When a THF–polymer mixture is diluted by a poorly solvating agent, say carbon tetrachloride, the immediate surroundings of the oxonium ion remain virtually unaltered, or only slightly modified. Therefore, for the same fraction $\alpha' = \alpha$ of monomer not converted to polymer, the rate of polymerization is approximately the same after dilution as it was in bulk polymerization, i.e.

$$-\mathrm{d}[\mathrm{THF}]_t/\mathrm{d}t = k_\mathrm{u}(\alpha' - \alpha_\mathrm{e}')I_0$$

where α' and α_e' are the ratios $[\mathrm{THF}]_t/[\mathrm{THF}]_0$ and $[\mathrm{THF}]_\mathrm{e}/[\mathrm{THF}]_0$, respectively, and $[\mathrm{THF}]_0$ is the initial concentration of THF after dilution.

The kinetic data are always reported in terms of calculated *bimolecular* rate constant, k_p, of propagation, i.e.

$$-\mathrm{d}[\mathrm{THF}]_t/\mathrm{d}t = k_\mathrm{p}(\alpha' - \alpha_\mathrm{e}')[\mathrm{THF}]_0 I_0$$

and, hence, $k_\mathrm{u} = k_\mathrm{p}[\mathrm{THF}]_0$ or $k_\mathrm{p} = k_\mathrm{u}/[\mathrm{THF}]_0$. Since k_u is independent of the initial monomer concentration, the treatment outlined here, and not the variation of bulk dielectric constant of the medium, accounts for the findings of Penczek's group, i.e., for increasing k_p on dilution of the polymerizing medium by an oxonium ion nonsolvating diluent. Indeed, the bulk dielectric constant of the medium should be of little significance in determining the propagation constant of polymerization performed under these conditions.

Acknowledgment. The financial support of the National Science Foundation is gratefully acknowledged.

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(12) The probability of finding THF around the oxonium ion is proportional to α and to the preferential solvating power of THF, β, as compared with the solvating power of a monomeric segment of poly-THF, $(1 - \beta)$. Thus the fraction of THF molecules in the solvating shell is given by $\alpha\beta/\{\alpha\beta + (1 - \alpha)(1 - \beta)\}$. This expression is reduced to α for $\beta = {}^1/_2$ and to 1 for $(1 - \beta) = 0$. The first-order relation $-\mathrm{d}[\mathrm{THF}]_t/dt \sim [\mathrm{THF}]_t - [\mathrm{THF}]_\mathrm{e}$ requires $\beta \approx {}^1/_2$. For $\beta \approx 1$, i.e., when the solvating power of THF greatly exceeds that of a monomeric segment of poly-THF, the propagation should be governed by zero-order kinetics.

Configurational Properties of Flexible Polymer Chains

ROBERT COOK* and MARY MOON

Department of Chemistry, Lafayette College,
Easton, Pennsylvania 18042. *Received June 9, 1978*

The theoretical study of simple polymer chain configurations by restricting each internal rotational angle to a finite number of possible values (e.g., either a trans, gauche plus, or gauche minus configuration[1]) is useful because it facilitates the rapid calculation of many chain properties. The details of this approach have been well developed by Flory.[2] Little attention has been given to the effect of this restriction on the results obtained, largely because of the difficulty of incorporating a continuous internal rotational angle potential into a tractable theory and also due to the apparent success of the Flory formalism. However, rotational angle flexibility, and the resulting enhanced flexibility of the chain, may be important features to include in the study of certain problems. Dielectric relaxation studies on macromolecules are frequently aimed at a study of the relaxation motions of short segments of chains. In order to explain the relaxation modes for certain polymers, internal rotations must be theorized, which in the strict three-state model require passage over energy barriers.[3] If some play in the internal rotational angles is allowed, then there will be a contribution to the dynamic properties which does not require passage over a barrier, and so the apparent barrier deduced from an Arrhenius plot would be lower than the real one. In another area the rate of intrachain fluorescence quenching for reasonably small chains (10–20 bonds) with fluorescent and quenching moieties on opposite ends[4] can be modeled by looking for those configurations which bring the ends of the chain within a certain distance. Preliminary studies of this problem strongly suggest that internal rotational angle flexibility may be essential to a successful theory, since it allows for quenching in situations where the three-state configuration would not.[5]

These problems and others suggest that a careful study of the effect of internal rotational angle flexibility would be valuable. In this note, some preliminary results are presented which indicate that, even for short chains, the distribution of end-to-end distances for a *single* configuration is considerable when small deviations are allowed in the internal rotational angles. A configuration c of a model n-bond polymethylene chain is defined by selecting the $n - 2$ internal rotational angles $\{\phi_i\}_\mathrm{c}$ to be either trans, gauche plus, or gauche minus. The end-to-end distance, r_c, is then calculated using unit bond lengths and 112° bond angles. In order to model a flexible chain, the internal rotational angles are modified by adding a deviation to each. The deviations are picked by a Monte Carlo method such that the probability of a given deviation is given by

$$P(\Delta\phi_i) = \frac{1}{a(2\pi)^{1/2}} \exp(-{}^1\!/_2(\Delta\phi_i)^2/a^2) \qquad (1)$$

where $\Delta\phi_i$ is the deviation (both positive and negative values are possible) to be added to ϕ_i, and a is the root mean square deviation, which is picked to determine the degree of flexibility. Values of a in the range of 10 to 20° correspond to what one would infer from the bond rotational energy function. This gives a new set, $\{\phi_i^\mathrm{f}\}_\mathrm{c}$, of rotational angles, and also a new end-to-end distance r_c^f. The process is repeated many times (25 000 for the data presented here) to give a set of flexible chain end-to-end distances which describe a distribution function $F(r_\mathrm{c}^\mathrm{f})$. In reporting the preliminary results of this study focus will be placed on the breadth of the distribution $F(r_\mathrm{c}^\mathrm{f})$ as a function of (1) the rigid three-state end-to-end distance and (2) the root mean square deviation parameter a.

In Figure 1 the $F(r_\mathrm{c}^\mathrm{f})$ for three ten-bond configurations with different rigid end-to-end distances are plotted. In each case the root mean square deviation, a, is taken as 10°. These particular configurations were chosen as being

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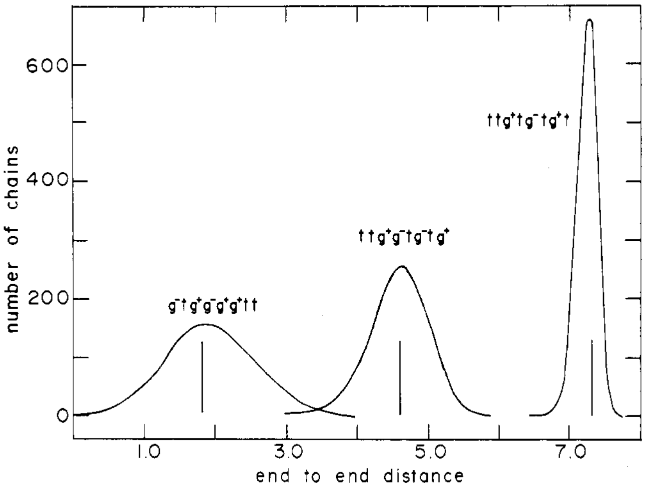

Figure 1. The distribution function $F(r_c^f)$ as a function of the end-to-end distance r_c^f for three configurations. The smoothed curves represent 25 000 chains, each with internal rotational angle root mean square deviation parameter a equal to 10°.

representative of chains of their respective lengths.[6] The most significant feature of this plot is that the distributions become broader as the rigid end-to-end distance (indicated by the single spike near the center of each curve) decreases. This feature can be easily understood by considering the possible "motions" allowed by the rotational angle flexibility. In the extended chains, the flexibility will result primarily in displacements of the end-to-end vector which are at angles nearly perpendicular to the rigid configuration end-to-end vector. For chains already bent back upon themselves the relative end-to-end motion can take any direction. Another feature noticeable is the skewing toward the center for compacted and elongated chains due to the fact that flexibility clearly will tend to shorten an extended chain and lengthen a compacted one. It might be suspected that the fraction of bonds with a trans conformation could be related to the breadth of the distribution. This is true only to the extent that the fraction of trans bonds affects the end-to-end length. Ten bond configurations of nearly the same end-to-end distance, but with differing numbers of trans bonds, were investigated. It was found that there was no significant variation in the breadth of the distribution from one configuration to another.

Since the individual fluctuations were picked with a Gaussian distribution, one might expect $F(r_c^f)$ to be Gaussian also. Allowing for the skewing described above, the Gaussian shape of the curves is confirmed. Assuming a functional form of the type $A\exp(-{}^1/_2\Delta^2/b^2)$ where Δ is the deviation from the center of the Gaussian curve, the parameter b can be determined as $0.849\Delta_{1/2}$ where $\Delta_{1/2}$ is the half-width of the curve at half-height. The results for studies on the ttg$^+$g$^-$tg$^-$tg$^+$ configuration using a root mean square deviation parameter of 5, 10, 15, and 20° for the ten-bond chain are plotted in Figure 2. Note the expected broadening for larger values of a. The curve fitting parameters b for these curves as well as for the other two configurations displayed in Figure 1 are also listed in Table I. There is a rough linear relationship between a, the flexibility index for individual bonds, and b, the index which measures the average flexibility in the end-to-end distance of a chain.

Given the Gaussian nature of the distributions, some conclusions can be drawn concerning the relationship of the breadth of the distribution $F(r_c^f)$ to the number of bonds. The complicating factor is that the distribution is also sensitive to the rigid end-to-end distance. To the extent that this dependence can be eliminated, one would expect for two chains of n_1 and n_2 rotational angles that $b_1 = (n_1/n_2)^{1/2}b_2$ at least in the limit of long chains.[7] This was confirmed by studying two configurations, one with 8 and the other with 16 gauche plus rotational angles. For samples of 25 000 chains each, b_{16} was found to be 1.4 times greater than b_8.

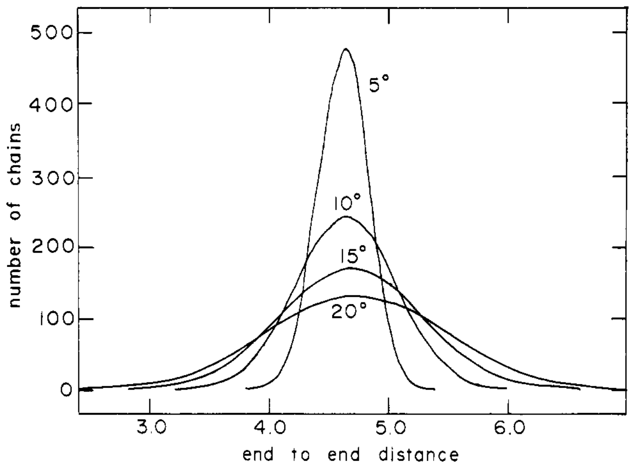

Figure 2. The distribution function $F(r_c^f)$ as a function of the end-to-end distance r_c^f for the conformation ttg$^+$g$^-$tg$^-$tg$^+$ with internal rotation angle runs deviation parameter a equal to 5, 10, 15 and 20°. The smoothed curves represent 25 000 chains each.

Table I
Values of b, the Total Chain Flexibility Fitting Parameter, for Four Values of a, the Root Mean Square Deviation of Individual Internal Rotational Angles[a]

configuration	r_c	5°	10°	15°	20°
g$^-$tg$^+$g$^+$g$^-$g$^+$tt	1.844	33.9	64.7	92.0	111.9
ttg$^+$g$^-$tg$^-$tg$^+$	4.621	20.9	41.4	59.2	76.0
ttg$^+$tg$^-$tg$^+$t	7.298	7.0	14.3	22.1	30.1

[a] Three different configurations with differing rigid end-to-end lengths r_c are displayed.

Thus our data demonstrate that chain flexibility gives rise to a relatively broad distribution of end-to-end distances for a single three-state configuration. Current work is focusing on the calculation of average chain parameters for flexible chains as a function of the number of bonds and the differences between these and the equivalent values calculated for the three-state model.

Acknowledgment. A part of this work was done at Dartmouth College and was supported by the National Science Foundation under Grant DMR-76-22985 in the Polymers Program, Division of Materials Research. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

We also wish to acknowledge several useful discussions with Dr. W. H. Stockmayer.

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described here were a strong function only of the rigid end-to-end distance.

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Scattering Functions for Gaussian Molecules. 2. Intermolecular Correlations

B. E. EICHINGER

Department of Chemistry, University of Washington, Seattle, Washington 98195. *Received May 12, 1978*

It is well known that radiation scattered from dense systems is dependent upon the radial distribution function for molecular centers.[1-4] If the system consists of Gaussian molecules the molecular structure factor makes an important contribution to the apparent intermolecular scattering function. The approach taken in the previous paper[5] is elaborated here, so as to include the effects of intermolecular interference; the calculation is based upon Gaussian statistics, but is otherwise general in respect to intermolecular correlations.

The pair correlation function, $p(\mathbf{r})$, for an array of m Gaussian molecules centered at $\sigma_1, \sigma_2, ..., \sigma_m$ may be written

$$p(\mathbf{r}) = [2/N(N-1)]Z^{-1}\sum_{i<j}\int \delta(\mathbf{r} - \mathbf{r}_i + \mathbf{r}_j) \times \exp[-\gamma \operatorname{Tr}(\mathbf{XKX}')] \prod_{j=1}^{m} \delta(\mathbf{X}J_l' - \sigma_l)\, \mathrm{d}\mathbf{X} \quad (1)$$

where $N = mn$, with n being the average number of beads in a molecule, and Z is the configuration integral or normalization constant. Here $\mathbf{X}$ is a $3 \times N$ dimensional matrix of coordinates, $\mathbf{K}$ is the Kirchhoff matrix for the molecular graph, which is the direct sum of m Kirchhoff matrices, each of dimension $n_l \times n_l$, and $J_l = (0, 0, ..., 1/n_l, 1/n_l, ..., 1/n_l, 0, ..., 0)$. The transpose of J_l is denoted by J_l'; the nonzero elements of this matrix are located at the n_l positions corresponding to the labels on the lth molecule. The product of δ functions fixes the centers of mass of the molecules at the respective σ_l. The parameter $\gamma = 3/2\langle l^2\rangle$, which implies use of the uniform expansion approximation $\langle l^2\rangle = \alpha^2\langle l^2\rangle_o$ away from the Θ temperature, or if you prefer the treatment is restricted to unperturbed molecules (this approximation is analogous to Albrecht's smoothed density models[2]).

The vector difference $\mathbf{r}_i - \mathbf{r}_j$ may be expressed as $\mathbf{X}c_{ij}'$, where $c_{ij} = (0, 0, ..., 0, 1, 0, ..., 0, -1, 0, ..., 0)$, with the +1 and −1 occurring at locations i and j, respectively. Use of the Fourier integral representation of the first δ function together with a normal coordinate analysis gives

$$p(\mathbf{r}) = [2/N(N-1)8\pi^3 Z]\sum_{i<j}\int \exp(i\mathbf{k}'\mathbf{r}) \times \exp[-\gamma \operatorname{Tr}(\mathbf{Q\Lambda Q}' + i\gamma^{-1}\mathbf{QT}'c_{ij}'\mathbf{k}')] \times \prod_{l=1}^{m} \delta(n_l^{-1/2}\mathbf{q}_l^{\circ} - \sigma_l)\, \mathrm{d}\mathbf{Q}\, \mathrm{d}\mathbf{k} \quad (2)$$

where $\mathbf{\Lambda}$ is the diagonal matrix of eigenvalues of $\mathbf{K}$, including the m zero eigenvalues, $\mathbf{k}' = (k_x, k_y, k_z)$ so that $\mathbf{k}'\mathbf{r} = \operatorname{Tr}(\mathbf{k}'\mathbf{r}) = \operatorname{Tr}(\mathbf{rk}')$, and the $\mathbf{q}_l^{\circ}$ are the center of mass coordinates of the normal coordinates $\mathbf{Q}$. Note that $\mathbf{T}'$, the matrix which diagonalizes $\mathbf{K}$ by a similarity transformation, is a direct sum of m matrices. The first row of each of those matrices is a constant vector $n_l^{-1/2}(1, 1, ..., 1)$. *Hence, upon performing the integrals over the* $\mathbf{q}_l^{\circ}$, the center of mass components of $\mathbf{QT}'$ are simply replaced by the appropriate σ_l, and $\mathbf{QT}'$ can be written as $\sigma + \mathbf{Q}_o\mathbf{T}_o'$, where

$$\sigma = (\sigma_1, \sigma_1, ..., \sigma_1, \sigma_2, ..., \sigma_2, ..., \sigma_m) \quad (3)$$

is a $3 \times N$ matrix, $\mathbf{Q}_o$ is a $3 \times (N-m)$ matrix obtained from $\mathbf{Q}$ by deletion of the $\mathbf{q}_l^{\circ}$, and $\mathbf{T}_o'$ is an $(N-m) \times N$ dimensional matrix obtained from $\mathbf{T}'$ by deletion of the $\mathbf{m}$ rows, one for each submatrix, that belong to the center of mass coordinates. Deletion of the zero eigenvalues from $\mathbf{\Lambda}$ yields the $(N-m) \times (N-m)$ matrix Λ_o.

The integrals over the $\mathbf{Q}_o$ may now be performed to give

$$p(\mathbf{r}) = [2/N(N-1)]\sum_{i<j}(\gamma/\pi g_{ij})^{3/2} \times \exp[-(\gamma/g_{ij})(\mathbf{r}' - \sigma c_{ij}')(\mathbf{r} - c_{ij}\sigma')] \quad (4)$$

where

$$g_{ij} = c_{ij}\mathbf{T}_o\mathbf{\Lambda}_o^{-1}\mathbf{T}_o'c_{ij}' = c_{ij}\mathbf{K}^{(-1)}c_{ij}' \quad (5)$$

The generalized inverse of $\mathbf{K}$ is $\mathbf{K}^{(-1)}$. It is now appropriate *to elaborate the counting somewhat. Let $i(k)$ be the ith* node on the kth chain. It is easy to compute eq 5 to show that

$$\mathrm{g}_{\mathrm{i(k),j}(l)} = k^{-1}{}_{i(k),i(k)} + k^{-1}{}_{j(k),j(k)} - 2k^{-1}{}_{i(k),j(k)} \qquad \text{for } k = l \quad (6a)$$

$$g_{i(k),j(l)} = k^{-1}{}_{i(k),i(k)} + k^{-1}{}_{j(l),j(l)} \qquad \text{for } k \neq l \quad (6b)$$

and from the definition of σ, one obtains

$$\sigma c'_{\mathrm{i(k),j(l)}} = 0 \qquad \text{for } k = l \quad (7a)$$

$$\sigma c'_{i(k),j(l)} = \sigma_k - \sigma_l \qquad \text{for } k \neq l \quad (7b)$$

The scattering function $P(\Theta)$ is defined as the Fourier transform of eq 4. A straightforward integration gives

$$P(\Theta) = [2/N(N-1)]\{\sum_{l=1}^{m}\sum_{i(l)<j(l)} \exp[-(g_{i(l),j(l)}/4\gamma)\mu^2] + \sum_{k<l}\sum_{i(k)}\sum_{j(l)} \exp[-(g_{i(k),j(l)}/4\gamma)\mu^2 + i(\sigma_k - \sigma_l)\cdot\mu]\} \quad (8)$$

where vector notation is now used. The sums are over all pairs of beads, with the elements of g_{ij} given by eq 6. The magnitude of the scattering vector is $\mu = (4\pi/\lambda) \sin \Theta/2$.

Equation 8 is general with respect to dispersity and connectivity, and therein lies its virtue. What has not been accounted for is the statistical mechanical average of $\Pi(\mathbf{X}J_l' - \sigma_l)$ in eq 1. The average of this quantity commutes with all the operations that have been carried out so long as the chain statistics are independent of intermolecular interactions.[2] In such a case, the sum over pairs of chains in eq 8 can be written in terms of a probability function, and that equation becomes

$$P(\Theta) = (n-1)/(mn-1)\langle P_1(\Theta)\rangle + n(m-1)/(mn-1)\langle F^2(\Theta)\rangle V^{-1}\int \rho(\mathbf{r})e^{i\mu\cdot\mathbf{r}}\, \mathrm{d}\mathbf{r} \quad (9)$$

where $\langle P_1(\Theta)\rangle$ is the average single chain scattering function,[5] and $\langle F^2(\Theta)\rangle$ is the average square of the molecular structure factor, one term of which is given by

$$F_k(\Theta) = n_k^{-1}\sum_{i(k)} \exp(-k^{-1}{}_{i(k),i(k)}\mu^2/4\gamma) \quad (10)$$

on account of eq 6. In eq 9, the spatial distribution function $\rho(\mathbf{r})$ is the fraction of pairs of molecules separated by the vector $\mathbf{r}$. This function need not be taken to be spherically symmetric, and will not be so for anisotropic media. If the molecules are anisotropic, the treatment of molecular statistics must be modified.[6,7] The integral is taken over the scattering volume V. It may be noted that $P(0) = 1$, since

$$V^{-1}\int \rho(\mathbf{r})\, \mathrm{d}\mathbf{r} = 1$$

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