Dependence of Unperturbed Dimensions and Dipole Moments of Polydialkylsiloxanes Upon Alkyl Group Length

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ABSTRACT: Unperturbed dimensions and dipole moments of polydialkylsiloxanes (alkyl = methyl, ethyl, *n*-propyl, isopropyl) have been investigated using rotational isomeric state theory. Polymers are treated as branched molecules in which each silicon atom constitutes a tetrafunctional branch point. All significant first- and second-order interactions are included in the configuration partition function. Higher order interactions not suppressed by second-order interactions are also evaluated and accounted for in the statistical weights used. Polydialkylsiloxanes can rigorously be treated by incorporating only two additional parameters (τ^* and f_2) into statistical weight matrices used previously for polydimethylsiloxane by Mark and Flory. These two parameters must be unity for polydimethylsiloxane but may differ from unity if side chains are articulated. Arbitrary variation of τ^* and f_2 produces characteristic ratios, $(\langle r^2\rangle_0/nl^2)_\infty$, ranging from 2 up to 40. A much more limited range is attained if τ^* and f_2 are confined to values suggested by estimates of first- and second-order interaction energies. An inevitable conclusion from such assignments is that the characteristic ratio for polydi-*n*-propylsiloxane cannot exceed that of polydiethylsiloxane. This prediction from rotational isomeric state theory is incompatible with experimental results reported by Lee and Emerson for polydi-*n*-propylsiloxane. Dipole moment measurements with polydi-*n*-propylsiloxane would be of assistance in resolution of this problem.

Configuration dependent properties for linear chain molecules in the unperturbed state are susceptible to rationalization via rotational isomeric state theory.[1,2] Articulated side chains introduce additional interactions which can be accomodated through formulations which utilize the direct product, or modifications thereof, and rectangular statistical weight matrices at branch points.[3,4] The requisite increase in complexity of matrix expressions may be great if all branches are large, as in the case of a "star"[4] or cross-linked polypeptide.[5] In contrast, comparatively minor modifications of the formalism utilized for linear chain molecules are required if branches are small, as has been shown for vinyl polymers containing articulated side chains.[6,7] Modifications can be reduced to five factors which are incorporated in statistical weight matrices for vinyl polymers in which side chains are unarticulated. Precise constitution of the five factors has been enumerated for articulated side chains containing two or three bonds.[7]

Our present concern is with polydialkylsiloxanes in which side chains are articulated. These polymers are of particular interest because unperturbed dimensions are reported to be strongly affected by an increase in side chain size (Table I). It will be shown that interactions involving articulated alkyl side chains can be accomodated exactly through introduction of only two factors into statistical weight matrices appropriate for polydimethylsiloxane. In this respect polydialkylsiloxanes constitute a simpler class of chain molecules than vinyl polymers. Conditions are defined under which side chains can appreciably modify unperturbed dimensions of polydialkylsiloxanes.

Configuration Partition Function

Statistical Weight Matrices. A segment from the interior of a polydialkylsiloxane chain is depicted in Figure 1. Silicon atoms are viewed as tetrafunctional branch points. Branches are indexed as shown in Figure 1. There are two bonds in branches $j-3$, j, and $j+3$, while the number of bonds in the remaining branches depicted depends on the nature of the alkyl substituent. As before,[3] n_j denotes the number of bonds in branch j, while ${}_j\mathbf{U}_i$ denotes the statistical weight matrix for bond i in branch j. Following exactly the formalism set forth for treating tetrafunctional branch points,[3] the contribution of one repeating unit to the configuration partition function can be written as

$$[({}_j\mathbf{U}_1 \ominus {}_{j+1}\mathbf{U}_1) \ominus {}_{j+2}\mathbf{U}_1][{}_j\mathbf{U}_2 \otimes ({}_{j+1}\mathbf{U}_2{}^{(n_{j+1}-2)}\mathbf{J}) \otimes ({}_{j+2}\mathbf{U}_2{}^{(n_{j+2}-2)}\mathbf{J})] \quad (1)$$

Here ⊗ denotes the direct product, ⊖ denotes formation of a rectangular statistical weight matrix as described in ref 3, **J** is a column whose every element is unity, and symbolism of the type ${}_j\mathbf{U}_a{}^{(b)}$ denotes the product of b successive statistical weight matrices, commencing with ${}_j\mathbf{U}_a$. This expression permits incorporation of all possible first- and second-order interactions and will accomodate assignment of any number of rotational states to bonds in Figure 1.

Subsequent development assigns three rotational states (trans at 0°, gauche± at ±120°) to all bonds about which rotation can occur. This assignment has proven effective in treating unperturbed dimensions[11] and dipole moments[12] of polydimethylsiloxanes. Backbone geometry has a tetrahedral configuration at each silicon atom, ∠Si–O–Si = 143°, and Si–O and Si–C bond length of 1.64 and 1.90 Å, respectively. These parameters differ from those adopted by Flory et al.[11] only in the slight decrease of ∠O–Si–O from 110° to the tetrahedral angle. Additional structural parameters are ∠Si–C–C = 112°, ∠C–C–C = 112°, and 1.53 Å for the C–C bond length.[1]

Three rotational states yield dimensions of 3 × 27 and 27 × 3 respectively for the first and second bracketed matrix in eq 1.[3] The operation in eq 1 therefore yields a 3 × 3 matrix. Repeated squaring of this matrix, along with definition of appropriate terminal matrices, will rapidly generate the configuration partition function for a large polydialkylsiloxane molecule. This 3 × 3 matrix may be generated identically as $\mathbf{U}_a\mathbf{U}_b$, where

$$\mathbf{U}_a = \begin{bmatrix} t_1 & \sigma_1 t_3 & \sigma_1 t_3 \\ t_3 & \sigma_1 t_2 & 0 \\ t_3 & 0 & \sigma_1 t_2 \end{bmatrix} \quad (2)$$

and

$$\mathbf{U}_b = \begin{bmatrix} 1 & \sigma_1 & \sigma_1 \\ 1 & \sigma_1 & \sigma_1\omega_1 \\ 1 & \sigma_1\omega_1 & \sigma_1 \end{bmatrix} \quad (3)$$

Order of columns is t, g$^+$, g$^-$ states for the bond in question, while rows are t, g$^+$, g$^-$ states for the preceding bond in the

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Table 1
Unperturbed Dimensions of Polydialkylsiloxanes

Alkyl group	Temp, °C	Solvent	$(\langle r^2\rangle_0/nl^2)_\infty$	Ref
Methyl	20	Methyl ethyl ketone	6.2 ± 0.1	8
	22.5	Fluorocarbon mixture	7.6 ± 0.2	8
Ethyl	25	Toluene	7.7 ± 0.8	10
n-Propyl	10	Toluene	14.4	9
	76	2-Pentanone	12.3	9

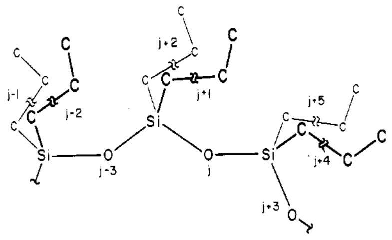

Figure 1. Diagrammatic depiction of C, O, and Si atoms in the interior of a polydialkylsiloxane chain. Indexing for branches is also shown.

main chain. Statistical weight matrix $\mathbf{U}_a$ is assigned to the first bond in branch j of Figure 1, while $\mathbf{U}_b$ is assigned to the second bond in branch j. Terms t_1, t_2, and t_3 in $\mathbf{U}_a$ include all necessary information concerning articulated side chains $j+1$ and $j+2$. It will prove advantageous to multiply the expression for $\mathbf{U}_a$ in eq 2 by the scalar $(t_3)^{-1}$, thus obtaining a more concise representation which can be written as

$$\mathbf{U}_a = \begin{bmatrix} \tau^* & \sigma_1 & \sigma_1 \\ 1 & \sigma_1 f_2 & 0 \\ 1 & 0 & \sigma_1 f_2 \end{bmatrix} \quad (4)$$

where $\tau^* = t_1/t_3$ and $f_2 = t_2/t_3$. Information concerning articulated side chains now resides in τ^* and f_2, which bear a similarity to parameters of the same designation arising in the treatment of vinyl polymers which bear articulated side chains.[7] The parameter τ^* modifies the weight of a sequence of trans placements, while f_2 affects the weight for consecutive gauche placements of the same sign. Interactions which contribute to τ^*, f_2, σ_1, and ω_1 will now be enumerated for polymers whose side chains are methyl, ethyl, n-propyl, and isopropyl.

Polydimethylsiloxane. Side chains for this polymer are not articulated, leading to $\tau^* = f_2 = 1$. Matrices $\mathbf{U}_a$ and $\mathbf{U}_b$ are now identical in form to those used by Flory[1] to treat polydimethylsiloxane. Null elements in $\mathbf{U}_a$ arise from severe interaction of silicon atoms and their methyl groups in $g^\pm g^\mp$ states.[11] The parameter σ_1 in $\mathbf{U}_a$ and $\mathbf{U}_b$ is defined as

$$\sigma_1 = \exp[-(E_{\mathrm{Si,O}} - E_{\mathrm{Si,CH_3}})/RT] \quad (5)$$

where $E_{\mathrm{Si,O}}$ and $E_{\mathrm{Si,CH_3}}$ denote first-order interaction energies of indicated groups. A second-order interaction of oxygen atoms produces statistical weight ω_1. Unperturbed dimensions[11] and dipole moments[12] of polydimethylsiloxanes have been reproduced using $E_{\mathrm{Si,O}} - E_{\mathrm{Si,CH_3}} = 850$ cal/mol and an energy of 1100 cal/mol for the second-order interaction. Significance of σ_1 and ω_1 is unchanged for higher polydialkylsiloxanes.

Polydiethylsiloxane. One first-order interaction and two second-order interactions contribute to τ^* and f_2 when ethyl side chains are present.

$$\tau^* = [\sigma_2(\sigma_2 + 4\omega_2) + 2\omega_2{}^2(1 + \omega_3)]\{\sigma_2[(1 + \omega_2)^2 + \sigma_2\omega_2] + 2\omega_2 + \omega_3(1 + \omega_2{}^2)\}^{-1} \quad (6)$$

$$f_2 = [\sigma_2\omega_2(4 + \sigma_2\omega_2) + 2(1 + \omega_3)]\{\sigma_2[(1 + \omega_2)^2 + \sigma_2\omega_2] + 2\omega_2 + \omega_3(1 + \omega_2{}^2)\}^{-1} \quad (7)$$

Characteristic ratios for polydimethylsiloxane and polydiethylsiloxane must be identical if $\omega_2 = 1$ because this circumstance yields $\tau^* = f_2 = 1$. Equations 6 and 7 also have the property that τ^* at $\omega_2 = y$ is identical to f_2 when $\omega_2 = 1/y$.

The first-order interaction is defined as

$$\sigma_2 = \exp[-(E_{\mathrm{O,CH_3}} - E_{\mathrm{CH_2,CH_3}})/RT] \quad (8)$$

where $E_{\mathrm{O,CH_3}}$ and $E_{\mathrm{CH_2,CH_3}}$ denote energies of first-order interactions of indicated groups. Separation of interacting methylene and methyl groups is 3.51 Å, a distance greatly exceeding that (3.17 Å) between methylene groups participating in the first-order interaction in polymethylene. Consequently $E_{\mathrm{CH_2,CH_3}}$ should be small. A distance of 3.37 Å separates the oxygen atom and methyl group. The van der Waals radius of an oxygen atom is ~0.6 Å smaller than that of a methylene group, while the $\mathrm{O \cdots CH_3}$ distance is only 0.14 Å smaller than the $\mathrm{CH_2 \cdots CH_3}$ distance. Thus $E_{\mathrm{O,CH_3}}$ will also be small.

Statistical weight ω_2 arises from second-order interaction of a silicon atom and methyl group as well as from mandatory third-order interactions of the methyl group with groups bonded directly to the silicon atom. Separation of silicon atom and methyl group is 3.75 Å. Mandatory third-order interactions occur at distances of 3.08 Å ($\mathrm{CH_2 \cdots CH_3}$) and 3.12 Å ($\mathrm{O \cdots CH_3}$). The $\mathrm{CH_2 \cdots CH_3}$ separation is slightly less than that (3.17 Å) of methylene groups which participate in the first-order interaction in polymethylene.[13] This interaction should have an energy near 500 cal/mol. A considerably smaller energy should attend the $\mathrm{O \cdots CH_3}$ interaction. Sequences of dihedral angles ${}_{j-3}\varphi_1$, ${}_{j-3}\varphi_2$, ${}_{j+1}\varphi_1$ which produce the $\mathrm{CH_2 \cdots CH_3}$ third-order interaction merit a statistical weight of either ω_2 or $\sigma_1\omega_2$. The necessity to suppress somewhat conformations which give rise to the repulsive $\mathrm{CH_2 \cdots CH_3}$ interactions dictates that $\omega_2 < 1$. Dihedral angles which produce the $\mathrm{O \cdots CH_3}$ third-order interaction merit a statistical weight of $\sigma_1\omega_2$. If ω_2 is made too small it will unduely suppress this conformation. A reasonable compromise would place E_{ω_2} at 200–600 cal/mol.

The second-order interaction whose statistical weight is ω_3 involves methyl groups separated by 3.22 Å. No mandatory third-order interactions occur. Comparison with the first-order interaction in polymethylene suggests E_{ω_3} should be in the vicinity of 500 cal/mol.

Polydi-*n*-propylsiloxane. Extension of side chains to n-propyl can be accomodated by eq 6 and 7 if each σ_2 is multiplied by c, where

$$c = (1 + 2\sigma_3\omega_4)[1 + \sigma_3(\omega_4 + \omega_5)]^{-1} \quad (9)$$

Unity is obtained for c if $\sigma_3 = 0$ or if $\omega_4 = \omega_5$. The upper limit for c is 2, and the only circumstance under which $c < 1$ is if $\omega_4 < \omega_5$.

First-order interaction of a silicon atom and methyl group at a distance of 3.25 Å gives rise to σ_3. An energy of about 0.2 kcal/mol would be obtained for a $\mathrm{C \cdots CH_3}$ interaction at this separation. Presumably E_{σ_3} will exceed 0.2 kcal/mol.

A second-order interaction between a methyl group and either an oxygen atom or a methylene group gives rise to statistical weights ω_4 and ω_5, respectively. Interacting groups are separated by nearly identical distances (2.96 Å for $\mathrm{O \cdots CH_3}$, 2.99 Å for $\mathrm{CH_2 \cdots CH_3}$). We anticipate $\omega_4 > \omega_5$ because the van der Waals radius for an oxygen atom is smaller than that of a methylene group by about 0.6 Å. On this basis $1 < c < 2$. Higher order interactions are unlikely to modify this conclusion. One of the three rotational states available to the Si–O bond will produce higher order interactions if the n-propyl side chain is in a conformation which merits inclusion of ω_4 in the statistical weight. However, the necessary combination of dihedral angles at the C–Si and Si–O bonds will already have been partially suppressed if ω_2 is made small. No modification of ω_4 due to higher order interactions is required.

Since multiplication of each σ_2 by c is the only modification required upon lengthening side chains from ethyl to *n*-propyl, polydiethylsiloxane and polydi-*n*-propylsiloxane must have identical characteristic ratios if *any one* of the following conditions exists: (a) $\sigma_2 = 0$, (b) $\omega_2 = 0$, (c) $\sigma_3 = 0$, or (d) $\omega_4 = \omega_5$. These circumstances are unlikely, in view of the foregoing consideration.

Polydiisopropylsiloxane. Terms t_1 and t_3 in eq 2 are zero for polydiisopropylsiloxane if $\omega_2 = 0$. Trans states are prohibited under these circumstances. Statistical weight matrices $\mathbf{U}_a$ and $\mathbf{U}_b$ may now be reduced to

$$\mathbf{U}_a = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (10)$$

$$\mathbf{U}_b = \begin{bmatrix} 1 & \omega_1 \\ \omega_1 & 1 \end{bmatrix} \quad (11)$$

where indexing for rows and columns is g$^+$, g$^-$. In the more likely event that $\omega_2 > 0$, $\mathbf{U}_a$ is given by eq 4 with

$$\tau^* = [2\sigma_2^2(1 + \omega_3) + \omega_2\omega_3(4\sigma_2 + \omega_2\omega_3)] \times [\sigma_2(\omega_3/\omega_2)(\sigma_2 + 1)(\omega_2^2 + 1) + 2\sigma_2(\sigma_2 + \omega_3) + \omega_3^2]^{-1} \quad (12)$$

$$f_2 = \{2\sigma_2[\sigma_2\omega_2(1 + \omega_3) + 2\omega_3] + \omega_3^2/\omega_2\} \times [\sigma_2(\omega_3/\omega_2)(\sigma_2 + 1)(\omega_2^2 + 1) + 2\sigma_2(\sigma_2 + \omega_3) + \omega_3^2]^{-1} \quad (13)$$

Unity is obtained for τ^* and f_2 if $\omega_2 = 1$.

Unperturbed Dimensions and Dipole Moments. Matrix methods were used to compute the mean square unperturbed end-to-end distance, $\langle r^2\rangle_0$, and mean square dipole moment, $\langle\mu^2\rangle$, as a function of number of Si–O bonds, n.[2] Dimensionless ratios at infinite degree of polymerization, $(\langle r^2\rangle_0/nl^2)_\infty$ and $(\langle\mu^2\rangle/nm^2)_\infty$, were evaluated by extrapolation to $1/n = 0$. A Si–O bond has length l and dipole moment m.

Results

Unperturbed Dimensions when $\sigma_1 = 0.238$ and $\omega_1 = 0.156$. Interaction energies used previously[11,12] to account for measured properties of polydimethylsiloxane in methyl ethyl ketone yield $\sigma_1 = 0.238$ and $\omega_1 = 0.156$ at 25 °C. Figure 2 depicts the manner in which $(\langle r^2\rangle_0/nl^2)_\infty$ depends on τ^* and f_2 when σ_1 and ω_1 have these values. A characteristic ratio of six is attained when $\tau^* = f_2 = 1$. Inequality of ∠O–Si–O and ∠Si–O–Si results in a closed polygon when there are about 22 consecutive trans placements.[11,12] This phenomenon explains the precipitous decline in dimensions as τ^* increases above unity, since τ^* is the statistical weight for trans placements at consecutive O–Si and Si–O bonds. A slight expansion can be effected by decreasing τ^* from unity. Once τ^* has become small enough to suppress the influence of cyclization, a further reduction has little effect on the dimensions.

Expansion can be more readily effected through formation of helices arising from sequential gauche placements of the same sign. Since the statistical weight for g$^\pm$g$^\pm$ placements at successive O–Si and Si–O bonds is $\sigma_1^2 f_2$, and $\sigma_1 \approx 1/4$, a large value must be assigned to f_2 before extension becomes apparent. A characteristic ratio of the size obtained for polydi-*n*-propylsiloxane could be attained only if f_2 were assigned an unrealistically large value.

Unperturbed Dimensions when $\sigma_1 = 0.66$ and $\omega_1 = 0.00$. Parameters used in the preceding section reproduce unperturbed dimensions in methyl ethyl ketone. Polydimethylsiloxane exhibits somewhat higher unperturbed dimensions in a low dielectric constant fluorocarbon mixture (Table I), presumably because specific solvent effects may occur with this polymer.[1] Experimental results obtained for polydiethylsiloxane and polydi-*n*-propylsiloxane in toluene should be compared with those for polydimethylsiloxane in the low dielectric constant medium. The surface in Figure 2 will be modified when σ_1 and ω_1 are assigned values which yield unperturbed dimensions in agreement with those measured in the fluorocarbon mixture. The required characteristic ratio for polydimethylsiloxane can be reproduced with $\sigma_1 = 0.66$ and $\omega_1 = 0.00$. Variation in τ^* and f_2 now produces characteristic ratios depicted in Figure 3.

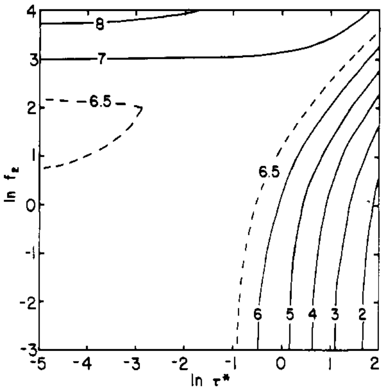

Figure 2. Dependence of $(\langle r^2\rangle_0/nl^2)_\infty$ on τ^* and f_2 when $\sigma_1 = 0.238$ and $\omega_1 = 0.156$. Solid contour lines denote characteristic ratios of 2–8, at intervals of 1. An additional contour line (dashed) is at a characteristic ratio of 6.5.

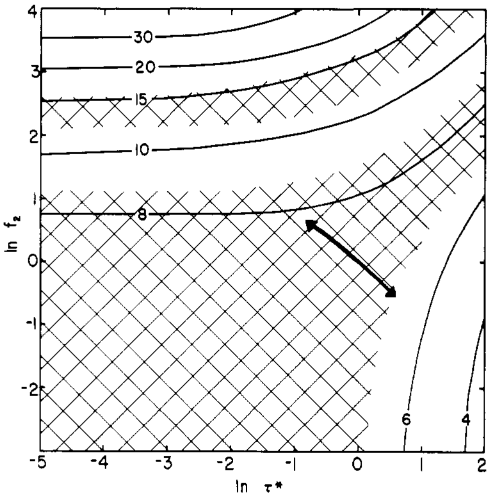

Figure 3. Dependence of $(\langle r^2\rangle_0/nl^2)_\infty$ on τ^* and f_2 when $\sigma_1 = 0.66$ and $\omega_1 = 0.00$. Solid contour lines are drawn at characteristic ratios of 4, 6, 8, 10, 15, 20, and 30. Light cross-hatched areas denote regions where the characteristic ratio is 7.7 ± 0.8 or 13.4 ± 2, corresponding to experimental values reported for polydiethylsiloxane[10] and polydi-*n*-propylsiloxane,[9] respectively. The heavy double-headed arrow is described in the text.

While extension of the chain is observed at all combinations of τ^* and f_2, the effect is most pronounced for large f_2 and small τ^*. Characteristic ratios as high as 40 are now computed. Extension of the chain is accomplished by development of helices consisting of gauche placements. As noted above, g$^\pm$g$^\pm$ placements at successive O–Si and Si–O bonds merit a statistical weight of $\sigma_1^2 f_2$. Elevation of σ_1 from 0.238 to 0.66 allows smaller values of f_2 to enhance the population of g$^\pm$g$^\pm$ states for successive O–Si and Si–O bonds. Gauche placements at successive Si–O and O–Si bonds merit statistical weights of $\sigma_1^2 f_2$ or $\sigma_1^2\omega_1 f_2$, depending upon whether they are of the same or opposite sign. A decrease in ω_1 from 0.156 to 0.00 suppresses g$^\pm$g$^\mp$ sequences for these bonds. Large f_2 will now produce long sequences of gauche placements of the same sign.

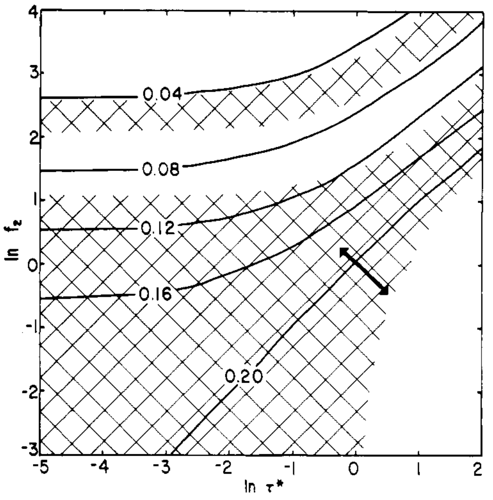

Figure 4. Dependence of $(\langle\mu^2\rangle/nm^2)_\infty$ on τ^* and f_2 when $\sigma_1 = 0.66$ and $\omega_1 = 0.00$. Solid lines are drawn at ratios of 0.04, 0.08, 0.12, 0.16, and 0.20. Minimum and maximum ratios attained for τ^* and f_2 displayed are 0.013 and 0.234, respectively. Light cross-hatched areas denote regions where $(\langle r^2\rangle_0/nl^2)_\infty$ is 7.7 ± 0.8 or 13.4 ± 2 (see Figure 3). The heavy double-headed arrow is described in the text.

The large cross-hatched region in Figure 3 denotes combinations of τ^* and f_2 for which the characteristic ratio is 7.7 ± 0.8, corresponding to the result obtained experimentally for polydiethylsiloxane.[10] Earlier discussion of second-order interactions involving methyl groups in this polymer permits approximation of ω_2 and ω_3 by ½. Pairs of τ^* and f_2 fall on the heavy double-headed arrow in Figure 3 if ω_2 and ω_3 are held constant at ½ and σ_2 is varied from 0 to 20. Earlier analysis of first-order interactions giving rise to σ_2 suggested it should differ little from unity. Similarity in unperturbed dimensions for polydimethylsiloxane and polydiethylsiloxane is easily rationalized by rotational isomeric state theory. Indeed, a contrary result is inconceivable.

The smaller cross-hatched region in Figure 3 denotes combinations of τ^* and f_2 yielding characteristic ratios in agreement with the results reported for polydi-*n*-propylsiloxane.[9] An increase in f_2 and/or a reduction in τ^* is required to move from the larger to the smaller cross-hatched area. Movement in the desired direction is obtained by decreasing σ_2, but even setting this statistical weight equal to zero will not cause the double-headed arrow in Figure 3 to rise as high as the 8 contour line. Since polydi-*n*-propylsiloxane simply requires replacement of each σ_2 by $c\sigma_2$, no assignment of c can effect a change of the required magnitude.

A more general statement of the foregoing conclusion is obtained by examination of $(\partial\tau^*/\partial\sigma_2)_{\omega_2,\omega_3}$ and $(\partial f_2/\partial\sigma_2)_{\omega_2,\omega_3}$, evaluated from eq 6 and 7. The *only* requirement for $(\partial\tau^*/\partial\sigma_2)_{\omega_2,\omega_3} > 0$ or $(\partial f_2/\partial\sigma_2)_{\omega_2,\omega_3} < 0$ is that ω_2 be less than unity. So long as $\omega_2 < 1$, we must also have c less than unity if f_2 or τ^* is to change in the direction required to move from the large to the small cross-hatched region in Figure 3. The size of c compared to unity is specified by the relative sizes of ω_4 and ω_5 (eq 9). Earlier discussion in connection with statistical weight matrices concluded that $\omega_4 > \omega_5$, which in turn requires $1 < c < 2$. Therefore lengthening of alkyl side chains from ethyl to *n*-propyl should actually *increase* τ^*, *decrease* f_2, and produce a *reduction* in unperturbed dimensions. The reported observation[9] that unperturbed dimensions for polydi-*n*-propylsiloxane are twice those of polydiethylsiloxane cannot be rationalized by rotational isomeric state theory unless unrealistic energies are assigned to at least one of the second-order interactions. It is difficult to see how this conclusion could be altered by invoking a large specific solvent effect on the unperturbed dimensions. Toluene was used as solvent for both polydiethylsiloxane and polydi-*n*-propylsiloxane.

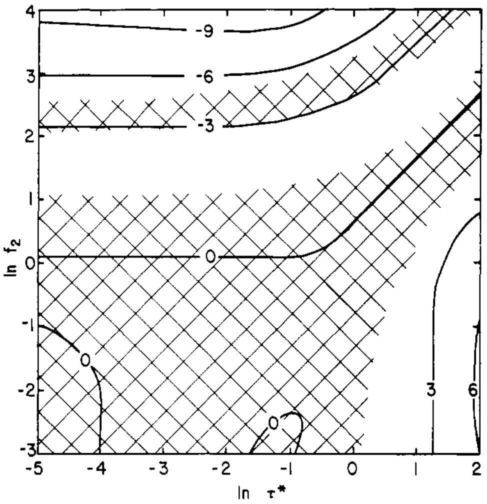

Figure 5. Temperature coefficient (10^3 d ln $\langle r^2\rangle_0$/dT) for the unperturbed dimensions. Cross-hatched regions, E_{σ_1}, and E_{ω_1} are as in Figures 3 and 4.

Characteristic ratios for polydiisopropylsiloxane fall between 7 and 8 if $\omega_2 = \omega_3 = $ ½ and $0 < \sigma_2 < 20$. However, significant extension will occur if ω_2 becomes small. Equations 10 and 11 describe the statistical weight matrices in the limit where $\omega_2 = 0$. If ω_1 is also zero, the only configuration available to the molecule will be that in which every internal main chain bond adopts a gauche state of the same sign. For this chain $\langle r^2\rangle_0/nl^2$ increases without limit as n increases.

Dipole Moments. Figure 4 depicts values of $(\langle\mu^2\rangle/nm^2)_\infty$ for polydialkylsiloxanes. Values of σ_1 and ω_1 are those used to obtain Figure 3. The experimental value for polydimethylsiloxane (deduced by extrapolation of results for small oligomers) is about 0.23, which is slightly higher than the result of 0.204 attained in Figure 4 at $\tau^* = f_2 = 1$. The large cross-hatched region denotes combinations of τ^* and f_2 which yield $(\langle r^2\rangle_0/nl^2)_\infty = 7.7 \pm 0.8$, the experimental value for polydiethylsiloxane.[10] It is easy to rationalize the preliminary result[15] that $(\langle\mu^2\rangle/nm^2)_\infty$ is of a similar size for polydimethylsiloxane and polydiethylsiloxane. Dipole moment ratios for these two polymers differ by less than 10% if $\omega_2 = \omega_3 = $ ½ and ¾ $< \sigma_2 < 10$ (double-headed arrow in Figure 4).

The smaller cross-hatched region in Figure 4 denotes combinations of τ^* and f_2 which yield $(\langle r^2\rangle_0/nl^2)_\infty$ within ±1 of results reported for polydi-*n*-propylsiloxane.[9] In this region the dipole moment ratio is smaller, by a factor of 3–5, than the result obtained with polydimethylsiloxane. We are unaware of an experimental measurement of dipole moments for polydi-*n*-propylsiloxane or its oligomers. Clearly such measurements would contribute substantially to a clarification of the status of polydialkylsiloxane chain statistics.

Temperature Dependence of the Unperturbed Dimensions. Figure 5 depicts $(\mathrm{d} \ln \langle r^2\rangle_0/\mathrm{d}T)_\infty$ as a function of τ^* and f_2, E_{σ_1} and E_{ω_1} being held constant at values used for Figures 3 and 4. A positive temperature coefficient is predicted for polydimethylsiloxane, in accord with with experiment.[16] A chain having a characteristic ratio of 7.7 ± 0.8 (large cross-hatched region) might have either a positive or a negative temperature coefficient, with the former being the more likely. If the characteristic ratio is 13.4 ± 1, a strongly negative temperature coefficient is predicted due to thermal disruption of the gauche helices.

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Rheooptical Studies on the Deformation Mechanism of Polymer Spherulite by Linear Elastic Theory[1a]

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ABSTRACT: A mathematical representation for the deformation mechanism of polymer spherulites is proposed in terms of the relationship between optical and mechanical responses to external mechanical excitations by using a linear elastic theory. The optical quantities observed from x-ray diffraction and polarized light scattering are found to be a sort of average of mechanical quantities, such as strains and stresses arising locally in the spherulites. In addition, the theoretical treatment is also tested with experimental results. Both the experimental results with regard to lattice deformations of crystalline regions and light scattering are found to be rather close to the calculated ones.

I. Introduction

The broad aim of this paper is to construct a theory for rheooptical studies that have revealed characteristic relaxation times of the responses of structural units in polymer solids to external mechanical excitations. The experimental results have been discussed in a number of papers.[2–7] The recent results of rheooptical investigations, using the dynamic x-ray diffraction technique[8,9] for dynamic orientation and lattice deformation of polyethylene crystal[10–12] as well as the dynamic light-scattering technique[13,14] for the deformation mechanism of polyethylene spherulites,[15,16] are the most definitive evidence confirming the notion that the α mechanical dispersion of polyethylene is actually related to the crystalline responses. However, the relationship between optical and mechanical responses to external mechanical excitation has never been developed in mathematical and quantitative terms. Quantitative description of the viscoelastic behavior of crystalline polymers in bulk is a very complicated and difficult problem, reflecting their complex structures.

The first investigation of the mathematical description of elastic behavior of a spherically isotropic system under general loading was carried out by Chen,[17] and its mathematical procedure was applied to the deformation mechanism of polyethylene spherulites by Wang.[18,19] Hence, this paper is concerned with a mathematical description of the relationship between the optical and mechanical responses using linear elastic theory. The investigation is mainly carried out for the problem in the deformation of polyethylene having a spherulitic crystalline texture in order to discuss the crystal lattice deformation within the spherulite and the polarized light scattering from the spherulitic texture in a quantitative manner. This treatment may not be sufficient, as discussed above, and therefore a more quantitative treatment supplementing the viscoelastic properties of the materials will be discussed in the succeeding paper.[20]

First, the five elastic constants C_{ij} for the spherically isotropic material will be determined by using an aggregation model proposed by Hibi,[21] and the mechanical constants in bulk, shear modulus G, bulk modulus K, Young's modulus E, and Poisson's ratio ν will be calculated by the method of Wang.[18]

Second, a mathematical representation of the crystal lattice strains within the spherulite will be discussed in terms of the geometric arrangement of the bulk specimen as revealed by x-ray optical coordinates. The calculated results will be tested vs. results obtained from dynamic x-ray diffraction measurements of a low density polyethylene (Sumikathen G201) and a high-density polyethylene (Sholex 5065).[22]

Finally, the light scattering from the spherulite will be calculated from a knowledge of the principal polarizability distribution within the spherulite, omitting the molecular orientation of the medium around the spherulite.

II. Elastic Constants of Polyethylene Lamella and in Bulk

Hooke's law in a polyethylene spherulite may be written by using a special spherical coordinate system suggested by Chen[17] and Wang[18] as follows:

$$
\begin{aligned}
\sigma_{\theta\theta} &= C_{11}\epsilon_{\theta\theta} + C_{12}\epsilon_{\phi\phi} + C_{13}\epsilon_{rr}\\
\sigma_{\phi\phi} &= C_{12}\epsilon_{\theta\theta} + C_{11}\epsilon_{\phi\phi} + C_{13}\epsilon_{rr}\\
\sigma_{rr} &= C_{13}(\epsilon_{\theta\theta} + \epsilon_{\phi\phi}) + C_{33}\epsilon_{rr}\\
\sigma_{r\theta} &= C_{44}\epsilon_{r\theta}\\
\sigma_{r\phi} &= C_{44}\epsilon_{r\phi}\\
\sigma_{\theta\phi} &= \tfrac{1}{2}(C_{11} - C_{12})\epsilon_{\theta\phi}
\end{aligned}
\tag{1}
$$

where the symbols σ_{ij}, ϵ_{ij}, and C_{ij} denote components of stress, strain, and elastic stiffness, respectively. The subscript 3 of

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