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Notes

Relationship between the Rotational Isomeric State and Wormlike Chain Models

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Some interest has been shown in relating the Kratky–Porod wormlike chain model[1,2] to the rotational isomeric state (RIS) model[3] or to real polymer molecules in solution. Maeda, Saitô, and Stockmayer[4] demonstrated that a relationship existed between RIS and wormlike chains. They defined a "shift factor" f, given by $n = fL/2a$ for n, the number of bonds of the RIS chain, and L and a, the contour length and persistence length, respectively, of the wormlike chain. They showed that for appropriate values of f, one could obtain very good agreement between both the second and fourth moments of the end-to-end vector of a number of sufficiently long RIS and wormlike chains. However, they were unable to give general rules for computing f and resorted finally to curve fitting. Along a somewhat different line, Yamakawa and co-workers[5-8] have compared wormlike chains to real chain molecules in solution and presented rules for determining the shift factor from various experimental properties. Recently, good agreement has been demonstrated[9] between certain RIS and wormlike star molecules. Mattice[10] examined a number of star molecules, finding many for which such agreement was lacking, and concluded that agreement was usually obtained for stars of large characteristic ratio. In this note, we give precise rules for the selection of the shift factor of Maeda et al.[4] for agreement between the second moments of wormlike and RIS chains. As has been recognized,[4,10] a good understanding of the relationship between the two models is desirable because of the relative simplicity of the wormlike model.

Two-bond correlations in a long RIS chain with all bonds identical can be written (cf. eq IV.16 of ref 3)

$$\langle \mathbf{l}_i \cdot \mathbf{l}_{i+j} \rangle = l^2 Z^{-1} \mathbf{L} \mathbf{M}^j \mathbf{R} \tag{1}$$

where **L**, **R**, and **M** are row, column, and square matrices, respectively, given by

$$\mathbf{L} = \mathbf{J}^* \mathbf{U}^{i-2} (\mathbf{E}_\nu \otimes \hat{\mathbf{l}}^{\mathrm{T}}) \tag{2}$$

$$\mathbf{M} = (\mathbf{U} \otimes \mathbf{E}_3) \|\mathbf{T}\| \tag{3}$$

$$\mathbf{R} = (\mathbf{E}_\nu \otimes \hat{\mathbf{l}}) \mathbf{U}^{n-j-i} \mathbf{J} \tag{4}$$

where $\hat{\mathbf{l}} = \mathbf{l}/l$ and all other notation follows ref 3. We set $1 \ll i \leq i + j \ll n$ so that the dominant eigenvalue, λ_1, of **U** determines the partition function, Z:[3]

$$Z = \Gamma_1 \lambda_1^{n-2} \tag{5}$$

where Γ_1 is defined in ref 3.

Let **A** be the diagonalizing similarity transformation of **M**. ($\mathbf{A}^{-1}\mathbf{M}\mathbf{A}$ is diagonal with elements m_μ.) Then

$$\langle \mathbf{l}_i \cdot \mathbf{l}_{i+j} \rangle = l^2 Z^{-1} \sum_\mu \Omega_\mu m_\mu^{\,j} \tag{6}$$

where

$$\Omega_\mu = \sum_{\sigma\rho} L_\sigma A_{\sigma\mu} A_{\mu\rho}^{-1} R_\rho \tag{7}$$

Because we have assumed that $1 \ll i$ and $i + j \ll n$, all of the i and j dependence in **L** and **R** appears in the factors λ_1^{i-2} and λ_1^{n-j-i}, respectively, so the i and j dependence of Ω_μ can be expressed as

$$\Omega_\mu = \lambda_1^{n-j-2} \Pi_\mu \tag{8}$$

Then

$$\langle \mathbf{l}_i \cdot \mathbf{l}_{i+j} \rangle = l^2 \sum_\mu K_\mu \alpha_\mu^{\,j} \tag{9}$$

for $K_\mu = \Pi_\mu / \Gamma_1$ and $\alpha_\mu = m_\mu / \lambda_1$. The corresponding expression for a wormlike chain of persistence length a is[2]

$$\langle \mathbf{u}(s') \cdot \mathbf{u}(s'') \rangle = \exp(-|s' - s''|/a) \tag{10}$$

for $\mathbf{u}(s)$ the unit vector tangent to the wormlike curve at the contour distance s. On the basis of the above, therefore, a sufficient condition for good agreement between the two models is the following:

(1) One of the K_μ is dominant, and (11a)

(2) the associated α_μ is near 1 (11b)

Condition 11a ensures that a single exponential will dominate in eq 9 and condition 11b ensures that $\sum_j \alpha_\mu^{\,j} \simeq \int \mathrm{d}x \, \exp(x \ln \alpha_\mu)$. Although condition 11 will certainly lead to good agreement between the two models, we actually find that agreement is more general.

The second moment of a wormlike chain of contour length L is given by[2,3]

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$$\langle R^2 \rangle = 2aL - 2a^2(1 - e^{-L/a}) \quad (12)$$

or in the first Daniels approximation[11] (appropriate for $e^{-L/a} \ll 1$)

$$\langle R^2 \rangle = 2aL - 2a^2 \quad (13)$$

As we shall see, RIS chains also give "first Daniels approximations" for which

$$\langle R^2 \rangle = nl^2 C_\infty - 2Dl^2 \quad (14)$$

for D a factor dependent on the particular RIS chain but independent of n or l. Exact agreement between eq 13 and 14 is obtained by setting

$$a = D^{1/2} l \quad (15)$$

and

$$L = \tfrac{1}{2} C_\infty D^{-1/2} nl \quad (16)$$

The shift factor[4] is given by

$$f = 4D/C_\infty \quad (17)$$

We conclude that good agreement may be obtained in the first Daniels approximation *whenever* $D > 0$, consistent with the observation of Mattice.[10] Condition 11 is a sufficient condition for agreement beyond the Daniels limit.

Several examples will illuminate the above arguments.

The Freely Rotating Chain

For this chain we have[3]

$$\langle \mathbf{l}_i \cdot \mathbf{l}_{i+k} \rangle = l^2 \alpha^k = l^2 \exp(k \ln \alpha) \quad (18)$$

and

$$\langle R^2 \rangle = \left(\frac{1+\alpha}{1-\alpha} \right) nl^2 - 2\alpha l^2 \frac{(1-\alpha^n)}{(1-\alpha)^2} \quad (19)$$

for $\alpha = \cos\theta$ and for θ the supplement of the bond angle. In this case, the "first Daniels approximation" results when $\alpha^n \ll 1$

$$\langle R^2 \rangle = \left(\frac{1+\alpha}{1-\alpha} \right) nl^2 - \frac{2\alpha l^2}{(1-\alpha)^2} \quad (20)$$

so just as in eq 15–17

$$a = \alpha^{1/2}(1-\alpha)^{-1} l \quad (21)$$

$$L = \tfrac{1}{2}(1+\alpha)\alpha^{-1/2} nl \quad (22)$$

and

$$f = 4\alpha/[(1+\alpha)(1-\alpha)] \quad (23)$$

Note that for $\alpha = {}^1/_3$, $f = {}^3/_2$ as determined by Maeda et al.[4]

The freely rotating chain provides an example of condition 11 leading to agreement beyond the Daniels approximation. There is, of course, only one K_μ, and when $\alpha \simeq 1$, the parameters chosen to force agreement within the Daniels limit, eq 21 and 22, agree well with the parameters that one would naturally choose in going to a continuous limit: $a = -(\ln \alpha)^{-1} l$ and $L = nl$. (This may be seen by expanding in powers of $1 - \alpha$.)

Independently Rotating Chains with Symmetric Bond Rotational Potentials

In this case eq 9 holds, with two eigenvalues being important.[3] We have (ref 3, eq I.53)

$$\langle R^2 \rangle = \left(\frac{1+\alpha}{1-\alpha} \right) \left(\frac{1+\eta}{1-\eta} \right) nl^2 - \left(\frac{\alpha\eta + \lambda_1}{\lambda_1 - \lambda_2} \right) P_1 l^2 + \left(\frac{\alpha\eta + \lambda_2}{\lambda_1 - \lambda_2} \right) P_2 l^2 \quad (24)$$

with

$$P_k = 2\lambda_k(1 - \lambda_k^{\,n})(1 - \lambda_k)^{-2} \quad (25)$$

The "Daniels approximation" in this case is $\lambda_k^{\,n} \ll 1$ (convergence requires $|\lambda_k| < 1$), or

$$P_k = 2\lambda_k(1 - \lambda_k)^{-2} \quad (26)$$

which is similar in form to the last term of eq 20. Then, to obtain appropriate values of a and L we employ

$$D = [(\alpha\eta + \lambda_2)\lambda_2(1-\lambda_2)^{-2} - (\alpha\eta + \lambda_1)\lambda_1(1-\lambda_1)^{-2}](\lambda_1 - \lambda_2)^{-1} \quad (27)$$

$$C_\infty = (1+\alpha)(1+\eta)(1-\alpha)^{-1}(1-\eta)^{-1} \quad (28)$$

and eq 15 and 16.

RIS Chains

In this case we have[12]

$$\langle R^2 \rangle = C_\infty n \langle l^2 \rangle - 2 \sum_{\mu,\sigma=1}^{s} \mathbf{m}_\mu^{\mathrm{T}} (\mathbf{B}_\mu^* \otimes \mathbf{E}_3)(\mathbf{E}_{3\nu} - \mathbf{S}_\mu^{\,x}) \times (\mathbf{E}_{3\nu} - \mathbf{S}_\mu)^{-2} \mathbf{R}_{\mu\sigma} (\mathbf{A}_\mu \otimes \mathbf{E}_3) \mathbf{m}_\sigma \quad (29)$$

an expression very similar in form to eq 19 or eq 24. Here the summation is over different types of bonds in a repeat unit, s is the number of bonds in a repeat unit, and $x = n/s$ is the number of repeat units. All notation is given in ref 12 or 13. When $s = 1$, $\mathbf{S}_1 = \mathbf{M}/\lambda_1$ for $\mathbf{M}$ given in eq 3 so the eigenvalues of $\mathbf{S}_1$ are just the α_μ of eq 9. In the RIS case, the "Daniels approximation" is $\mathbf{S}_\mu^{\,x} \simeq \mathbf{0}$. Convergence requires $\mathbf{S}_\mu^{\,x} \rightarrow \mathbf{0}$ with x. On this basis we can expect agreement between the two types of chains whenever D in eq 14 is positive and whenever $\alpha^x \ll 1$ for α the largest of all the eigenvalues of each $\mathbf{S}_\mu$ in eq 27. Since $\mathbf{S}_\mu^{\,x} \rightarrow \mathbf{0}$, $|\alpha| < 1$ always, and α^x will converge rapidly except when $|\alpha| \simeq 1$. Agreement at lower values of x will be fortuitous or result when condition 11 is satisfied.

Useful expressions for C_∞ and D may be determined from the work of Matsuo[12,13]

$$C_\infty = 1 + \frac{2}{s\langle l^2 \rangle} \sum_{\mu,\sigma=1}^{s} \mathbf{m}_\mu^{\mathrm{T}} (\mathbf{B}_\mu^* \otimes \mathbf{E}_3)(\mathbf{E}_{3\nu} - \mathbf{S}_\mu)^{-1} \mathbf{R}_{\mu\sigma} (\mathbf{A}_\mu \otimes \mathbf{E}_3) \mathbf{m}_\sigma \quad (30)$$

$$D = \frac{1}{s\langle l^2 \rangle} \sum_{\mu,\sigma=1}^{s} \mathbf{m}_\mu^{\mathrm{T}} (\mathbf{B}_\mu^* \otimes \mathbf{E}_3)(\mathbf{E}_{3\nu} - \mathbf{S}_\mu)^{-2} \mathbf{R}_{\mu\sigma} (\mathbf{A}_\mu \otimes \mathbf{E}_3) \mathbf{m}_\sigma \quad (31)$$

These equations involve the single eigenvalue expression for Z,[12,13] eq 5, and so are not accurate for short chains but will be adequate in most cases within the Daniels approximation.

We have not attempted similar comparisons for fourth moments or for star molecules but expect very similar results. One should not expect the shift factors applicable in these cases to agree with those for the second moments. In fact, shift factors different from the ones calculated for second moments have been observed for both fourth moments[4] and star molecules.[9]

The only important difference between eq 30 and 31 is the exponent of the $\mathbf{E}_{3\nu} - \mathbf{S}_\mu$ term. It may be that the signs of the two terms are correlated, so that $C_\infty < 1$ implies an increased probability that $D < 0$. This would agree with the statement of Mattice[10] that chains with small C_∞ cannot be made to agree with a wormlike chain.

In conclusion, we see that the equations for the second moment of wormlike and RIS chains both contain two terms. The first is the C_∞ term proportional to L or n (the first term in each of eq 12, 19, 24, and 29). The second is independent of L or n except for factors such as $1 - e^{-L/a}$, $1 - \alpha^n$, or $\mathbf{E} - \mathbf{S}^x$, which may be neglected in all but short chains. This common mathematical structure leads to the similarity of the two models. Therefore, eq 12–14 provide excellent approximations to RIS chains within the Daniels approximation. Once C_∞ and D are determined, by eq 30 and 31 for example, they will provide simple expressions for $\langle R^2 \rangle$ for all but short chains.

Yamakawa and co-workers[14-25] have developed the so-called helical wormlike model, and they have been successful in demonstrating agreement between their model and with both polymer molecules in solution[18,24,25] and RIS chains.[14,16,19,23] Agreement with RIS chains was seen both beyond the Daniels approximation and with $D < 0$. Although we have not studied the problem, it is probable that the additional adjustable parameters available in the helical wormlike chain model account for its improved ability to match RIS behavior.

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Low-Frequency Raman Spectroscopic Study of Ionomers

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Introduction

Ionomers are defined as polymers with nonpolar backbones containing up to 10 mol % salt group substituents, either present as pendant groups or directly incorporated into the main chain. It has been well established that the mechanical properties of these polymers, such as modulus, tensile strength, and melt elasticity, are significantly affected by the presence of these salt group substituents.[1,2] It is generally accepted that ionomers are phase separated and that the driving force for this phase separation is electrostatic in nature. Information obtained by electron microscopy, small-angle X-ray measurements, and infrared spectroscopy has led to the proposal of several morphological models.[3-6] However, each model differs considerably in its description of the nature and size of the phase-separated ionic domains. Therefore, additional characterization methods are still needed.

Table I
Mole Percent of Carboxylic Group and Degree of Ionization of Ethylene–Methacrylic Acid Copolymer and Its Salts

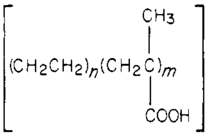
acid or salt	mol % carboxylic group	degree of ionization, %
acid	2.3	
Na	4.0	50.7
K	6.1	69.9
acid	6.1	

Recently, a number of low-frequency vibrational spectroscopic analyses showing spectroscopic features sensitive to the concentration and chemical nature of salt groups present have been carried out.[7-10] In contrast to pure modes, such as CH_2 and C=O stretching modes, vibrational bands in the low-frequency region are delocalized in nature; i.e., they involve a number of atoms. The positions and shapes of such bands are conformationally dependent and may also be quite sensitive to both the specificity and magnitude of intermolecular interactions. However, because of their complex nature, band assignments in this region are often unclear.

Ethylene–methacrylic acid copolymer and its salts have been studied in the past.[1,2,11] The structure of this polymer involves a number of phases. They are (1) the lamellar structure involving crystalline polyethylene, (2) the amorphous phase of polyethylene, and (3) the ionic domains. We have carried out a Raman spectroscopic study of this ionomer. Our preliminary results are reported here.

Experimental Section

Ethylene–methacrylic acid copolymer (1) and salts were supplied by du Pont. The neutralization of the copolymer containing 6.1 mol % methacrylic acid was accomplished in dilute xylene solution by the addition of freshly prepared potassium methoxide. Copolymer compositions are collected in Table I. These samples were dried under vacuum for several days and then used for Raman spectroscopy.



$$\left[(CH_2CH_2)_n(CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOH}{|}}{C}})_m \right]$$

1

The degree of neutralization of the ethylene–methacrylic acid ionomers used was estimated from the ratio of the intensity of the C=O stretching vibration associated with the carboxyl group (1700 cm^{-1}) to that of the asymmetric vibration of the carboxylate ion (1560 cm^{-1}). The values (Table I) obtained for our samples are in the same range found previously.[11,12]

Raman spectra were obtained with a computer-controlled Jobin-Yvon HG.2S laser Raman spectrometer, which offers the advantage of having extremely high discrimination against Rayleigh scattering, yielding high signal-to-noise ratios in the low-frequency region. However, the Raman spectra were usually difficult to obtain because of the high fluorescence background

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