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Moments and Distribution of the End-to-End Vector for Short Poly(methylphenylsiloxane) Chains of Different Tacticities

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ABSTRACT: Moments of the end-to-end vector and the distribution function of the end-to-end distance have been obtained for short poly(methylphenylsiloxane) chains with different lengths and tacticities (intermediate between the purely syndiotactic and isotactic chains), using a slightly modified version of a previously established quasi-analytical scheme. Sharp changes in the conformational characteristics (values of the moments and the cyclization probability, shape of the distribution function, asymmetry, etc.) are observed as the isotactic chain limit is approached.

Introduction

Most interesting conformational characteristics of a flexible polymer are directly related to the distribution function of the end-to-end vector, $F(\mathbf{R})$, with $\mathbf{R}$ expressed in a reference frame embedded in the first bonds of the chain.[1] In fact, very useful information is provided by the simpler function $F(R)$, the distribution function of the end-to-end distance. Thus, from $F(R)$ one can obtain different averages of R that intervene in the calculation of equilibrium of hydrodynamic properties. Moreover, a detailed knowledge of $F(R)$ is required to describe non-Gaussian effects in networks at high elongations (strain–stress curves.[2–4] Equilibrium charge transfer and cyclization processes are also determined by $F(\mathbf{R})$ or $F(R)$.[5] For long chains, $F(\mathbf{R})$ is spherically symmetric and $F(R)$ is Gaussian. However, the evaluation of these functions for realistic models of short chains, as the rotational isomeric model (RIS), is a difficult task.

In recent years, calculations for $F(R)$ and $F(\mathbf{R})$ have been performed for different short polymer chains by two different methods: (a) direct Monte Carlo simulations on conformational samples;[4,6] (b) inference from statistical moments of R that have been previously obtained according to exact iterative procedures[7–9] (quasi-analytical, i.e., non-Monte Carlo methods). Though method (b) is not exact (its accuracy depends on the number of moments employed to infer the distribution function), the results obtained so far have been shown to be sufficiently accurate to avoid costly simulations. In this way we have been able to obtain results with this inference method for polymethylene,[8,9] poly(oxyethylene),[2,10] poly(dimethylsiloxane),[2,10] and poly(methylphenylsiloxane) (PMPS) chains.[10,11] The latter chains were studied considering molecules with regular stereochemical configurations; isotactic, i.e., ...*ddd*... or ...*lll*... sterochemical sequences, or syndiotactic, i.e., ...*dldldl*... sequences (*d* refers arbitrarily to a Si atom with a phenyl group in front the plane of the chain backbone and *l* corresponds to the phenyl group behind that plane).

However, the study of $F(\mathbf{R})$ for asymmetric chains with intermediate, nonregular stereochemical structures has not been yet performed because the computational effort required for such a study is considerably greater. Thus in these cases, the results should be averaged over samples of Monte Carlo generated chains with different stereochemical sequences but with the same replication probability, p_r (p_r is defined as the probability that a repeat unit being added to the growing chain will have the same configuration, *d* or *l*, as its predecessor).

In this paper we present results for PMPS chains with different values of p_r. Our goal is to show that even in these cases, in which a further Monte Carlo average is necessary, the inference method can be usefully applied. Moreover, we discuss some interesting features of the results concerning the very different conformational characteristics exhibited by PMPS chains with different stereochemical structures.

Methods

For a given stereochemical sequence, the calculation of different moments of $\mathbf{R}$ and its distribution function can be accomplished by means of the procedures explained in ref 10 and 11. However, we have performed some slight modifications in our scheme to evaluate moments from real and imaginary terms associated to each bond in the iterative equations. These modifications are introduced in order to avoid the use of redundant statistical weight matrices and are inspired in those previously employed by Flory et al.[1,12,13] within their scheme of Cartesian coordinate transformation matrices. (A scheme that is not efficient to obtain the high moments required for an adequate inference of $F(\mathbf{R})$.[6,9])

This way, matrices U_d, U_l, U_{ll}, U_{dl}, U_{ld}, and U_{dd}, defined in ref 11, that contain statistical weights associated to the different bond pairs are substituted by

$$U = QU_d = U_lQ$$
$$U_m = QU_{ll} = U_{dd}Q$$
$$U_r = U_{dl} = QU_{ld}Q$$

with

$$Q = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{1}$$

so that U_r and U_{dl} are identical, while U and U_m are obtained from matrices U_{dd} and U_{ll} by interchanging rows 2 and 3. U is now associated to bond pairs O–Si–O bracketing an Si atom of either *d* or *l* stereochemical configuration. U_m is employed for Si–O–Si bond pairs containing a meso (*dd* or *ll*) sequence of asymmetric Si atoms, while U_r is employed for Si–O–Si bond pairs containing a racemic (*dl* or *ld*) sterochemical sequence.

Using U, U_m, and U_r implies changes both in the direction of the bond-based coordinate systems and in the sign of rotational angles associated to the bond pairs. It can be shown that a left-side multiplication by matrix Q (i.e., an interchange of rows 2 and 3) on a weight matrix associated to the N bond rotation is equivalent to reverse the y_{N-1} axis direction (change a). On the other hand, a right-side multiplication by Q on such a matrix (interchange of columns 2 and 3) is equivalent to reverse the y_N axis direction. Also, in this case, the different φ_j^{N-1} rotational angles should reverse their signs (change b). The net effect of both types of changes is equivalent as can be

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Table I
Event Moments $\langle R^{2p} \rangle$ (Å^{2p}) for PMPS Chains of N Bonds and Three Different Values of p_r; T = 30 °C, δ_φ = 15°[a]

	p_r = 0.25		p_r = 0.50		p_r = 0.75	
p	N = 20	N = 40	N = 20	N = 40	N = 20	N = 40
1	3.00 ± 0.08 (02)	6.65 ± 0.07 (02)	2.71 ± 0.08 (02)	5.7 ± 0.1 (02)	2.44 ± 0.08 (02)	4.7 ± 0.1 (02)
2	1.04 ± 0.04 (05)	6.1 ± 0.1 (05)	9.0 ± 0.4 (04)	4.7 ± 0.2 (05)	7.5 ± 0.4 (04)	3.3 ± 0.1 (05)
3	4.1 ± 0.2 (07)	6.7 ± 0.2 (08)	3.3 ± 0.2 (07)	4.7 ± 0.3 (08)	2.6 ± 0.2 (07)	2.9 ± 0.2 (08)
4	1.7 ± 0.1 (10)	8.2 ± 0.3 (11)	1.3 ± 0.1 (10)	5.2 ± 0.4 (11)	9.9 ± 0.9 (09)	3.0 ± 0.2 (11)
5	7.3 ± 0.5 (12)	1.08 ± 0.04 (15)	5.5 ± 0.5 (12)	6.4 ± 0.5 (14)	4.0 ± 0.4 (12)	3.3 ± 0.2 (14)
6	3.3 ± 0.3 (15)	1.50 ± 0.06 (18)	2.4 ± 0.2 (15)	8.5 ± 0.8 (17)	1.7 ± 0.2 (15)	4.1 ± 0.3 (17)
7	1.5 ± 0.1 (18)	2.2 ± 0.1 (21)	1.1 ± 0.1 (18)	1.2 ± 0.1 (21)	7.2 ± 0.9 (17)	5.2 ± 0.5 (20)
8	7.4 ± 0.7 (20)	3.4 ± 0.2 (24)	5.0 ± 0.5 (20)	1.7 ± 0.2 (24)	3.2 ± 0.5 (20)	7.0 ± 0.6 (23)
9	3.6 ± 0.3 (23)	5.3 ± 0.3 (27)	2.4 ± 0.3 (23)	2.6 ± 0.3 (27)	1.5 ± 0.2 (23)	9.9 ± 0.9 (26)
10	1.8 ± 0.2 (26)	8.5 ± 0.5 (30)	1.2 ± 0.1 (26)	4.0 ± 0.5 (30)	7.1 ± 0.1 (25)	1.4 ± 0.2 (30)

[a] Power of ten that multiplies entries is in parentheses.

verified by performing such changes on the Cartesian coordinate transformation matrix from reference frame N to reference frame $N - 1$ with rotational angle φ_j^{N-1}

$$(\boldsymbol{T}_N)_j = \begin{pmatrix} \cos\theta_{N-1} & \sin\theta_{N-1} & 0 \\ \sin\theta_{N-1}\cos\theta_{N-1} & -\cos\theta_{N-1}\cos\varphi_j^{N-1} & \sin\varphi_j^{N-1} \\ \sin\theta_{N-1}\sin\theta_{N-1} & -\cos\theta_{N-1}\sin\varphi_j^{N-1} & -\cos\varphi_j^{N-1} \end{pmatrix} \quad (2)$$

Thus, change a or b means that the third column of $(\boldsymbol{T}_N)_j$ is multiplied by −1. If both changes are applied on $(\boldsymbol{T}_N)_j$, the matrix remains unaltered.[13] Consequently, introducing matrix $\boldsymbol{U}_r$ as $\boldsymbol{U}_{N-1}$ does not require any further modification of previous schemes, but in order to employ matrices $\boldsymbol{U}$ or $\boldsymbol{U}_m$ as $\boldsymbol{U}_{N-1}$ we have to reverse the y_N axis direction along with the sign of the rotational angles $\varphi_n{}^N{}_{-1}$ (choosing b between the two alternative possible changes). Reversing the y_N axis direction means a change in the sign of polar coordinate ϕ_N that defines $\mathbf{R}$ with respect to the local frame based in bond N. (In our iterative scheme $F(\mathbf{R})$ is defined in the reference frame of bond N, though the results are valid for a reference frame based on bond 1 for practical cases where the molecular parameters are introduced backward; see ref 11). Consequently, from the spherical harmonic expansion of $F(\mathbf{R})$[10]

$$F(\mathbf{R}) = \sum_l \sum_m 2\epsilon_m[F_{lm}{}^{(R)}Y_{lm}{}^{(R)}(\Theta_N,\Phi_N) - F_{lm}{}^{(I)}Y_{lm}{}^{(I)}(\Theta_N,\Phi_N)] \qquad \epsilon_m = 1 - (1/2)\delta_{m,0} \quad (3)$$

it can be shown that the coefficients $F_{lm}{}^I(R)$ must change their signs to obtain the correct results for $F(\mathbf{R})$. Moreover, this modification should be extended to the imaginary moments defined in ref 11 and also to the imaginary iterative elements associated to them.

All these changes can be summarized as follows: when we use matrices $\boldsymbol{U}$ and $\boldsymbol{U}_m$ we should reverse signs for the different $\varphi_j{}^{N-1}$ rotational angles and also for the $I_N{}^{(p)}[l,m,\varphi_j{}^{(N-1)}]$ elements included in our iterative scheme to obtain moments of chains with different number of bonds, N. Then, eq 32 and 33 of ref 11 should be substituted by

$$R_N{}^{(p)}[l,m,\varphi_j{}^{(N-1)}] = (-1)^m \sum_{q,l'} \binom{p}{q} b_N{}^{p-q}(z^{p-q})_m{}^{ll'} \times \sum_{m'} \exp[-1/2(m')^2\delta^2\varphi] P_{mm'}{}^{(l')}(\theta_{N-1}) \times \{\cos[m'\varphi_j{}^{(N-1)}][\boldsymbol{U}_{N-1}{}^T\mathbf{R}_{N-1}{}^{(q)}(l',m')]_j + (-1)^{t_N}\sin[m'\varphi_j{}^{(N-1)}][\boldsymbol{U}_{N-1}{}^T\mathbf{I}_{N-1}{}^{(q)}(l',m')]_j\} \quad (4)$$

and

$$I_N{}^{(p)}[l,m,\varphi_j{}^{(N-1)}] = (-1)^m \sum_{q,l'} \binom{p}{q} b_N{}^{p-q}(z^{p-q})_m{}^{ll'} \times \sum_{m'} \exp[-1/2(m')^2\delta^2\varphi] Q_{mm'}{}^{(l')}(\theta_{N-1})\{(-1)^{t_N} \times \cos[m'\varphi_j{}^{(N-1)}][\boldsymbol{U}_{N-1}{}^{\mathrm{T}}\mathbf{I}_{N-1}{}^{(q)}(l',m')]_j - \sin[m'\varphi_j{}^{(N-1)}][\boldsymbol{U}_{N-1}{}^{\mathrm{T}}\mathbf{R}_{N-1}{}^{(q)}(l',m')]_j\} \quad (5)$$

where the different symbols are defined in ref 11, except the factor t_N (whose introduction represents the only modification of the previous formulas). $t_N = 0$ should be used when N is associated to a Si–O–Si bond pair containing a racemic diad while $t_N = 1$ should be employed otherwise.

The choice of diads in the Monte Carlo generation of a chain with given stereochemical sequence is performed according to the previous definition of the replication probability. Whenever a new Si atom is introduced a random number between 0 and 1 is chosen. If this number is smaller than p_r the new asymmetric center is assigned to be of the same stereochemical character than its predecessor and the diad is taken as meso. However, when the random number is greater than p_r the new unit is taken as of different stereochemical character that the previous one (racemic diad). A standard procedure in these Monte Carlo samplings consists in rejecting a given sequence (once the definition of its stereochemical sequence is completed) if the fraction of meso diads differs by more than 5% from p_r.[14] However, we have verified that the average results obtained this way are practically identical with those calculated with the whole sample of generated sequences. Therefore, we have not made use of the rejection criterion. Once the definition of diads is completed the assignment of $\boldsymbol{U}_{N-1}$ and t_N can be performed for the different bonds according to the rules established in the preceding paragraphs.

Results and Discussion

Equations 4 and 5 together with the expressions given in ref 10 and 11 allow us to obtain the different moments as specified in those references. We employ the set of molecular parameters of the RIS model proposed for PMPS by Mark and Ko,[14] which we also used previously.[10,11] We have verified for several individual chains that our results for these moments are identical with those obtained employing weight matrices $\boldsymbol{U}_d$, $\boldsymbol{U}_l$, $\boldsymbol{U}_{dd}$, $\boldsymbol{U}_{ll}$, $\boldsymbol{U}_{ld}$, and $\boldsymbol{U}_{dl}$ and the older formulas[11] for $R_N{}^{(p)}$ and $I_N{}^{(p)}$. Then the validity of our modified scheme described above is confirmed. A summary of even moments obtained as averages over samples of 12 Monte Carlo generated stereochemical sequences is given in Table I. Values of the characteristic ratio obtained from the long-chain limit of our results for $\langle R^2 \rangle$ have been compared with those obtained previously by Mark and Ko[14] through the conventional scheme of Cartesian coordinate transformation matrices. Bot sets of results are coincident for the whole range of value of p_r. It can be observed that the values of $\langle R^{2p} \rangle$ are smaller as p_r increases. This can be explained as a consequence of the predominant weight that corresponds to an "all-trans" closed conformation for isotactic sequences.[11]

Table II
Different Averages of Components of ⟨R⟩ (Å) and ⟨RR^T⟩ (Å^2) for PMPS Chains with Different Values of N and p_r; δ_φ = 15°

	$p_r = 0$		$p_r = 0.25$		$p_r = 0.50$		$p_r = 0.75$		$p_r = 1$	
	$N = 20$	$N = 40$	$N = 20$	$N = 40$	$N = 20$	$N = 40$	$N = 20$	$N = 40$	$N = 20$	$N = 40$
$\langle x \rangle$	1.7707	1.8036	1.0 ± 0.3	1.4 ± 0.2	−0.1 ± 0.4	0.9 ± 0.3	−0.8 ± 0.4	−0.3 ± 0.3	−0.6697	−0.5291
$\langle y \rangle$	1.1926	1.2457	0.7 ± 0.1	1.0 ± 0.1	0.4 ± 0.1	0.6 ± 0.1	0.3 ± 0.1	0.19 ± 0.03	−0.0537	−0.0570
$\langle z \rangle$	7.9427	8.1037	6.4 ± 0.4	7.0 ± 0.2	4.6 ± 0.5	5.8 ± 0.6	3.4 ± 0.5	4.0 ± 0.4	2.4655	2.8672
$\langle x^2 \rangle$	98.901	246.09	91 ± 1	218 ± 5	87 ± 2	180 ± 5	80 ± 2	159 ± 6	52.721	99.112
$\langle y^2 \rangle$	93.503	240.35	90.7 ± 0.1	214 ± 4	89.0 ± 0.8	180 ± 4	81 ± 1	162 ± 5	53.576	100.09
$\langle z^2 \rangle$	139.79	287.82	115 ± 6	249 ± 7	95 ± 6	203 ± 8	81 ± 6	166 ± 8	54.610	101.97
$\langle xy \rangle$	3.8449	3.9875	1.5 ± 0.6	2.3 ± 0.4	0.0 ± 0.3	0.8 ± 0.4	−0.8 ± 0.2	−0.4 ± 0.1	0.0572	0.0193
$\langle xz \rangle$	−4.5586	5.0514	−12 ± 3	−6 ± 2	−17 ± 3	−7 ± 2	−16 ± 2	−15 ± 2	−7.6125	−8.8725
$\langle yz \rangle$	6.4808	6.8304	4.4 ± 0.7	5.1 ± 0.7	3.0 ± 0.8	3.6 ± 0.7	2.4 ± 0.7	1.3 ± 0.2	−0.3598	−0.3760

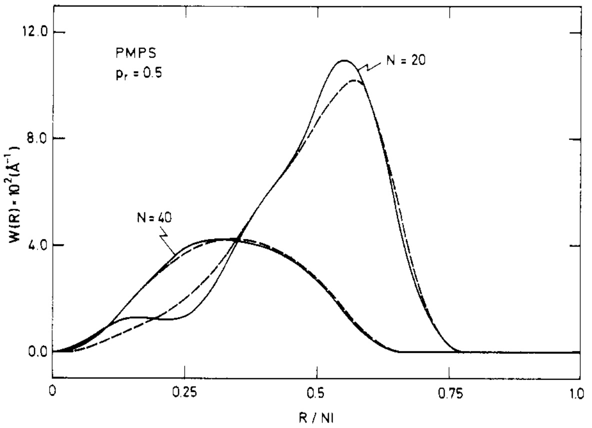

Figure 1. Radial distribution of R for PMPS chains of 20 and 40 bonds; p_r = 0.5, T = 30 °C. (Solid lines, $\delta\varphi$ = 0°; broken lines, $\delta\varphi$ = 15°.)

The results shown in Table I have been calculated by using a rotational angle fluctuation[8,11] characterized by its root-mean square value, $\delta\varphi$ = 15°. The values are greater than those obtained without fluctuations ($\delta\varphi$ = 0°). Differences are especially significant (40% for p = 10) for the highest values of p_r. Of course, fluctuations in the rotational angles tend to open the "all-trans" structure. Other effects concerning this all-trans prominence in chains close to the isotactic limit will be discussed later.

The inference of $F(R)$ and $F(\mathbf{R})$ is performed from our values for the stereochemically averaged moments according to previously described methods.[7,9,10] We employ a number M = 10 of even moments to infer $F(R)$, as we did in previous calculations for other types of chains.[2,8-11] This number has been selected as sufficiently high to obtain a good convergence of the inference method, according to our previous experience. (In fact we have obtained for this case values of $F(R)$ with M = 9, and they do not differ significantly from the M = 10 results.) In Figures 1 and 2 we present the radial distribution function $W(R) = 4\pi R^2 F(R)$ of chains with different values of p_r and N versus R/Nl (l is the Si-O bond length value). It should be remarked that the computational time required to obtain these results is about 20% of that needed in a direct evaluation of the distribution function from Monte Carlo generated conformations (also with randomly chosen stereochemical sequences). In Figure 2 we have included the results corresponding to purely syndiotactic and isotactic chains.[11] The transition from unimodal to bimodal distribution as p_r increases is clearly shown. We have plotted the results obtained without fluctuating rotational angles for which this effect is explicitly observed (for $\delta\varphi$ = 15° only the p_r = 1 curve shows bimodal shape). Thus, the shape of the distribution functions changes dramatically as p_r approaches the limit p_r = 1, corresponding to an isotactic chain. The bimodal shape for N = 20, p_r = 1 is due to the predominant closed all-trans conformation, responsible of the peak at the smallest value of R. The effect is also visualized in Figure 3, where we have plotted values of the cyclization probability, $F(0)$, as a function of p_r; chains with p_r close to unity exhibit considerably higher values of $F(0)$, even when fluctuating rotational angles are introduced.

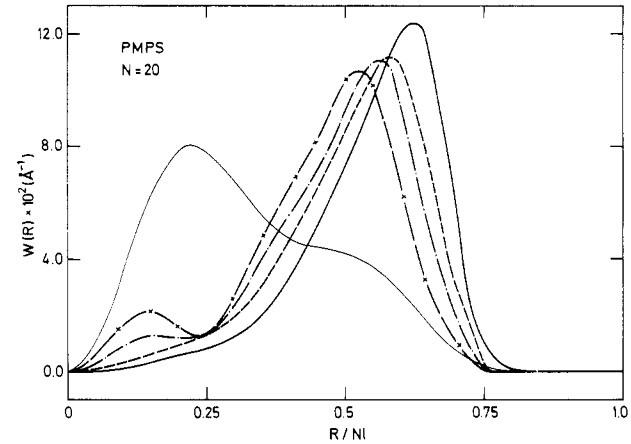

Figure 2. $W(R)$ for the N = 20 chain ($\delta\varphi$ = 0°): (—) p_r = 0; (- - -) p_r = 0.25; (-·-) p_r = 0.50; (-×-) p_r = 0.75; (—) p_r = 1.

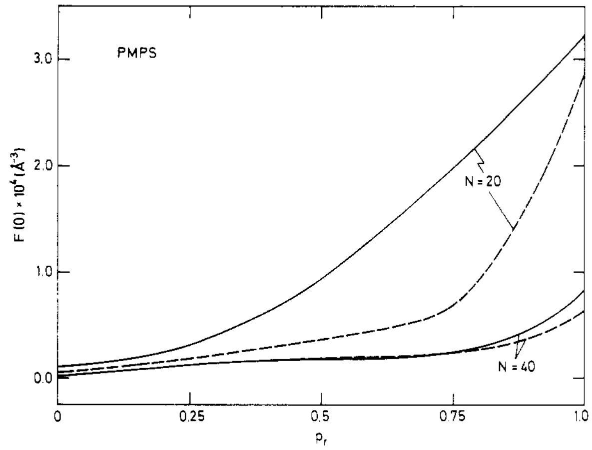

Figure 3. Variation of the cyclization probability with tacticity for chains of 20 and 40 bonds. (Solid lines, $\delta\varphi$ = 0°; broken lines, $\delta\varphi$ = 15°.)

Asymmetry of $F(\mathbf{R})$ with respect to a frame associated with the first bonds can be studied from averages of Cartesian coordinates of the persistence vector ⟨**R**⟩ and the tensor ⟨**RR**^{T}⟩. Our results for these averages (obtained with $\delta\varphi$ = 15°) are contained in Table II. Again, we can observe that the results for different values of p_r cover the gap between those corresponding to the syndiotactic and isotactic chains, the latter limit being reached in a more abrupt way. A noticeable oscillation of these averaged results with the number of bonds (Figure 4) can be at-

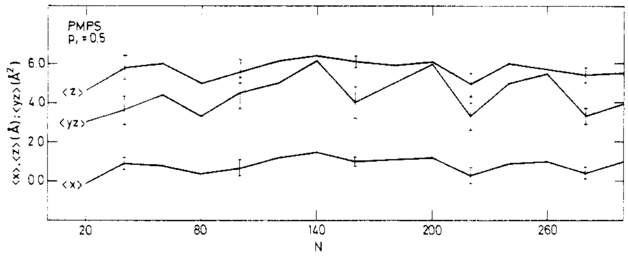

Figure 4. Variation of some components of $\langle \mathbf{R} \rangle$ and $\langle \mathbf{R}\mathbf{R}^T \rangle$ with N; $\delta\varphi = 15°$, $p_r = 0.5$. Illustrative errors bars are included.

tributed to the high influence of the stereochemical definition of the first diads on those asymmetry effects. This way, a Monte Carlo sample of stereochemical sequences which gives excellent reproduction of even moments $\langle R^{2p} \rangle$ may yield a less satisfactory description of spherically asymmetric averages. Though these oscillations are only slighly higher than the statistical errors associated to our averages, they are significant enough to preclude an asymptotically well-defined diagonalization of $\langle \mathbf{R}\mathbf{R}^T \rangle$ for the longest chains, diagonalization which was customarily used to define the three principal axes in other polymers.[6,9,10]

As a concluding remark, we can state that the quasi-analytical scheme to obtain moments and distribution functions of **R** established in previous work for simpler chains is also useful to obtain these quantities in the case of chains with nonregular stereochemical structures. Consequently, we have been able to perform such calculations for atactic PMPS chains with different replication probabilities. Though some subtle characteristics related with the asymmetry of **R** may require wider Monte Carlo samples of stereochemical sequences, most of the conformational properties of these chains can be successfully calculated with this numerically efficient scheme. A dramatic increase of the cyclization probability and non-Gaussian effects for chains close to the isotactic limit is the main prediction of our calculations. The lack of extensive experimental work on conformational properties of PMPS chains with well-known tacticity precludes, however, a direct comparison of these calculations with experimental data.

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Coil Dimensions of Poly(2-vinylnaphthalene) in Solution and Their Influence on Triplet Photophysics

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ABSTRACT: A quantitative determination of the coil dimensions of poly(2-vinylnaphthalene) (P2VN) in different solvents and solvent mixtures has been made by using disymmetry coefficients determined from measurements of Rayleigh light scattering. The polymers were prepared by using standard methods of anionic polymerization. Triplet luminescence spectra were recorded in these different solvents at 77 K and ambient temperatures. Pulse-probe methods were used to determine concentrations of transient triplets as a function of time following laser excitation. The specific rate constants for triplet–triplet annihilation were evaluated by assuming exclusively intramolecular processes and were found to increase regularly with decreasing coil radius. Ratios of the intensities of delayed fluorescence to phosphorescence in these solvents were also consistent with the conclusion that triplet–triplet annihilation increases in rate as the effective coil volume decreases. It is concluded that triplet exciton migration does not occur exclusively along the chain contour and that nonneighbor processes make a significant contribution.

Introduction

The focal point of this particular study is upon average interchromophore separation distances in poly(2-vinylnaphthalene) in good and poor solvents and the effect which a variation in these distances might have upon the photophysics of triplet states of the naphthalene chromophore produced by laser photoexcitation. It is well-known that an important component of the triplet state photophysics of vinyl aromatic polymers is that of energy migration, often described as random exciton hopping.[1] It seems important to sharpen the image of this process and try to learn whether or not the steric constraints imposed by the presence of the aromatic chromophore on every third backbone carbon atom moderate, in any way, the randomness of the migratory process.

The basic question that the study is intended to address is whether the migration process most closely resembles a one-dimensional neighbor-to-neighbor process or a three-dimensional randomly oriented process. These, of course, are the extremes of behavior which are to be expected. In any real system one must be prepared to deal with intermediate cases. To approach this question a decision was made to test the effect of altering average interchromophore separation distances in isolated polymer molecules by the use of good and poor solvents for P2VN. To a first approximation, one expects the average neighbor-neighbor distance to be unaffected by a variation in average coil radius. That is, these distances would be

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