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KERR EFFECTS OF FLEXIBLE MACROMOLECULES

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Detailed calculations of the effects of different conformations on the Kerr constant have become available only recently. These calculations can be utilized to evaluate the usefulness of Kerr constant measurements in characterizing configurations of macromolecules. Experimental scientists would like to know, in particular, if Kerr measurements are more sensitive to changes in conformation than other methods and for what types of molecules. These sensitivities must be judged against the results for more common characterization methods.

Kerr effect measurements are more complicated properties than most more common methods. In particular, as we will see, they depend upon both the dipole moments and the optical and static polarizability anisotropies of the molecules. This dependence occurs in two terms, one which dominates for polar molecules, involving the optical anisotropy and the square of the dipole moment and another which is normally important only for nonpolar molecules. The Kerr constant usually is most sensitive to conformations in molecules with large dipole moments; sensitivity is greatest if there is a large difference in the dipole moments of the configurations being compared. There is a greater sensitivity to differences in dipole moments, because of the square dependence, than to differences in optical anisotropies.

The presentation here consists of the following parts: 1) The formalism for the detailed calculation of the configurational average of the Kerr constant is briefly outlined. 2) The question of the tensor additivity of bond polarizabilities and the range of their interactions are taken up in some detail for the n-alkanes.

3) Results are reviewed which indicate that the Kerr constants for polar vinyl chain molecules depend strongly upon their stereoregularity. 4) Polypeptide Kerr constants and their dependences upon composition are treated, as well as their changes through the helix-coil transition.

CONFIGURATIONAL AVERAGE OF THE KERR CONSTANT

The usual approach is to develop molecular properties in a series expansion in the external electric field and retain only the lowest order terms. Nagai and Ishikawa (1965) originally developed the expressions appropriate for treating Kerr constants. Their expression for the molecular anisotropy at a temperature T is

$$\Delta\alpha = (1/10)\ [\langle \underline{\mu}^T \hat{\underline{\alpha}}\ \underline{\mu} \rangle\ (E/kT)^2 + \langle \mathrm{Trace}(\hat{\underline{\alpha}}\ \hat{\underline{\alpha}}') \rangle\ (E^2/kT)] \quad (1)$$

μ is the molecular dipole moment, α is the molecular polarizability, the $\hat{}$ indicates the traceless form, E is the magnitude of the electric field, the prime on the last α designates that it is the static polarizability, ^{T} indicates the row vector, and the brackets <> indicate the average, in the absence of the electric field, of the quantities enclosed. The molar Kerr constant is obtained from eq (1) with a proportionality constant (Le Fevre and Le Fevre, 1955; Le Fevre, 1965)

$${}_mK = (2\pi N/135kT)\ [\ \langle \underline{\mu}^T \hat{\underline{\alpha}}\ \underline{\mu} \rangle/kT + \langle \mathrm{Trace}(\hat{\underline{\alpha}}\ \hat{\underline{\alpha}}') \rangle\ ] \quad (2)$$

where N is Avogadro's number.

The molecular dipole moments and optical anisotropies are themselves composed of contributions from each of the molecular subunits. There is an alternative approach of combining atomic polarizabilities (Applequist et al., 1972); results for alkanes have been presented by Ladanyi and Keyes (1979). Here, however, we take sums of bond or group contributions.

$$\underline{\mu} = \sum_i \underline{\mu}_i \quad \text{and} \quad \hat{\underline{\alpha}} = \sum_i \hat{\underline{\alpha}} \quad (3)$$

The details of the matrix formalism for calculating these averages have been presented in several places, most usefully in the monograph by Flory (1969) and in the review by Jernigan and Thompson (1976). We will not repeat the details here. The independence implicit in eq (3) has been a matter of some controversy. For the bond polarizabilities, this additivity is often termed the valence optical method. The validity of the additivity of bond dipoles is much better established than is the additivity of bond polarizabilities. Next it is our purpose to attempt to indicate the effects of interactions between bond polarizabilities and to explore the range of the interactions which may affect this additivity.

INTERACTIONS BETWEEN POLARIZABILITY TENSORS

Here the form of the interactions between polarizabilities is to be the induced dipole-induced dipole interactions of Silberstein (1917) and presented in a formalism similar to that of Mortensen (1968). The total electric field at bond j will be the intrinsic field E^o plus that arising from interactions with all other bonds i.

$$\underline{E}_j = \underline{E}^o + \sum_{i \neq j} \left(-\underline{\mu}_i / r_{ij}^3 + 3 \underline{r}_{ij} \underline{r}_{ij}^T \underline{\mu}_i / r_{ij}^5 \right) \tag{4}$$

μ_i is the dipole moment of bond i and r_{ij} is the distance between bond centers. The bonds to be included in the sum over index i are arbitrary to a significant extent. Rowell and Stein (1967) treated ethane and included interactions between all bonds; their result showed large enhancements of the polarizabilities. We have chosen here to exclude interactions between bond pairs whose distances are fixed. Since the only conformational variables here will be backbone bond rotations, interactions between bonds on the same atom will not be explicitly included. This is equivalent to taking the intrinsic bond polarizability to be an effective one that already includes the effects of configurationally invariant interactions. Practical considerations dictate that an upper bound be imposed upon the interaction range. A large body of evidence supports the premise that macromolecules at theta conditions can be well represented by considering only short range interactions (Flory, 1969). For the linear alkanes, this range corresponds to interactions among three and four neighboring carbon-carbon bonds and their pendant carbon-hydrogen bonds. The conformations of these fragments are specified by one or two backbone rotation angles. Those considerations to limit the range of the interactions are appropriate for van der Waals interactions; here we are assuming this same range of interaction to be appropriate for induced dipole-induced dipole interactions. We hope that the range of interactions treated here is adequate. Our calculations should correspond most closely to either pure liquids or theta conditions.

If the intrinsic bond polarizability of bond j is $\underline{\alpha}_j^o$, then the moment induced in bond j is given by

$$\underline{\mu}_j = \underline{\alpha}_j^o \underline{E}_j = \underline{\alpha}_j^o \left[\underline{E}^o + \sum_{i \neq j} \left(-\underline{I}/r_{ij}^3 + 3 \underline{r}_{ij} \underline{r}_{ij}^T / r_{ij}^5 \right) \underline{\mu}_i \right] \tag{5}$$

with I as the identity matrix of order 3. By defining a dipole-dipole interaction tensor, this becomes

$$\underline{E}^{o} = (\underline{\alpha}_{j}^{o})^{-1}\,\underline{\mu}_{j} + \sum_{i\neq j} \underline{J}_{ji}\,\underline{\mu}_{i} \tag{6}$$

which can be reexpressed in matrix form as

$$\underline{\mu} = \underline{A}^{-1}\,\underline{E}^{o} \tag{7}$$

with

$$\underline{A} = \begin{bmatrix} (\underline{\alpha}_{1}^{o})^{-1} & \underline{J}_{12} & \cdots & \underline{J}_{1n} \\ \underline{J}_{21} & (\underline{\alpha}_{2}^{o})^{-1} & \cdots & \underline{J}_{2n} \\ \vdots & \vdots & & \vdots \\ \underline{J}_{n1} & \underline{J}_{n2} & \cdots & (\underline{\alpha}_{n}^{o})^{-1} \end{bmatrix} \tag{8}$$

The entries in this matrix are the inverse of the intrinsic polarizability tensors, on the diagonal, and the dipole-dipole interaction tensors with the interacting bonds indicated by the pair of subscripts on J.

$$\underline{M} = \begin{bmatrix} \underline{\mu}_{1} \\ \underline{\mu}_{2} \\ \vdots \\ \underline{\mu}_{n} \end{bmatrix} \tag{9}$$

The effective bond polarizabilities are derived by identifying them with the dipole moment induced by unit electric field; this means that the effective or net polarizability is identical to the inverse of the matrix A.

We will apply this formalism to treat the interactions within alkane chains. For the ten bond fragment $C_i-(CH_2)_{i+1}-(CH_2)_{i+2}-(CH_2)_{i+3}-C_{i+4}$ we have determined with the method above the polarizability tensor for the group $(CH_2)_{i+2}-C_{i+3}$, with interactions between the bond polarizabilities permitted. Terminal groups are treated with a similar 10 bond fragment, in which one of the C-C bonds has been replaced by a C-H bond. The terminal C-C bond on each end is taken to be in a fixed configuration; therefore for the terminal group, there is only one rotation angle and the number of interactions is reduced. Results are given in Table I. The mean polarizabilities, $\bar{\alpha}$ = (1/3) Trace(α), have been increased by the interactions quite uniformly by approximately 20%; whereas the square anisotropies, γ^2, display a greater than fourfold increase over the independent case. Furthermore, the value of γ^2 for

Table I. Nearest Neighbor Conformational Dependence of the Polarizability Tensors of (CH_2-C)

Conformation	$\bar{\alpha}$	γ^2
trans, trans	2.10	2.99
trans, gauche+	2.13	3.36
gauche+, trans	2.11	3.07
gauche+, gauche+	2.15	3.54
gauche+, gauche-	2.15	3.60

for Le Fevre Bond Polarizabilities,

$\alpha_{C-C} = (0.99,\ 0.27,\ 0.27)$

$\alpha_{C-H} = (0.64,\ 0.64,\ 0.64)$

the (CH_2-C) group is almost determined by the rotation angle included within this group, with the preceding bond rotation having less effect. That is, 2.99 is similar to 3.07; whereas 3.36, 3.54 and 3.60 are alike. Of course, these invariants do not give a complete indication of how the individual tensor components of the polarizability tensor vary. Also we should report that more anisotropic bond polarizabilities result in larger interactions and consequently in much stronger dependences on configuration. Now we wish to average the configuration dependent polarizability tensors over all available configurations. The alkanes have the advantage of having well studied configuration statistics (Flory, 1969). These are briefly outlined below.

The n-Alkane Configurational Statistics

The configurational variations in the flexible n-alkanes are adequately described in terms of two simple parameters which can be ascribed to three bond and four bond interactions (Flory, 1969). The statistical weights for three bond interactions are 1 for the planar trans form and σ for each of the two gauche states. Four bond interactions are accounted for with an additional statistical weight of ω for adjacent pairs of gauche states of opposite sense. These statistical weights can be organized into a matrix to permit generation of a partition function as follows:

$$\underline{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \qquad (10)$$

The order of both the row and column matrix indices is trans, gauche+, and gauche-. The partition function is generated by an appropriate number of U's in a product.

$$Z = (1\ 0\ 0)\ U^{n-2} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \qquad (11)$$

where n is the number of C-C bonds in the backbone. In the calculations to be presented here we have taken $\sigma = 0.424$ and $\omega = 0.0323$ for a temperature of 20 .

A partition function of this type has been utilized in conjunction with the geometry and methods set forth in the monograph by Flory (1969) to calculate averages of the requisite molecular properties. These are, specifically, the mean square polarizability anisotropy (Jernigan and Flory, 1967) and the Kerr constant (Flory and Jernigan, 1968). For the nonpolar alkanes we need only the nonpolar term in eq (2).

In the usual formalism (Jernigan and Thompson, 1976; Flory, 1969) for calculating the averages, each term in the above statistical weight matrix U is multiplied by the polarizability tensor corresponding to the bond type indicated by the index on U and formed into a larger generator matrix. Here we have obtained polarizability tensors that depend upon a pair of backbone bond rotations; each of these is placed into the larger matrix after being multiplied by the corresponding statistical weight from U for that pair of rotational angles. This results in more complicated matrices, but they are no larger in size than those required for previous calculations with configuration independent bond polarizability tensors. In a manner of speaking, this calculation removes some redundancy in the usual equations and takes more complete advantage of the matrix formalism.

Results for n-Alkane Polarizability Interactions

The choice of bond polarizability tensors, even for such simple bonds as carbon-carbon and carbon-hydrogen is a difficult matter (Jernigan and Thompson, 1976). We have chosen for the results here to use the bond polarizabilities of Le Fevre et al. (1966) and Bunn and Daubeny (1954). The Le Fevre C-H bond is taken to be isotropic with a bond polarizability of 0.64 A^3 ; the C-C bond has a parallel component of 0.99 A^3 and a perpendicular one of 0.27 A^3 . These yield 0.72 for the value of $\Gamma = \Delta\alpha_{C-C} - 2\,\Delta\alpha_{C-H}$ which is similar to the somewhat lower value determined experimentally by Patterson and Flory (1972). The Bunn and Daubeny values are: for a C-C bond $\alpha_{\parallel} = 0.968$, $\alpha_{\perp} = 0.263$ and for a C-H bond $\alpha_{\parallel} = 0.7815$ and $\alpha_{\perp} = 0.5731$. For all cases we have arbitrarily taken $\alpha' = 1.1\ \alpha$. The units of all results presented in this paper are as follows, unless otherwise specified: molar Kerr constants in 10^{-10} cm^5 $statvolt^{-2}$ mol^{-1} , polarizabilities in A^3 , and

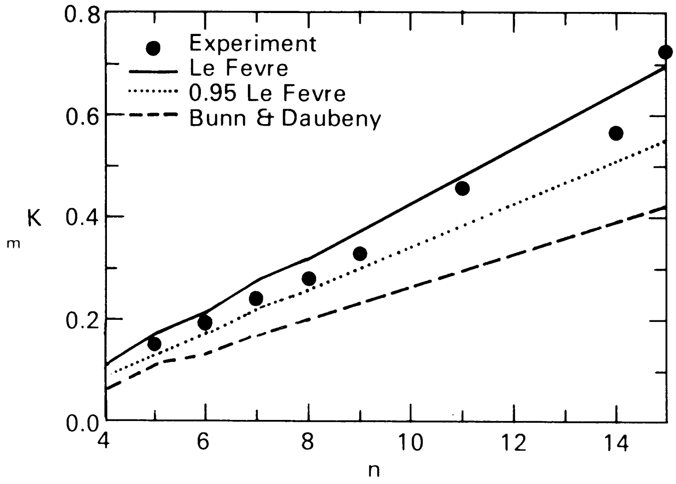

Fig. 1. Chain length dependence of the Kerr constants for the n-alkanes, with short range interactions between bond polarizability tensors. The curves were calculated for the indicated sets of polarizability tensors.

mean square anisotropies in A^6. In Fig. 1 we present results for these bond polarizabilities, with interactions limited in range as described above, for both the Le Fevre and the Bunn and Daubeny bond polarizabilities. In addition we have also calculated results with an arbitrary reduction in each of the Le Fevre bond polarizability values of 5%. The solid curve, for Le Fevre polarizabilities, is slightly higher than most of the experimental values (Stuart, 1962); whereas a reduction of only 5% in each of the bond polarizabilities yields results slightly below the experiments. The strong sensitivity of the results to the exact values of the bond polarizabilities appears because of the interactions. The sensitivity of the individual group polarizability tensors to the conformation is not a strong one. Mostly the interactions serve simply to increase the overall polarizability anisotropy. The exact conformational dependences of two invariants of the group polarizability tensor were given in Table I.

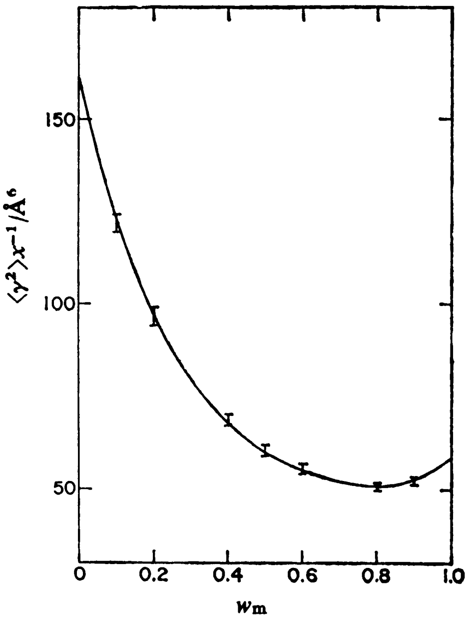

Fig. 2. Dependence on stereoregularity of the mean square optical anisotropy per unit for poly(p-chlorostyrene). w_m is the probability of a meso dyad, a dd or ll pair. The value $w_m = 1$ corresponds to a completely isotactic chain. Results are averages of 20 Monte Carlo chains, each of 100 units. (Reproduced by permission, Saiz, Suter and Flory, 1977).

VINYL POLYMERS

The two vinyl polymers of most interest are the polar ones, poly(vinyl chloride), $\mathrm{-[CHClCH_2]-}$, and poly(p-chlorostyrene), $\mathrm{-[CH_2(p\text{-}C_6H_4Cl)CH]-}$. Each unit of these polymers possesses an asymmetric carbon atom. Extensive calculations of dimensions and dipole moments and their dependences upon composition and stereoregularity have been presented by Mark (1974). Variations in tacticity can change mean square dipole moments by a factor of 4 or 5. Unfortunately the dipole moments are often nearly constant over a substantial range of tacticity.

Tonelli (1977) has calculated Kerr constants for a wide variety of vinyl copolymers and considered variations of both stereoregularity and composition. For the nonpolar polypropylene, stereoregularity in the chain produces a maximum variation in K_m of 25%. By contrast the highly polar poly(vinyl chloride) ranges from 0.306 for an isotactic chain and 0.71 for an atactic chain to -134 for a syndiotactic chain. By comparison with dipole moment results this is an enormous range. Random 50:50 copolymers of these two units give values ranging from -6.46 for a syndiotactic molecule to 1.1 for the isotactic form. In general the Kerr constants

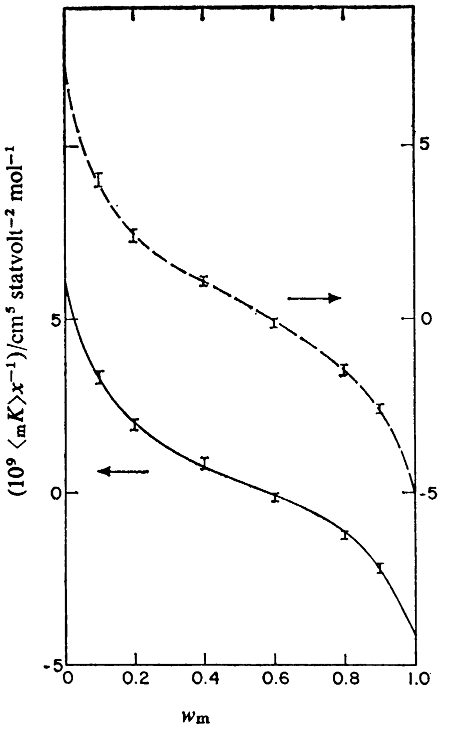

Fig. 3. Molar Kerr constants per unit for para-halogenated polystyrenes. The dashed curve is for poly(p-bromostyrene), and the solid curve is for poly(p-chlorostyrene). Samples were generated as indicated in the Legend for Fig. 2. (Reproduced by permission, Saiz, Suter and Flory, 1977).

appear to show greater sensitivity to both sequence and stereoregularity than do the calculated dipole moments.

In Figs. 2 and 3 are displayed results (Saiz et al., 1977) of the effect of tacticity on the optical properties of the para-halogenated polystyrenes. The mean square anisotropy evidences behavior similar to that calculated for other properties of vinyl polymers. Unfortunately these curves are nearly constant over a broad range in tacticity, indicating that determination of tacticity by those methods can be uncertain. From Fig. 2, values of $\langle\gamma^2\rangle/x$ are very similar for all values of $w_m > 0.5$. The most interesting feature evidenced by the Kerr constants in Fig. 3 is their markedly different dependence on tacticity. In particular, the slopes of the curves indicate that the Kerr constants of these polymers can be utilized to distinguish between samples of high isotacticity. Those authors obtained good agreement between experimental Kerr constants for samples, whose tacticities had been estimated by depolarized light scattering and other methods, and the calculated

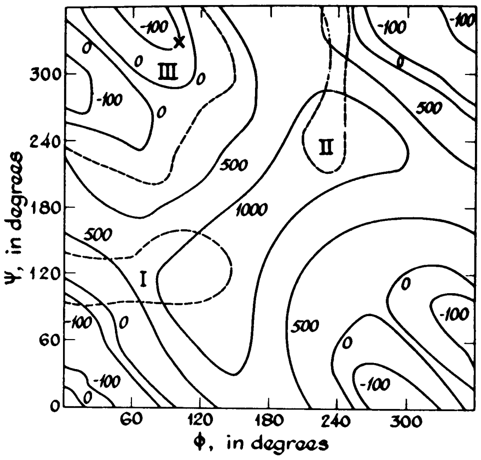

Fig. 4. Kerr constant contour map of the peptide N-acetyl-L-alanine-N'-methylamide in units of cm^5 $statvolt^{-2}$ mol^{-1} x 10^{-12}. ϕ and ψ are the peptide backbone rotation angles about bonds N-C^α and C^α-C', respectively. The dashed lines enclose those energetically favored conformations with an energy of 5 kcal mol^{-1} or less. (Reproduced by permission, Ingwall, Czurylo and Flory, 1973).

Kerr constants for the corresponding tacticity.

Other molecules for which calculations have been performed are chain molecules with oxygen as well as carbon in their backbones (Ishikawa and Nagai, 1971; Kelly et al., 1977).

POLYPEPTIDES

A polarizability tensor for the peptide bond was derived by Ingwall and Flory (1972); recently an alternative, somewhat more anisotropic tensor has been reported by Khanarian (1980). The calculations reported here were performed with the former values. Reproduced in Fig. 4 is the Kerr constant contour map for N-acetyl-L-alanine-N'-methylamide (Ingwall et al., 1973). The areas inside the dotted lines correspond to the usual favored conformations, I) right handed alpha helix, II) left handed alpha helix and III) beta strand. It is noteworthy that most of the helix conformations have Kerr constants greater than +10; whereas a substantial portion of the beta strand domain has negative Kerr constants. This strong sensitivity to conformation makes the method a particularly attractive one for studying polypeptides and proteins.

We have utilized the Ingwall and Flory polarizability tensors set forth for glycine and alanine to calculate the effect of com-

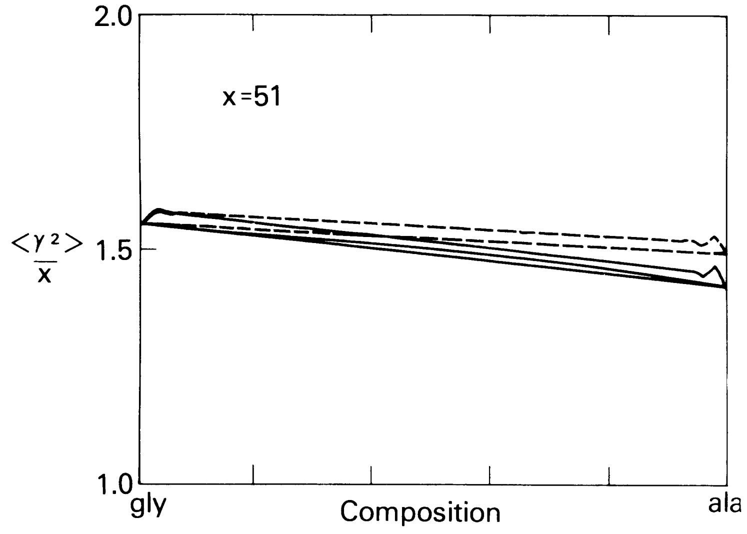

Fig. 5. Mean square polarizability anisotropy per peptide for various copolymers of glycine and alanine. The dotted curve correspond to an energy increment of 0.7 kcal mol^{-1} for the beta strand region for alanine. The top curve is the sum of the scalar anisotropies for the two blocks. The other dotted curve is for both the random copolymer and the properly calculated block copolymer. The top solid curve is for the scalar sum of the anisotropies of the two blocks. The middle solid curve is for the properly calculated block copolymer, and the lowest curve is for the random copolymer.

position on the Kerr constant for an alanine-glycine copolymer, for both random sequences and for block copolymers. Much larger effects would be expected for amino acids with polar side chains. The chain treated is CH_3-(CO-NH-CHR)$_{x-1}$ CO-NH-CH_3 . For alanine it is necessary to specify the value of Γ for the CH_2-C unit; in these calculations we have taken a value of 0.55. Ingwall et al. (1973) found that it was necessary, in order to obtain agreement with the Kerr constants for N-acetyl-L-alanine-N'-methylamide and N-acetyl-L-leucine-N'-methylamide, to increase the energy of the region III by 0.7 kcal mol^{-1}; this may correspond to a solvent effect. We have calculated the energies with the same method of Brant et al. (1967). In Fig. 5 are shown results for the mean

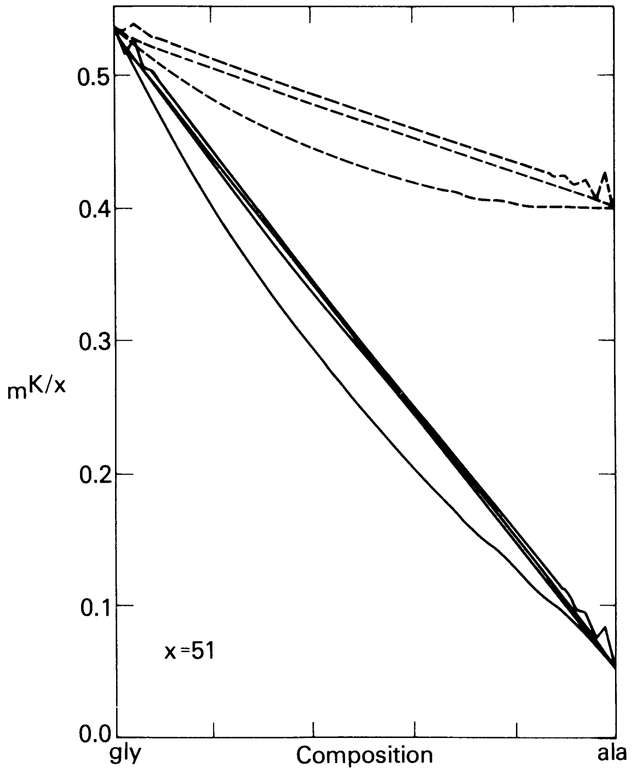

Fig. 6. Calculated Kerr constants per peptide for copolymers of glycine and alanine. As in Fig. 5, the dotted curves correspond to calculations in which an energy of 0.7 kcal mol^{-1} has been added to the beta strand region for alanine. The top and bottom solid curves are for the same cases as those in Fig. 5. For the solid curves the two nearly indistinguishable curves in the middle are for properly calculated block copolymers, the lower one for $(\text{gly})_i(\text{ala})_{x-i-1}$ and the upper for $(\text{ala})_{x-i-1}(\text{gly})_i$. The top dotted curve is for the sum of scalar Kerr constants of the two blocks; the middle dotted curve is for properly calculated block copolymers; and the lowest dotted curve is for the random copolymer.

square anisotropy appropriate to depolarized light scattering measurements. The results are quite linear and nearly independent of composition, especially for the case with region III at a higher energy. In Fig. 6 are displayed the corresponding Kerr constant results. These show substantially more variation in passing from poly(glycine) to poly(alanine). In addition, results for the random sequence copolymer, the lowest curves in each set, evidence substantial curvature. The mean square polarizability anisotropies in the previous figure did not indicate significant similar effects.

Helix-Coil Transitions

We have chosen to treat the helix-coil transition in the simplest possible manner (Poland and Scheraga, 1970). The partition function formulated by Zimm and Bragg(1959) is

$$Z = (1\ 0)\begin{bmatrix} 1 & \sigma s \\ 1 & s \end{bmatrix}^{x-1}\begin{bmatrix} 1 \\ 1 \end{bmatrix} \tag{12}$$

This generates all occurrences of the two conformations, helix and coil along the molecule. Because of the substantial independence of each virtual bond in a polypeptide, it is possible to treat the random coil by independently averaging each residue over an energy map such as that indicated in abridged form in Fig. 4. We have

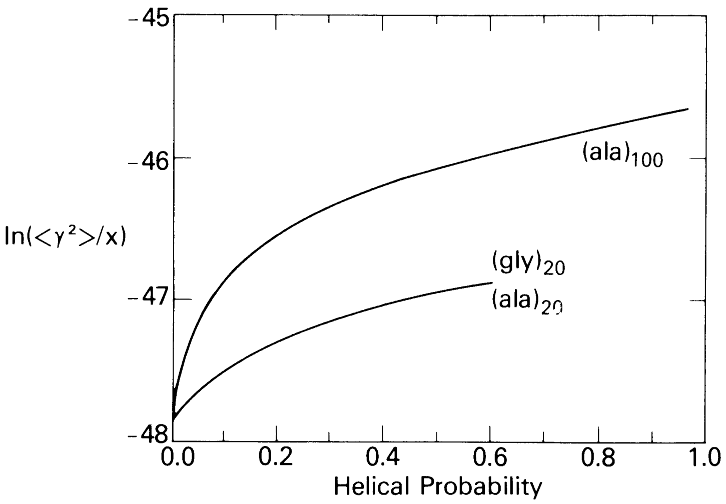

Fig. 7. Values of the mean square polarizability anisotropy per peptide through the helix-coil transition. $\langle\gamma^2\rangle$ is expressed in units of cm^6. Both glycine and alanine curves are coincident. The lower curve is for 21 peptide bonds and the upper one for 101. The abscissa is the fraction of residues in helical form.

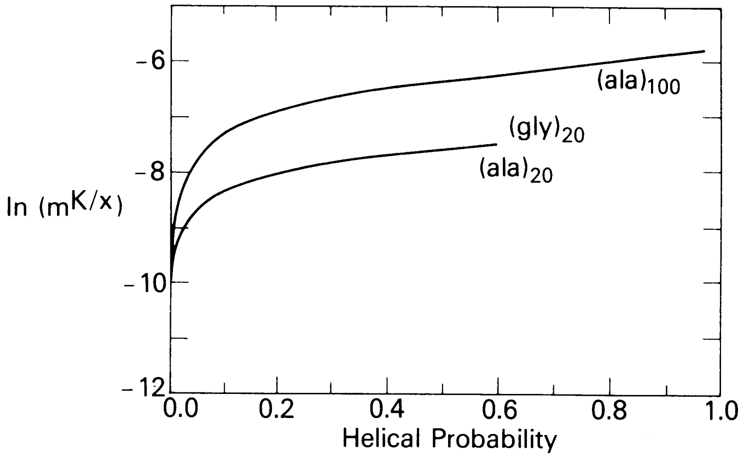

Fig. 8. The Kerr constants for finite polypeptide chains through the helix-coil transition. $_mK$ is expressed in units of cm^5 statvolts^{-2} mol^{-1}. Designations are the same as those in Fig. 7.

chosen a Kerr constant value from the contour map in Fig. 4 for the helix conformation at ϕ =122, ψ =133. Calculations are for a temperature of 25 and $\sigma = 10^{-4}$. The averages in eq (2) are easily obtained with the partition function in eq (12). Results for both the mean square polarizability anisotropy and the molar Kerr constant are presented in Figs. 7 and 8. Both figures are for the same set of parameters. The most noteworthy feature is that the Kerr constant curve increases more sharply at significantly smaller helix fractions than does the mean square polarizability anisotropy. This occurs because the latter quantity, for a rigid rod, depends on the square of the molecular weight, but the Kerr constant, for rigid polar molecules, depends on the cube of the molecular weight. Hence Kerr constant measurements are more sensitive to initial stages of the onset of rigidity than are most other methods.

DISCUSSION AND SUMMARY

From the evidence collected here, it is apparent that the Kerr constant is most sensitive to conformation in those polymers with large dipole moments. This effect is especially sizable in the results presented for polar vinyl polymers.

For nonpolar molecules, interactions of the bond polarizabilities, through induced dipole-induced dipole interactions, may be important. The determination of the effective range of such interactions remains as an experimental problem. The results calculated here, for the n-alkanes with short range interactions between bond polarizabilities, fit the experimental data well; however, similar results can be obtained with many combinations of the parameters. Only further careful experimental determinations of bond polarizabilities will be able to resolve this issue.

In polar molecules, the potential for significant interactions is even greater. In addition to induced dipole-induced dipole interactions, there is the possibility of a hyperpolarizability contribution to the induced interactions.

If interactions of these types are in fact important, they may possibly account for the broad range of values of bond polarizabilities reported for nearly identical chemical bonds. A possible alternative to the present approach would be a quantum mechanics evaluation of the dependences of group polarizabilities on conformations.

Also it should be pointed out that the physical state and details of solution conditions can play an important role in determining the relative importance of interactions. Two reports make evident this possibility. Buckingham and Sutter (1976) concluded, from gas phase measurements on n-alkanes, that bond polarizabilities are not additive. In the gas state, the range of interactions for the largest molecules may be longer than at theta conditions because of the possibility that the molecules are more collapsed. By contrast, Meeten (1968) concluded that, for solutions of n-alkanes, the mean second hyperpolarizabilities were additive.

The calculations presented on the helix-coil transition in polypeptides make it clear that different experimental methods may monitor different stages in that transition. Because the molecular weight dependence of the Kerr constant for helix is different than for mean square moments, the Kerr effect is expected to be more sensitive to the initial onset of rigidity.

The polar peptides (Khanarian, 1980) present an excellent opportunity for study of their conformations by Kerr measurements. The abundance of small polypeptides isolated recently from biological sources makes this method particularly important.

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