Theoretical Investigation Including Computer Simulation of a Rigid Rod Polymer

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ABSTRACT: A theoretical approach has been applied to elucidate the molecular conformations, associated flexibility, and dynamics of poly(*p*-hydroxybenzoic acid) (pHB) esters. Properties such as the radius of gyration and persistence length which are characteristic of the stiffness of a macromolecule were calculated on the basis of two different theoretical methods: Molecular dynamics and the well-known rotational isomeric state model of Williams and Flory[1] augmented by the more recent scheme for the matrix computations.[2] The analysis of the results obtained by the latter method reflects a strong dependence on the choice of the structural parameters of the system. The purpose of this paper is to make a realistic estimate of the intrinsic stiffness of the backbone of pHB esters by use of molecular dynamics calculations.

Introduction

Aromatic polyesters belong to the class of stiff polymers and have highly extended polymer chains.[3,4] The physical reason for this statement is the preference of the ester groups for the planar trans configurations and the assumption of a considerable torsional potential barrier opposing rotations about the ester bonds. Variation of the torsional angle is widely ignored, e.g., the polymer is treated a priori as rigid and planar,[4] although it is known that those fluctuations affect the chain dimensions significantly.[5,16]

The goal in this paper is first to examine carefully the dependence of properties like the root-mean-squared radius of gyration $\langle r_g^2 \rangle^{1/2}$ and the persistence length on the choice of parameters used in the rotational isomeric state (RIS) model. Second we show that computer simulation of polymer chains by the molecular dynamics method[6] provides characteristic fluctuation values offering a basis for a consistent description in the framework of the RIS model. Molecular dynamics has been developed for the configuration space of disordered systems. It is widely used for studying the statistical thermodynamics of liquids and has been also applied to biological systems.[7,8] This is an acceptable way of treating a large number of coupled degrees of freedom and the dynamics of the system displays fluctuations and flexibility of the internal coordinates of a molecule. These results are also used in the abovementioned Flory formalism.

Theory

In molecular dynamics it is necessary to express the potential energy of the system in terms of an analytical function. An accepted approach is given by the representation of the energy V as a function of the internal degrees of freedom and interatomic distances as it is implemented in the AMBER code:[9]

$$V = \sum_{\mathrm{b}} f_{\mathrm{b}}(r_{\mathrm{b}} - r_{\mathrm{b\,eq}})^2 + \sum_{\mathrm{v}} f_{\mathrm{v}}(\delta_{\mathrm{v}} - \delta_{\mathrm{v\,eq}})^2 + \sum_{\mathrm{d}} f_{\mathrm{d}}(1 - \cos(n_{\mathrm{d}}\varphi_{\mathrm{d}} - \delta_{\mathrm{d}})) + \sum_{i,j} \frac{1}{4\pi\epsilon} \frac{q_i q_j}{r_{ij}} + \sum_{i,j} \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \quad (i < j) \quad (1)$$

This sum represents (in this order) the potentials given by stretching of bonds, bending of bond angles, torsion of bonds, and electrostatic interactions. The last term expresses van der Waals' interactions and polarizabilities. The potential and force field parameters in eq(1) (f_{b}, $r_{\mathrm{b\,eq}}$, f_{v}, $r_{\mathrm{v\,eq}}$, f_{d}, n_{d}, δ_{d}, q_i, A_{ij}, B_{ij}) are derived from microwave spectroscopy, neutron diffraction, and molecular mechanical calculations for the equilibrium bond lengths and angles. Torsional constants are derived from microwave and NMR studies and noncovalent bond parameters from crystal packing calculations. Standard parameters are given in the AMBER package and published in ref 10. The most significant of the parameters used are listed in Table I. The "united atom" force field was used to decrease the calculation time, i.e., the hydrogen atoms are implicitly considered in the parameters of the carbon atoms. The partial charges q_i were calculated by the MNDO method (see Table II).

Table I
Bending and Torsional Force-Field Parameters of Intramolecular Coordinates q

q^a	f_q
φ_1	90 kcal/(mol rad^2)
φ_2	80 kcal/(mol rad^2)
$\phi_4{}^b$	$V_q/2 = 10$ kcal/mol

[a] The mean-square values of q are shown in Table III. [b] ϕ_4, see ref 15 and 17.

Table II
Partial Charges[a] of the Atoms (Numbers According to Figure 1)

q_1	-0.401	q_6	0.173
q_2	0.251	q_7	-0.155
q_3	-0.053	q_8	0.545
q_4	0.173	q_9	-0.480
q_5	-0.053		

[a] The partial charges were scaled up by a factor of 1.3, an empirical value fitting the AMBER force field.

To obtain the trajectory $\vec{x}(t)$ describing the system under the influence of an external perturbation, Newton's equations

$$\vec{F}(t)/m = \frac{-\mathrm{grad}\ V}{m} = a(t) = \delta\vec{v}(t)/\delta t = \delta^2\vec{x}(t)/\delta t^2 \quad (2)$$

are integrated by applying the Verlet algorithm.[11] The initial conditions are defined by a set of initial coordinates and velocities which are related to a chosen temperature T on the basis of

$$\tfrac{3}{2}kT = \tfrac{1}{2}mv^2 \quad (3)$$

Finite difference steps, Δt, of 10^{-15} s were taken to get a reliable representation of the trajectory. The time-dependent expansion of the velocity and the coordinates is

Table III
Mean Bond Angle Values, Fluctuations, Radius of Gyration of a Chain of 30 Monomers, $\langle r_g \rangle$, Persistence Length, a, and Characteristic Ratio, c_∞, According to Method I

	$\langle \varphi_1 \rangle$	$\Delta\varphi_1$	$\langle \varphi_2 \rangle$	$\Delta\varphi_2$	$\langle \phi_4 \rangle$	$\Delta\phi_4$	$\langle r_g \rangle$, Å	a, Å	c_∞
a	110.9°	0°	118.3°	0°	0°	0°	53	706	223
b	111.8°	2.74°	120.0°	3.50°	0°	8.76°	50	256	82
c	112.74°	2.70°	121.1°	3.49°	−0.67°	15.09°	48	142	45
d	112.13°	4.34°	121.67°	9.91°	−1.01°	22.09°	42	65	20

[a] See ref 4. [b] Values directly calculated from the force-field parameters according to (11) and (12). [c] Time-averaged molecular dynamics geometries, ring is rigid. [d] Molecular dynamics geometries.

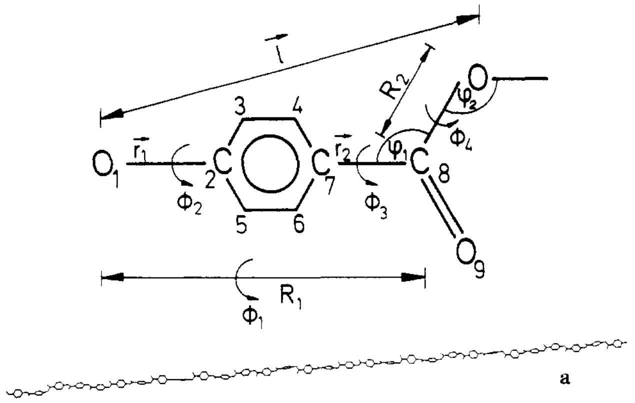

Figure 1. pHB monomer unit; $R_1 = 5.57$ Å, $R_2 = 1.36$ Å. The length of the virtual bond $\vec{l}$ is approximately 6.2 Å. The assignment of the internal parameters is in accord with method I. (a) Initial conformation of 30 pHB monomers.

done by the "leap frog" algorithm;[12] it performs a Taylor expansion of $\vec{v}(t + \mathrm{d}t/2)$ and $\vec{x}(t + \mathrm{d}t)$ to update the positions of the atoms and the associated conformational fluctuations. It assures a good numerical stability in the transfer to the differential equation (2) and it also offers the possibility to scale the velocities to keep a constant temperature T ("coupling to a thermal bath").[12] After a sufficiently long molecular dynamics run the system will be in equilibrium. Tracing the trajectory, one can extract the structural, statistical thermodynamic, and spectroscopic properties as time-averaged quantities. The dynamic properties such as structural fluctuations can be monitored directly by viewing the conformational motion.

For the calculation of the persistence length we chose three different methods. The first one (I) adopts the rotation matrix formalism which can be described in the following way. The rotational matrix for bonding R_1 (according to Figure 1)

$$\mathbf{T}_1 = \begin{bmatrix} \langle \cos \varphi_1 \rangle & \langle \sin \varphi_1 \rangle & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{4}$$

corresponds to a free rotation about R_1, this is plausible because the rotation ϕ_2 is symmetric about ±90° and the rotation ϕ_3 is symmetrical about 0° and 180°, which causes the rotation ϕ_1 about R_1 to be symmetric about ±90°. The deviations in the mean rotation and bond angles are taken into account by

$$\langle \cos \delta \rangle \approx \cos \langle \delta \rangle \left(1 - \frac{1}{2}\langle \Delta^2 \delta \rangle\right) \tag{5}$$

The rotation matrix for bonding R_2 is given by

$$\mathbf{T}_2 = \begin{bmatrix} \langle \cos \varphi_2 \rangle & \langle \sin \varphi_2 \rangle & 0 \\ \langle \sin \varphi_2 \rangle \langle \cos \phi_4 \rangle & -\langle \cos \varphi_2 \rangle \langle \cos \phi_4 \rangle & \langle \sin \phi_4 \rangle \\ \langle \sin \varphi_2 \rangle \langle \sin \phi_4 \rangle & -\langle \cos \varphi_2 \rangle \langle \sin \phi_4 \rangle & -\langle \cos \phi_4 \rangle \end{bmatrix} \tag{6}$$

In $\mathbf{T}_1$ and $\mathbf{T}_2$, φ_i exceptionally denotes the complement of the bond angle. All angle fluctuations are regarded to be independent. The entire rotation matrix is given by

$$\mathbf{T} = \mathbf{T}_1 \mathbf{T}_2 \tag{7}$$

The virtual bond vector is

$$\vec{l} = |\vec{l}| \begin{bmatrix} x \\ y \\ z \end{bmatrix} \tag{8}$$

where $|\vec{l}|$ is considered as the length of one monomer. The characteristic ratio is given by[13]

$$c_\infty = (x \quad y \quad z)((\mathbf{E} + \mathbf{T})(\mathbf{E} - \mathbf{T})^{-1}) \begin{bmatrix} x \\ y \\ z \end{bmatrix} \tag{9}$$

where $\mathbf{E}$ is the unit matrix of order 3. The persistence length is then calculated by[13]

$$a = |\vec{l}|(c_\infty + 1)/2 \tag{10}$$

In the first model we evaluated the fluctuations in the bond angles φ_1 and φ_2 within the classical harmonic approximation

$$\tfrac{1}{2} k_B T = \tfrac{1}{2} k_f (\Delta\varphi_i)^2 \tag{11}$$

In the calculation of φ_1 we took into account that a fluctuation of φ_1 also causes fluctuations of the complementary angles. The force constants related to k_f by $f_q = {}^1/_2 k_f$ are shown in Table I.

The mean-square deviation of the dihedral angle ϕ_4 was obtained by applying the potential energy equipartition principle, using the analytic expression of the force field:

$$\frac{1}{2} k_B T = \frac{V\phi_4}{2}(1 + \cos(2\phi_4 - 180°)) \tag{12}$$

Since (12) just gives the linear deviation of $\langle \phi_4 \rangle$ we evaluated the mean-square deviation by fitting the potential curve to a parabola. We obtained a factor of $\pi^{1/2}/2^{1/2}$ for the correction of $\Delta\phi_4$. These values are listed in Table III, row *b*.

The second method (II) to obtain the persistence length follows the theory of Porod and Kratky[14] for a wormlike chain on the basis of the molecular dynamics trajectory, $x(t)$. This model considers the polymer chain as a sequence of infinitesimally small segments. If α is the angle between two of those in sequence and L the contour length between the ith and the $(i + n)$th element of the chain, then

$$(\cos \alpha)^n = \exp(-L/a) \tag{13}$$

Assuming free rotation about the infinitesimal elements leads to

$$\cos \omega = (\cos \alpha)^n \tag{14}$$

where ω is the angle between element i and $(i + n)$. The persistence length is then given by

$$a = -L/\ln(\cos \omega) \tag{15}$$

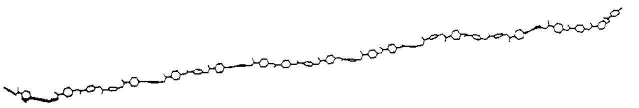

Figure 2. Snapshot of the molecular dynamics conformation of the pHB ester chain consisting of 30 monomers after 2.0 ps.

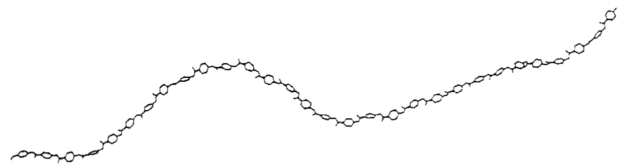

Figure 3. Snapshot of the molecular dyanamics conformation after 37.5 ps.

For each conformation the average is taken over the values calculated from every pair of monomers which is separated by least two monomer units. The outermost monomers are not taken into account, so the inner monomers are more strongly represented in the average. The contour length, L, in our calculation is the sum of n monomers of the length $|\vec{l}|$ (Figure 1) between the initial and end points of the included polymer segment.

The *third method* (III) requires an iteration procedure to obtain the persistence length from the expression of the mean-square end-to-end distance,[14]

$$\langle r^2 \rangle = 2a(L - a + a \exp(-L/a)) \quad (16)$$

The calculation of the fluctuations shown in Table II was always done within the approximations described in method I. The radius of gyration is given by

$$\langle s^2 \rangle_{0n}/nl^2 = (x \quad y \quad z)\left[\frac{n+2}{6(n+1)}(\mathbf{E}+\mathbf{T})(\mathbf{E}-\mathbf{T})^{-1} - \frac{1}{n+1}\mathbf{T}(\mathbf{E}-\mathbf{T})^{-2} + \frac{2}{(n+1)^2}\mathbf{T}^2(\mathbf{E}-\mathbf{T})^{-3} - \frac{2}{n(n+1)^2}\mathbf{T}^3(\mathbf{E}-\mathbf{T}^n)(\mathbf{E}-\mathbf{T})^{-4}\right]\begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (17)$$

Results and Discussion

We performed molecular dynamics calculations for chain molecules consisting of 20 and 30 monomers in vacuum at a constant temperature (300 K). The essential force field parameters we used are displayed in Table I. The coordinates of the systems topological data were stored every 0.05 ps and the dynamics were monitored over 110 ps. The initial structure is characterized by a sequence of trans-planar monomers, rotated about 68°, producing a "linear straight" chain (Figure 1a), derived from the classical procedure of energy minimization using the force field parameters of Table I. This structure is in good agreement with the theoretical MNDO conformational analysis done for phenyl benzoate[15] which predicts a rotational angle of 60°.

Perturbation of the system by adding kinetic energy until the scaled velocities correspond to room temperature causes the chain to bend. Figures 2–5 present snapshots of the internal structure at moments during the molecular dynamics run. The velocities are distributed randomly in the initial state, with the consequent motion of the atoms then determined by the action of the force field (1). Figures 2–5 also give an impression that the polymer chain does not stay highly extended, which will reduce the persistence length by a considerable amount. On a much shorter time scale, consecutive snapshots of conformations show wavelike propagation of displacements along the polymer chain. Analyzing the geometries created during the molecular dynamics run and taking the time average of the conformations the system went through, we obtain the mean values of the bond and dihedral angles given in Table III. The analysis starts when the system is in equilibrium, i.e., when the persistence length, which is very high in the beginning because of the stretched starting conformation, is no longer decreasing.

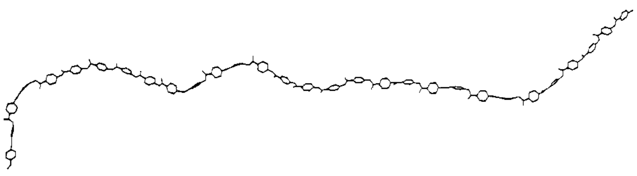

Figure 4. Snapshot of the molecular dynamics conformation after 45.5 ps.

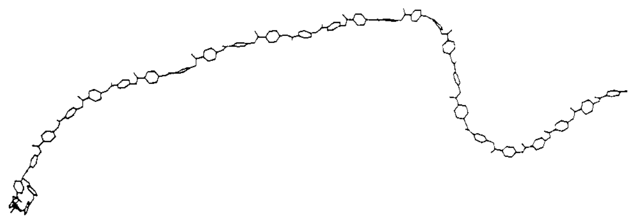

Figure 5. Snapshot of the molecular dynamics conformation after 84.5 ps.

We notice that the choice of the parameters φ_1, φ_2, and ϕ_4 and their fluctuations used in the RIS model effects the characterstic ratio c_∞ and the persistence length rather strongly. Starting out with the assumption that the molecule is totally rigid,[4] i.e., the fluctuations $\Delta\varphi_1$, $\Delta\varphi_2$, and $\Delta\phi_4$ are equal to zero, we obtain the persistence length a = 706 Å so that poly(p-hydroxybenzoic acid) (pHB) could be described as stiff. Taking the structural parameters of our force field and calculating the mean-square deviation from these values, within the harmonic approximation as described in method I, the persistence length decreases to 256 Å. The parameters displayed in rows c and d of Table III are obtained by averaging the trajectory of the molecular dynamics. Treating the ring as being rigid (Table IIIc), we get a persistence length of 142 Å. The most realistic result is obtained by regarding R_1 as a virtual bond (as depicted in Figure 1), representing the fluctuations of the ring by φ_1, φ_2, and ϕ_4. The resulting persistence length is 65 Å. The calculation of a according to formula 15 on the basis of the same 740 conformations as taken into account in rows c and d of Table III gives a persistence length of 64 Å. The result of 44 Å obtained by considering the end-to-end distance of each conformation (formula 16) is far too small as predicted by Birshtein.[5] The conclusion one can draw out of this is that methods I and II are in good agreement if one chooses the values put into the RIS model carefully with respect to the potential barriers and equilibrium geometries. The time-averaged internal coordinates of the molecular dynamics used with the RIS model give very reasonable results. The comparison with the result of method II, where the pure molecular dynamics data were used, proved that the averages of the internal coordinates and the persistence length are reliable. Our calculated persistence length agrees acceptably with a result recently published by Krigbaum and Tanaka[18] for a related structure: they found the persistence length of poly(phenylhydroquinone-*co*-terephthalic acid) in the range 60–150 Å. There is rather lively discussion in the literature about the experimental results for the persistence length for poly(p-benzamide) (p-BA) and poly(p-phenyleneterephthalamide) (p-PT) depending on the technique used for the measurement. The reported results[19] cover the range 325–1050 Å for *p*-BA and 113-650 Å for *p*-PT.

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Notes

Segmental Orientation in Networks Cross-Linked in Solution

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Introduction

Two of the most important new techniques for studying segmental orientation in strained polymers are fluorescence polarization[1-3] and nuclear magnetic resonance (NMR) spectroscopy.[4-7] Deuterium NMR in particular has now been used to investigate some important general issues regarding rubberlike elasticity, but reliable analysis of such results requires proper account of polymer reference volumes. An analysis of data of this type[7] is the subject of the present communication.

Specifically, deuterium NMR spectroscopy was recently used to study quadrupolar splitting, $\Delta\nu$, and the chain orientation function, S, in elongated poly(dimethylsiloxane) (PDMS) networks having either deuterated chain segments or swollen with a deuterated solvent.[7] Some networks had been prepared by end-linking PDMS chains in solutions with toluene, which was then removed prior to the elasticity measurements. Both $\Delta\nu$ and S were found to decrease substantially with a decrease in the volume fraction, v_{2C}, of polymer present during network formation. The decreases were attributed to decreased trapping of inter-chain entanglements due to the presence of diluent.[7] Apparently neglected in the analysis, however, was the fact that the reference volume, V_0, of the network (during cross-linking) was not the same as its volume, V, during the elasticity measurements. For example, $V < V_0$ means that the chains are "supercontracted"[8] at the beginning of the elasticity measurements. Qualitative consideration suggested that this difference could well account for the experimental observations, and the quantitative elasticity calculations described below were therefore undertaken.

Theory

The effects of the differences in volumes are more easily analyzed through the polymer volume fractions

$$v_{2C} = V_d/V_0 \tag{1}$$

$$v_2 = V_d/V \tag{2}$$

where V_d is the volume of the dry polymer network, V_0 is its reference volume, and V is the volume of the network during the elasticity measurements. The volume fraction v_{2C} thus characterizes the system during cross-linking, and v_2, in this case,[7] characterizes it during the elongation–NMR measurements.

The orientation function, S, for a phantom network, in which junction fluctuations are not constrained by chain interpenetrations,[3] is given by[1,2]

$$S = D[\Lambda_x^2 - (\Lambda_y^2 + \Lambda_z^2)/2] \tag{3}$$

where D is a configurational factor, and Λ_x^2, Λ_y^2, and Λ_z^2 are components of the microscopic deformation tensor. These three latter quantities are given by

$$\Lambda_t^2 = (1 - 2/\phi)\lambda_t^2 + (2/\phi) \qquad t = x, y, z \tag{4}$$

where ϕ is the junction functionality. The λ_t's are extension ratios relative to the unstretched network in its reference volume, V_0, and for elongation along the x axis can be written

$$\lambda_x = (v_{2C}/v_2)^{1/3}\alpha \tag{5}$$

$$\lambda_y = \lambda_z = (v_{2C}/v_2)^{1/3}\alpha^{-1/2} \tag{6}$$

where the elongation, α, is now relative to the unstretched network at its volume, V. Thus, for a phantom network,

$$S = (1 - 2/\phi)(v_{2C}/v_2)^{2/3}D(\alpha^2 - \alpha^{-1}) \tag{7}$$

The critical point is that the ratio v_{2C}/v_2 cannot be ignored when networks are studied at a degree of swelling significantly different from that at which they were prepared.

Since the phantom network model is generally appropriate only at very high elongations or very high degrees of swelling,[3] it is useful also to consider the more realistic

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