq 22.

For $\langle S^4\rangle$ the terms when i and j are on the side chains are the same as eq B5. Adding terms for i on the backbone with j on a side chain plus i and j both on the backbone, we get

$$\langle S^4\rangle - \langle S^2\rangle^2 = \text{eq B5} + \frac{4a^4}{3N^4}\sum_{k=1}^{f}\sum_{i=1}^{n_k} i^2\Big\{\sum_{l=1}^{k}\sum_{j=1}^{m_l}\Big[j + \sum_{p=1}^{l-1}(m_p+n_p)\Big]^2 + \sum_{l=k+1}^{f+1}\sum_{j=1}^{m_l}\Big[j + \sum_{p=1}^{f}(m_{p+1}+n_p)\Big]^2\Big\} + \frac{2}{3}\,\frac{a^4}{N^4}\sum_{k=1}^{f+1}\sum_{i=1}^{m_k}\Big[N - i - \sum_{p=1}^{k-1}(m_p+n_p)\Big]^2\Big\{\sum_{j=1}^{i}\Big[j + \sum_{p=1}^{k-1}(m_p + n_p)\Big]^2 + \sum_{l=1}^{k-1}\sum_{j=1}^{m_l}\Big[j + \sum_{p=1}^{l-1}(m_p+n_p)\Big]^2\Big\} + \frac{2}{3}\,\frac{a^4}{N^4}\sum_{k=1}^{f+1}\sum_{i=1}^{m_k}\Big[k + \sum_{p=1}^{k-1}(m_p+n_p)\Big]^2\Big\{\sum_{j=i+1}^{m_k}\Big[j + \sum_{p=k}^{f}(m_{p+1}+n_p)\Big]^2 + \sum_{l=k+1}^{f+1}\sum_{j=1}^{m_l}\Big[j + \sum_{p=1}^{f}(m_{p+1}+n_p)\Big]^2\Big\} \quad \text{(B7)}$$

When the sums in eq B7 are evaluated for $m_p = m$ and $n_p = n$ and terms containing $\lambda^{6-n}(1-\lambda)^n$ for $n = 0 \rightarrow 6$ are collected, we get eq 23.

An H-shaped molecule has 4 equal arms with a backbone connecting them (see Figure 4b). Let λ be the fraction of material in the backbone. Then using methods the same as those detailed above, we find

$$g_1 = \lambda^3 + 3\lambda^2(1-\lambda) + 9/4\lambda(1-\lambda)^2 + 5/8(1-\lambda)^3 \quad \text{(B8)}$$

$$g_2 = [\lambda^6 + 6\lambda^5(1-\lambda) + 15\lambda^4(1-\lambda)^2 + 65/4\lambda^3(1-\lambda)^3 + 495/64\lambda^2(1-\lambda)^4 + 21/16\lambda(1-\lambda)^5 + 46/256(1-\lambda)^6]/g_1^2 \quad \text{(B9)}$$

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$$\langle \mathbf{r}_i \mathbf{r}_j \rangle = a^2 \delta_{ij}$$

$$\langle \mathbf{r}_i \mathbf{r}_j \mathbf{r}_k \mathbf{r}_l \rangle = a^4[\delta_{ij}\delta_{jk}\delta_{kl} + \delta_{ij}\delta_{kl}(1-\delta_{ik}) + \tfrac{1}{3}(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl})(1-\delta_{ij})]$$

where δ_{ij} is the Kronecker delta function.
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Random Coil Configurations of Aromatic Polyesters: Temperature Coefficient of the Unperturbed Dimensions of Poly(diethylene glycol terephthalate) Chains

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ABSTRACT: Hydroxyl-terminated poly(diethylene glycol terephthalate) chains having number-average molecular weights of 7200 were end-linked into noncrystallizable trifunctional networks using an aromatic triisocyanate. The networks thus obtained were studied with regard to their stress–strain isotherms at 62, 70, and 88 °C. For elongation ratios up to 400% none of the isotherms displayed an increase or upturn in the reduced forces $[f^*]$, indicating that the polymer does not crystallize under stress, probably due to very unfavorable kinetic conditions. Force–temperature measurements at constant length and pressure are also reported for these networks. The ratio of the energy contribution to the total tension, f_e/f, calculated from these measurements and the thermal expansion coefficient were used to calculate the temperature coefficient of the mean-square end-to-end distance. It was found that $d \ln \langle r^2 \rangle_0 / dT = (1.01 \pm 0.14) \times 10^{-3}\ \mathrm{K}^{-1}$. A similar value was obtained for this coefficient from thermoelastic measurements carried out on swollen networks. The analysis of the temperature coefficient of poly(diethylene glycol terephthalate) in terms of the rotational isomeric state model confirms the results obtained from ^{1}H NMR studies, according to which the gauche states about CH_2–CH_2 bonds in the polymer chain have an energy significantly lower than these states about similar bonds in poly(oxyethylene).

Introduction

Studies on the random configurations of aromatic polyesters are meager due to the difficulties involved in the experimental determination of their configuration-dependent properties.[1–6] Most of these materials are highly crystalline and melt well above room temperature, so they are insoluble in ordinary solvents.[7] Measurements of configurational properties in solution are therefore precluded. Even in the cases in which the determination of a particular property can be carried out in bulk, as, for example, in the measurements of the temperature coefficient of the unperturbed dimensions by thermoelastic experiments, it is necessary to make the pertinent experiments above the melting temperature at which most of the molecular networks prepared from these polymers would undergo chemical and physical aging.

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