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Notes

Configurational Statistics of Polymer Chains Accounting for All Rotational States. General Extension to Finite Chains and Copolymers

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The statistical properties of chain molecules with interdependent rotational potentials may be calculated either within the rotational isomeric state (RIS)[1] scheme or by accounting for all rotational states (ARS scheme).[2] The latter method has been applied hitherto only to infinite chains consisting of equivalent monomer units since these systems allow simplifications in the mathematical procedure (the ring closure of the infinite chain and the evaluation of the partition function through the maximum eigenvalue of the correlation matrix U).[3,4] Copolymer chains have been treated within this framework, but practical expediency only permits fixing of the frequency of occurrence of very short sequences of structural units.[5]

It is the purpose of the present note to show that the matrix correlation techniques employed within either scheme are essentially isomorphic, so that all RIS approaches suggested to treat chains of finite length and/or containing different monomer units in any specified sequence may be easily translated into the ARS language.

The formal equivalence between the two methods follows from the fact that they differ from each other only in the choice of an appropriate set of orthonormal basis functions for the representation of the statistical weight function $w(\varphi_{i-1},\varphi_i)$: Dirac delta functions in one case (RIS) and Fourier components in the other (ARS). Imaginary exponentials may well replace the sine/cosine functions[3] but any other orthonormal basis set could be adopted if appropriate.

From a practical point of view we shall devote particular attention to indicate how to calculate the second moment of the distribution of any vectorial property associated with the chain bonds.

Use is made of definitions already given in ref 2 for what concerns the Fourier method of accounting for all rotational states and in ref 1 for what concerns the step-by-step matrix multiplication to generate the partition function of a polymer chain; the reader is therefore referred to these publications for all details.

In the approximation of first-neighbor correlation we may express the configurational potential energy pertaining to a chain with $N + 1$ bonds in the configuration specified by the values $\varphi_2,\varphi_3,...,\varphi_N$ of the rotational angles as

$$E(\varphi_2,\varphi_3,...,\varphi_N) = E(\varphi_2,\varphi_3) + E(\varphi_3,\varphi_4) + ... + E(\varphi_{N-1},\varphi_N) \quad (1)$$

and the configurational partition function is then given by

$$Z_{N+1} = \int_0^{2\pi}\int_0^{2\pi}...\int_0^{2\pi} w(\varphi_2,\varphi_3)w(\varphi_3,\varphi_4)...w(\varphi_{N-1},\varphi_N)\, d\varphi_2\, d\varphi_3\, ...\, d\varphi_N \quad (2)$$

where

$$w(\varphi_{i-1},\varphi_i) = \exp[-E(\varphi_{i-1},\varphi_i)/RT] \quad (3)$$

We may expand the periodic function $w(\varphi_{i-1},\varphi_i)$ into a double-Fourier series whose coefficients may be arranged in a matrix $\mathbf{U}_i$ of order $(2\bar{n}_{i-1} + 1) \times (2\bar{n}_i + 1)$, where $\bar{n}_{i-1}$ and $\bar{n}_i$ are the largest Fourier indices pertaining to the expansions along φ_{i-1} and φ_i, respectively;[2] in principle, $\mathbf{U}_i$ may therefore be rectangular but, for simplicity, we shall assume henceforth $\bar{n}_{i-1} = \bar{n}_i = \bar{n}$. The statistical weight function may then be written

$$w(\varphi_{i-1},\varphi_i) = \Phi_{i-1}\mathbf{U}_i\Phi_i^{\mathrm{T}} \quad (4)$$

where Φ_i is the row vector defined in eq 7 of ref 2 and Φ_i^{T} is its transpose. The multiple integration of eq 2 may be written as in eq 9 of ref 2

$$Z_{N+1} = (2\pi)^{N-3}\int_0^{2\pi}\Phi_2\, d\varphi_2\, [\prod_{i=3}^{N}\mathbf{U}_i]\int_0^{2\pi}\Phi_N^{\mathrm{T}}\, d\varphi_N \quad (5)$$

or

$$Z_{N+1} = (2\pi)^{N-1}\mathbf{J}\prod_{i=3}^{N}\mathbf{U}_i\mathbf{J}^{\mathrm{T}} \quad (6)$$

where $\mathbf{J}$ is a $(2n + 1)$-dimensioned row vector with the first element equal to 1, all others being equal to 0, and $\mathbf{J}^{\mathrm{T}}$ is its transpose. Comparing eq 6 with eq 24 of ref 1 shows their apparent formal equivalence. Equation 6 may be applied to chains of at least four bonds, while for three-bond systems it becomes

$$Z_3 = 2\pi a_2^{\,0} \quad (7)$$

where

$$a_2^{\,0} = \frac{1}{2\pi}\int_0^{2\pi} w(\varphi_2)\, d\varphi_2 \quad (8)$$

The calculation of the configurational average of any function $f(\varphi_i)$ involves the calculation of an integral of the type $\int_0^{2\pi}\Phi_i^{\mathrm{T}}f(\varphi_i)\Phi_i\, d\varphi_i$ (see eq 13 of ref 2) which defines a matrix Ψ_i (eq 14 of ref 2); this in turn has the form given

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in eq 17 and 18 of ref 2. The matrix $\mathbf{\Psi}_i$ defined in the ARS scheme is the equivalent of the diagonal $\mathbf{F}_i$ matrix defined in eq 1 (Chapter IV) of ref 1; in fact they both contain a representation of the function which must be averaged and occupy the same place in the matrix product which performs this average. In particular we are interested in the function defined by the rotation matrix $\mathbf{T}(\varphi_i)$ which transforms the components of any vector, expressed in the reference frame connected with the $(i + 1)$th bond, into those appropriate to the ith bond. In this case the $\mathbf{\Psi}_i$ matrix assumes the specific form defined in eq 23 of ref 2 and may be indicated with τ_i. With these definitions it is easy to prove that

$$\langle \mathbf{T}(\varphi_i) \rangle_{N+1} = Z_{N+1}^{-1}(2\pi)^{N-1}(\mathbf{J} \otimes \mathbf{E}_3) \times \left[\prod_{j=3}^{i}(\mathbf{J}_j \otimes \mathbf{E}_3)\right]\tau_i\left[\prod_{j=i+1}^{N}(\mathbf{U}_j \otimes \mathbf{E}_3)\right](\mathbf{J}^T \otimes \mathbf{E}_3) \quad (9)$$

A formal equivalence may be found again between eq 9 and 8 of ref 1 and we see that the matrix τ_i plays, in eq 9, the same role as $\|\mathbf{T}\|_i$ in eq 8 of ref 1. For sake of brevity we ignore intermediate manipulations and write an equation formally similar to eq 28 of ref 1

$$\langle M^2 \rangle_{N+1} = 2Z_{N+1}^{-1}(2\pi)^{N-1}\mathbf{A}\mathbf{G}_1\mathbf{G}_2...\mathbf{G}_{N+1}\mathbf{A}^* \quad (10)$$

where $\mathbf{A}$ is a row of $5(2n + 1)$ elements, only the first of them being 1, while the others are 0 and $\mathbf{A}^*$ is a column of $5(2n + 1)$ elements, where only the $(8n + 5)$th is 1 while the others are 0. $\mathbf{G}_i$ is a generator matrix formally similar to that defined in eq 24 of ref 1 but with $\|\mathbf{T}\|_i$ substituted by τ_i; $\mathbf{U}_1$, $\mathbf{U}_2$, and $\mathbf{U}_{N+1}$ are unit matrices and $\mathbf{G}_{N+1}$ has all elements 0 except those of the last pseudocolumn. Equation 10 may be used, as in the case of the RIS scheme, to describe chains of finite number $(N + 1)$ of bonds while the sequence of $\mathbf{G}_i$ matrices may be constructed in order to produce any given sequence of structural units, provided the corresponding $w(\varphi_{i-1},\varphi_i)$ function is known. Consequently copolymer chains with any composition may be treated.

In the case of a three-bond chain the average value of $\mathbf{T}(\varphi_2)$ is

$$\langle \mathbf{T}(\varphi_2) \rangle = (a_2{}^0)^{-1}(a_2{}^0\mathbf{T}_0 + \tfrac{1}{2}a_2{}^1\mathbf{T}_c + \tfrac{1}{2}b_2{}^1\mathbf{T}_s) \quad (11)$$

where $a_2{}^0$ is defined in eq 7, $a_2{}^1$ and $b_2{}^1$ are the coefficients of the cos φ_2 and sin φ_2 terms of the Fourier expansion of $w(\varphi_2)$, and $\mathbf{T}_0$, $\mathbf{T}_c$, and $\mathbf{T}_s$ are defined in eq 22 of ref 2.

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Glass Transition Temperature of Anionic Polyisoprene

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We are currently investigating the glass transition temperature (T_g) of ABA poly(styrene-*b*-isoprene) block copolymers (SIS) as a function of their molecular characteristics.[1] Generally, block copolymers exhibit two T_g's corresponding approximately to those of the parent homopolymers. When the T_g values of the block polymers differ from those of the homopolymers, this indicates a change in morphology due to an evolution in the miscibility of the two phases.

In order to establish these changes, it is useful for comparison purposes to know the relationship between T_g and the molecular weight of the parent homopolymers. Such a relationship was first established by Fox and Flory[2] as follows:

$$T_g = T_g{}^\infty - K\bar{M}_n{}^{-1}$$

in which $T_g{}^\infty$ is the glass transition temperature of a polymer with infinite molecular weight, $\bar{M}_n$ is the number-average molecular weight, and K is a constant characteristic of a given polymer. For polystyrene and some other polymers, the K values are well-known.[3]

However, the literature contains little information about the molecular weight–T_g relationship of polyisoprene (PI). Different microstructures exist for this polymer which also play a role in the T_g value. Wood[4] found T_g's varying from −74 to −69 °C, but the molecular weights of his samples were not given. Essel[5] noted an increase in T_g with the overall 3,4- and 1,2-configuration content for a PI ($\bar{M}_n$ = 160 000). Dannis[6] and Haas et al.[7] found a difference ΔT_g of about 15 °C between cis-1,4 and trans-1,4 isomers. Morgan et al.[8] confirmed Haas' findings with T_g values of −60 and −42 °C, respectively. Cowie[9] reported data on samples with different chain lengths: for *trans*-1,4-polyisoprenes, in the molecular weight range 17 000–110 000, a constant T_g of −66 °C was found.

In this note, we report T_g values for a series of PI with molecular weights ranging from 3000 to 75 000 and of known microstructure. These polymers were obtained by anionic synthesis in benzene at 50 °C, with *n*-butyllithium as the initiator. Mass distribution was examined by gel permeation chromatography (GPC, Waters chromatograph, Styragel columns, THF). Two different calibration curves were used: one was the universal calibration curve,[10] and the other was deduced from the polystyrene curve. Since in THF, the polystyrene and polyisoprene curves are parallel,[11] a fixed molecular ratio of 1.35 can be used for the two polymers. Concordance was satisfactory. Polydispersity ranges from 1.10 to 1.22. The number of isomeric units in polyisoprene was determined by ^{1}H NMR in benzene-d_6 solution (Cameca 250-MHz spectrometer). As olefinic proton signals at 5.25 and 4.82 ppm, due, respectively, to the 1,4 and 3,4 units,[12] do not overlap, their ratio could be determined directly from the spectrum. The cis-1,4 and trans-1,4 content was calculated by Assioma's method.[13] Glass transition temperatures were determined by using a Perkin-Elmer DSC-1 differential scanning spectrometer, calibrated with *n*-octane. T_g values were measured at several heating rates (v = 2, 4, 8, 16 and 32 °C/min). From a plot of T_g vs. $v^{1/2}$,[14] the extrapolated zero heating rate value was taken as being the value of T_g. Its accuracy was ±2 °C.

Table I and Figure 1 show the T_g values of PI with high 1,4 content (over 85%) and various molecular weights. As a first approximation, all T_g's fall within a −70.5 to −64.5 °C range. The difference between these limits is very small, about 6 °C, and not systematic. Thus, Flory's law does not apply to this particular molecular weight range. Our values confirm those found by Wood[4] and Cowie.[9]

Table II and Figure 2 give T_g's in terms of the microstructure of the polyisoprene samples. Some PI of known microstructure that are listed in Table I also appear in

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