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Dependence of some conformational properties of polyglycine on composition and sequence of secondary structure

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The values of four conformational properties, unperturbed dimensions $\langle r^2 \rangle_0$, dipole moment $\langle \mu^2 \rangle$, mean squared optical anisotropy $\langle \gamma^2 \rangle$ and molar Kerr constant $\langle {}_mK \rangle$, have been calculated for polyglycine chains of $x = 100$ repeat units with varying composition of α-helix, β-sheet and random coil conformations. The influence of the conformational sequence on these properties has been investigated by calculating the four above-mentioned properties together with the end-to-end vector for several polyglycine oligomers.

1. Introduction

In previous papers [1,2] dealing with the influence of secondary structure on the theoretical values of some conformational properties for polyglycine chains, the sensitivity of the dimensions, dipole moments, optical anisotropy and especially the Kerr constant to the different conformations (α-helix [3], β-sheet [4] or random coil) of the repeat units was investigated. Polyglycine chains with all their units in one of the conformations or with varying composition of two of the above-mentioned structures (i.e., α-helix/random coil, β-sheet/random coil and α-helix/β-sheet) were investigated. The choice of the simplest polypeptide, polyglycine, was made in order to diminish the number of parameters to be considered in the calculation; thus, the influence of primary structure on the magnitudes of these conformational properties, exhaustively studied before [5–9], was omitted.

The combined results obtained for these four magnitudes covered a considerable range of values and offered the possibility of being used as a way of determining secondary structures. Moreover, for polyglycine chains with different composition of two rigid conformations, i.e., α-helix/β-sheet chains, the dispersion in the results [2], indicated a marked effect of the conformational sequence. Hence, the calculated values of the conformational properties depend not only on the relative amounts of each of the conformations but in some cases on their order. This sequence effect was already reported for the primary structure [8] and the fact that it has been observed for the secondary structure should open up, at least in principle, interesting perspectives for studying the conformations that polypeptides may adopt. Hence, these calculations can be utilized to evaluate the usefulness of the studied properties in characterizing conformations of polypeptides. The sensitivity to changes in conformation of these properties must be judged

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against the results of more common characterization methods.

In this paper, two approaches have been taken in order to examine both composition and sequence effects of secondary structure of polyglycine on the above-mentioned conformational properties. In the first, the dimensions, dipole moments, optical anisotropy and the Kerr constant of polyglycine chain with varying compositions of the three conformations, α-helix, β-sheet and random coil, have been calculated. In the second, the same four magnitudes and the end-to-end vector were studied for polyglycine oligomers with the aim of investigating the sequence effect.

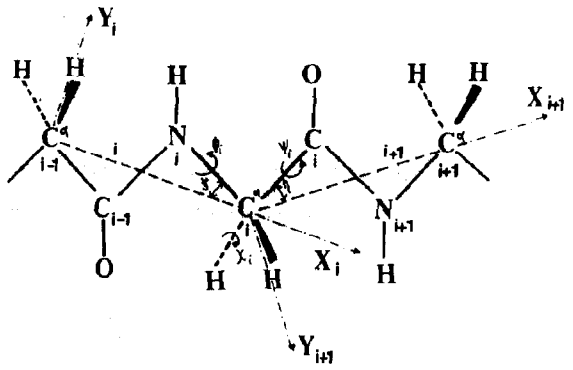

Fig. 1. A segment of a polyglycine chain in its planar all-*trans* conformation ($\phi_i = \psi_i = 0$). Virtual bonds connecting consecutive α-carbons are shown by dashed lines. Coordinate systems are represented by dotted-dashed lines. z-axes complete right-handed frames.

2. Scheme of calculations

Values of the five conformational properties studied for polyglycine chains comprising x units in a given conformation may be calculated using Flory's method of matrix multiplication [10,11] as follows.

The end-to-end vector $\boldsymbol{r}$ which connects the ends of the chain may be evaluated by serial multiplication of generator matrices

$$\boldsymbol{r} = \prod_{i=1}^{x} \boldsymbol{A}_i \tag{1}$$

where $\boldsymbol{A}_i$ represents a 4×4 generator matrix defined [11] as

$$\boldsymbol{A}_i = \begin{bmatrix} \boldsymbol{T} & \boldsymbol{l} \\ \boldsymbol{0} & 1 \end{bmatrix}_i \quad 1 < i < x \tag{2}$$

where $\boldsymbol{l}_i$ represents the length of unit i written in the coordinate system affixed to bond i. $\boldsymbol{T}_i$ is the matrix that by premultiplication transforms a vector from the $i+1$ to the i bond coordinate system (see fig. 1). $\boldsymbol{A}_1$ and $\boldsymbol{A}_n$ in eq. 1 represent, respectively, the first row and last column of the $\boldsymbol{A}$ matrices defined by eq. 2.

The square of the end-to-end distance is given by the scalar product of $\boldsymbol{r}$ with itself and may be evaluated by serial multiplication of generator matrices

$$r^2 = \prod_{i=1}^{x} \boldsymbol{G}_i \tag{3}$$

where the $\boldsymbol{G}_i$ represent 5×5 generator matrices defined elsewhere [10,12].

The square of the dipole moment of the chain μ^2 may be evaluated by an expression similar to eq. 3 with substitution of the dipole moment vector of unit i, $\boldsymbol{\mu}_i$ [6], for $\boldsymbol{l}_i$ in the generator matrices $\boldsymbol{G}_i$.

The square optical anisotropy, γ^2, is defined as [13–15]

$$\gamma^2 = 3/2 \,\mathrm{Trace}\,(\hat{\boldsymbol{\alpha}}\hat{\boldsymbol{\alpha}}) \tag{4}$$

where $\hat{\boldsymbol{\alpha}}$ is the anisotropic part of the polarizability tensor $\boldsymbol{\alpha}$ of the molecule. Computation of γ^2 for the chain, which requires previous knowledge of the contributions to the anisotropic part of the polarizability tensor $\hat{\boldsymbol{\alpha}}_i$ of each repeat unit [7], may be accomplished as

$$\gamma^2 = 3/2 \prod_{i=1}^{x} \boldsymbol{P}_i \tag{5}$$

where $\boldsymbol{P}_i$ is an 11×11 generator matrix defined elsewhere [10,12,16].

The last conformational magnitude studied, the Kerr constant of a given molecule, governs the birefringence produced by an electric field in a sample of independent and uncorrelated molecules and can be calculated as [17,18]

$${}_mK = \frac{2\pi N}{15kT}\left\{\frac{\boldsymbol{\mu}^T\hat{\boldsymbol{\alpha}}\boldsymbol{\mu}}{kT} + \frac{\epsilon - 1}{n^2 - 1}\mathrm{Trace}(\hat{\boldsymbol{\alpha}}\hat{\boldsymbol{\alpha}})\right\} \tag{6}$$

where N is Avogadro's number, k Boltzmann's constant, T the absolute temperature, ϵ the static dielectric constant of the medium, n its refractive index and μ the permanent dipole moment. The term $\mu^T\hat{\alpha}\mu$ can be calculated as

$$\mu^T\hat{\alpha}\mu = \prod_{i=1}^{x} Q_i \tag{7}$$

where the Q_i are the 26×26 generator matrices defined elsewhere [10].

Eqs. 1, 3, 5 and 7 are used as written for ordered conformations such as α-helix or β-sheet, however, in the case of random coil units averages of these equations over all the conformations of the chain must be performed. Because of the substantial independence of each virtual bond in polyglycine, it is possible to treat the random coil by independently averaging each repeat unit [19]. Hence, averages can be obtained by replacing the generator matrices A_i, G_i, P_i and Q_i by their corresponding $\langle A_i \rangle$, $\langle G_i \rangle$, $\langle P_i \rangle$ and $\langle Q_i \rangle$ over the skeletal bonds ϕ_i and ψ_i (see fig. 1). As is customary, the absolute values of the magnitudes for the whole chain were transformed into values for the repeat unit defined as $C_x = \langle r^2 \rangle_0 / xl^2$, $D_x = \langle \mu^2 \rangle / x\mu_0^2$, $G_x = \langle \gamma^2 \rangle / x$ and $K_x = \langle {}_mK \rangle / x$ where x is the degree of polymerization, l the virtual bond length and μ_0 the dipole moment of the repeat unit. C_x and D_x are dimensionless and G_x and K_x are given in the corresponding units.

3. Secondary structures

Three possible conformations for the repeat unit have been considered. The α-helix can be generated using values of 124.8 and 134.8° for the rotation ϕ_i and ψ_i, respectively [1] (we have used Flory's convention [10] for these angles; see fig. 1); these values together with the geometrical parameters given by Scheraga and co-workers [20] permit one to obtain the corresponding transformation matrix as

$$T_\alpha = \begin{bmatrix} -0.010 & -0.582 & -0.813 \\ -0.335 & 0.768 & -0.546 \\ 0.942 & 0.267 & -0.203 \end{bmatrix}$$

which is the one used throughout this work.

In order to generate a parallel β-sheet, rotation angles of $\phi_i = 65.05°$ and $\psi_i = 289.1°$ [2] together with the geometrical parameters given by Scheraga et al. [20] have been used. Thus, the transformation matrix can be written as

$$T_\beta = \begin{bmatrix} 0.427 & -0.074 & 0.901 \\ -0.074 & -0.996 & -0.047 \\ 0.901 & -0.047 & -0.431 \end{bmatrix}$$

The third possibility considered for the structure of a unit is random coil, i.e., it is assumed that the chain is not in a fixed structure but, instead, each bond can adopt several orientations according to the interaction of the atoms whose positions depend upon those orientations and, as explained above, the calculations for this structure require the use of averaged matrices. In the present work, we have used the $\langle T \rangle$ matrix reported by Saiz et al. [5].

$$\langle T \rangle = \begin{bmatrix} 0.379 & -0.156 & 0 \\ 0.086 & -0.449 & 0 \\ 0 & 0 & -0.201 \end{bmatrix}$$

4. Results and discussion

4.1. Polyglycine chains

We present in this section the results calculated for polyglycine chains whose repeat units can adopt α-helix, β-sheet or random coil conformations. The compositions of the chains were characterized by the fractions f_α, f_β and f_c of units in α-helix, β-sheet and random coil conformations, respectively. It is sufficient to give two of the fractions to specify a given chain, since $f_\alpha + f_\beta + f_c = 1$. The values presented below were obtained for chains with $x = 100$ repeat units whose conformations were assigned using a random numerical procedure, with the restriction of the predetermined values of the fractions f_α, f_β and f_c. Each of the fractions f_α, f_β and f_c has been varied between 0 and 1 with increments of 0.05. Ten chains of the same composition were independently generated, and all the values presented are averages over those 10 chains. The choice of averages of 10 chains [2] was made in order to de-

crease the sequence effect in the calculated magnitudes but not to exclude it, since we are interested not only in the influence of the conformational chain composition but also in the conformational sequence. Thus, the dispersion of the calculated values will provide us with a way to estimate the relative importance of the sequence effect.

Figs. 2–5 represent the results obtained for unperturbed dimensions, dipole moment, optical anisotropy and Kerr constant, respectively. All these figures are triangular diagrams since they automatically ensure that the condition $f_\alpha + f_\beta + f_c = 1$ is fulfilled. The three apexes represent those polyglycine chains with all their units in the same conformation – α-helix, β-sheet or random coil, i.e., $f_\alpha = 1$, $f_\beta = 1$ or $f_c = 1$, respectively. The edges correspond to those polyglycine chains with two possible conformations for their repeat units, i.e., the opposite edge to the apex for which $f_\alpha = 1$, represents all the polyglycine chains without α-helix units and thus $f_\beta + f_c = 1$. A polyglycine chain of any composition can be represented by a point in the interior of the triangle. The lines parallel to each side of the triangle represent those chains with a fixed fraction of one of the conformations and varying composition of the other two. An important property of a triangular diagram is the significance of a straight line joining an apex to a point on the opposite edge. Any point along the indicated line represents a composition that is progressively richer in the component of the apex as it goes from the edge to the apex, while the other two components remain present in the same initial proportions.

In all these figures the circles, squares and triangles represent the calculated values of C_x, D_x

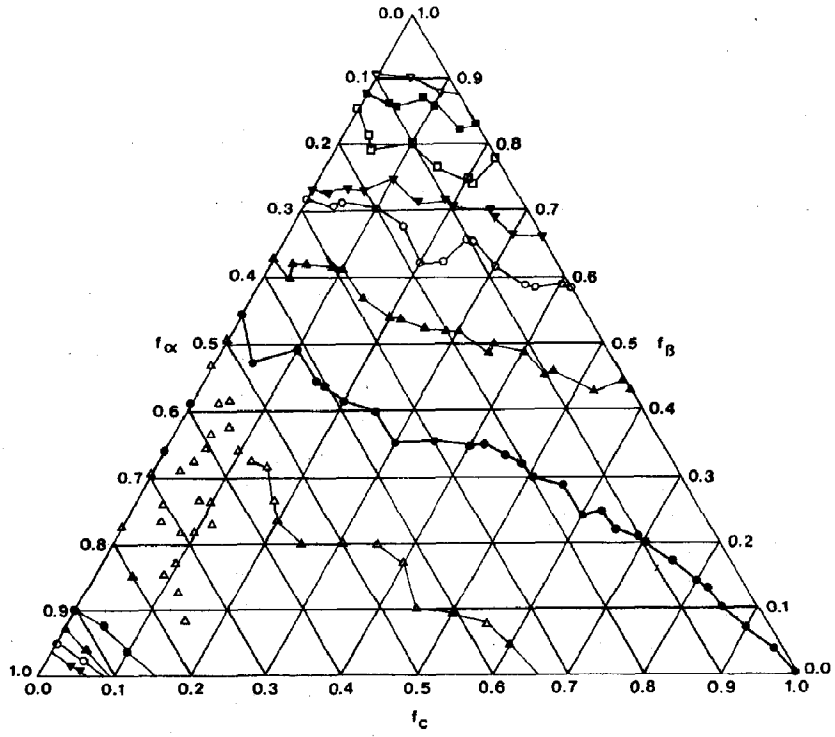

Fig. 2. Dependence of C_x on chain conformation; f_α, f_β and f_c represent the fractions of α-helix, β-sheet and random coil, respectively. Similar values of C_x are represented by like symbols; $C_x = 13.0$ (▽), $C_x = 10.0$ (■), $C_x = 7.0$ (□), $C_x = 5.0$ (▼), $C_x = 4.0$ (○), $C_x = 3.0$ (▲), $C_x = 2.2$ (●), $C_x = 1.5$ (△).

and G_x and natural logarithm of K_x; the lines are plotted only to facilitate the following of the variation of the magnitude and are not adjusted by any numerical procedure.

The values calculated for C_x are represented in fig. 2. Those chains with different composition which give similar values for C_x are represented by the same symbol and joined by a solid line when possible. A heavier line indicates the chain for which $C_x = 2.16$, the value of an all random coil polyglycine chain. As can be seen in this figure, this line bisects the angle at $f_c = 1$, thus all the polyglycine chains with the same proportion of α-helix and β-sheet conformations ($0 < f_\alpha = f_\beta < 0.5$) not only have the same value of C_x but it also coincides with that for a chain in random coil ($f_c = 1$). Thus, regardless of the proportion of random coil conformations, those chains with equal proportions of the two rigid conformations α-helix and β-sheet have a value of C_x similar to the asymptotic value of C_x for random coil chains. Qualitatively, the explanation is straightforward, since the effect of each interruption of a rigid polyglycine chain by other conformations causes the chains to fold and thus, to vary its direction [2], the result being a plegate chain with dimensions similar to those of a random coil.

As can be seen in the lower part of fig. 2, for a value of the fraction of α-helix higher than 0.5 and lower than 0.9 ($0.5 < f_\alpha < 0.9$) the dimensions of the chain keep decreasing, acquiring remarkably low values, much smaller than for random coil chains. It is worth pointing out that even in chains with a high content of α-helix such as 85%, it is sufficient for 15% of random coil or β-sheet units to lower drastically the value of C_x from the corresponding value to an all α-helix chain ($C_x = 17.4$). If $f_\alpha > 0.9$ (left apex in fig. 2) the value of C_x increases, tending towards the value for an all α-helix chain ($C_x = 17.4$). On the other hand, for the upper part of the figure (i.e., $0 < f_\alpha < 0.5$ and $0.5 < f_\beta < 1$) the dimensions increase as the fraction of f_c diminishes and thus f_β increases, since the β-sheet is the most extended conformation. In this part of the figure, the value of f_β is dominant, i.e., as f_β increases C_x grows, and the fact that the remaining units ($1 - f_\beta$) are α-helix or random coil is secondary in importance. The value of C_x for an all β-sheet ($C_x = 71.4$) is drastically lowered with a few units in another conformation; thus, for $f_\beta \simeq 0.9$, $C_x = 13.0$.

Summarizing these results, increasing values of C_x from 2.16 to 17.4 will indicate a chain content of β-sheet increasing from 0.5 to 0.9 or a content of f_α greater than 0.9. Values of C_x less than 2.16 will indicate values of f_α between 0.5 and 0.9. This magnitude cannot provide information on the content of random coil conformations. As we are going to see this information can be improved with the results obtained for the other three magnitudes.

Fig. 3 shows the results obtained for D_x. The difference between figs. 2 and 3 can be explained by taking into account the differences between the lengths and dipole moments for the three conformations of interest. To the most extended conformation, β-sheet, corresponds the lowest dipole moment ($D_x = 0.21$ for an all β-sheet chain) which is very close to the value for a random coil chain ($D_x = 0.37$), whereas the highest value of the dipole moment concerns the α-helix conformation ($D_x = 81.3$). As in fig. 2, a heavier line indicates the values of D_x corresponding to a polyglycine chain in random coil conformation. This line corresponds to polyglycine chains with a low content of α-helix conformation, $f_\alpha < 0.2$, and proportion $f_\alpha/f_\beta \simeq 1/3$. If f_α increases, the value of D_x increases until $D_x = 81.3$ (corresponding to a pure α-helix chain) irrespective of the relative proportions of f_β and f_c. This is easily explained since, as stated above, the random coil or β-sheet conformations produce chains with very low dipole moments. Thus, the value of D_x for a given polyglycine chain will give information on the content of α-helix provided that this content is greater than 20%, therefore this magnitude together with C_x would provide a description of the α-helix and β-sheet contents of the chain over an adequate range.

The values obtained for G_x are depicted in fig. 4. Given that the values of this magnitude for α-helix chains ($G_x = 140.0 \times 10^{-6}$ nm^6) and β-sheet ($G_x = 172.2 \times 10^{-6}$ nm^6) are much greater than that for random coil ($G_x = 3.27 \times 10^{-6}$ nm^6), the lowest value obtained is for an all random chain ($f_c = 1$) so there is no heavier line as in figs.

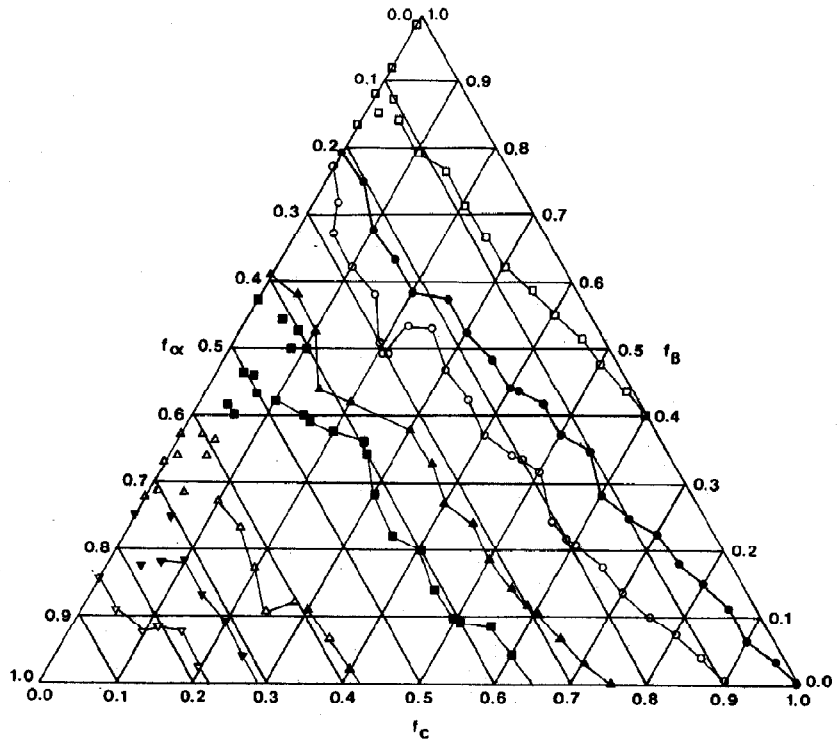

Fig. 3. Dependence of D_x on chain conformation (see legend to fig. 2). $D_x = 5.0$ (▽), $D_x = 3.0$ (▼), $D_x = 2.0$ (△), $D_x = 1.0$ (■), $D_x = 0.8$ (▲), $D_x = 0.5$ (○), $D_x = 0.37$ (●), $D_x = 0.2$ (□).

2 and 3. As f_c increases, i.e., conformation units in α-helix or β-sheet are added to the chain, G_x increases. Thus, for all lines joining the apex $f_c = 1$ and the opposite edge (three dashed lines plotted in fig. 4), which represent values of f_c decreasing from $f_c = 1$ to $f_c = 0$, each with the same f_α/f_β value, G_x increases. However, the dispersion of the points is great due to the different contributions of α-helix or β-sheet units to the total value of the anisotropy, as can be seen from one line to another. The optical anisotropy may be used as a probe of the random coil content of the chain, especially together with the dimensions and dipole moment which provide information about the contents of α-helix and β-sheet.

The results obtained for the three magnitudes studied thus far complement each other in the sense of deducing the chain conformation, although within a wide margin of error. Nevertheless, these wide limits can be reduced by studying the fourth considered magnitude, the Kerr constant. The results obtained for this magnitude are represented in fig. 5. As will be readily apparent from even a cursory examination of figs. 3 and 5, a similar behavior of D_x and K_x is observed. This similar behavior is easily understood if we consider the great importance of the dipole moment term in the total value of the Kerr constant.

As stated above the Kerr constant can be computed as the sum of two contributions (eq. 5), one depending on the product $\boldsymbol{\mu}^T\hat{\boldsymbol{\alpha}}\boldsymbol{\mu}$ and the other proportional to trace $(\hat{\boldsymbol{\alpha}}\hat{\boldsymbol{\alpha}})$. When the polymer studied has a permanent dipole moment, as in the case of polyglycine, the second term is negligible compared to the first and the K_x results are similar, but for a scale factor, to those of D_x which depend on the product $\boldsymbol{\mu}\boldsymbol{\mu}$. The major difference is the enormous variation in K_x, which forces us to use ln K_x, instead of K_x, ranging between $K_x = 1.83 \times 10^7$ (ln $K_x = 16.7$) for an

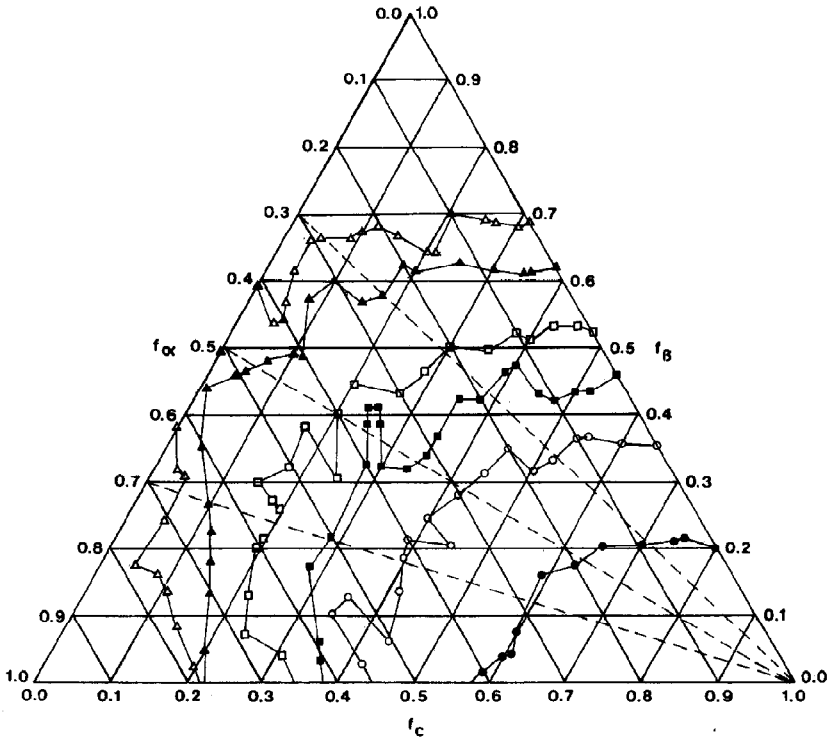

Fig. 4. Dependence of G_x on chain conformation (see legend to fig. 2). $G_x = 11.0$ (△), $G_x = 9.0$ (▲), $G_x = 7.0$ (□), $G_x = 6.0$ (■), $G_x = 5.0$ (○), $G_x = 4.0$ (●).

α-helix chain and 275.8 (ln $K_x = 5.62$) for a random coil chain both in units of 10^{-27} m^5 V^{-2} mol^{-1}.

The Kerr constant, together with the three other magnitudes, thus offers great possibilities from the theoretical point of view as a way of determining secondary structures in polypeptides. However, there is a disadvantage of this magnitude; the influence of the sequence for a chain with a given value of f_α, f_β and f_c, which is noticeable in the other three magnitudes, becomes greater for the Kerr constant, especially for those chains with a high content of α-helix or β-sheet conformations, leading to extensive dispersion of the points. This sequence effect hinders the interpretation of the results but, from another point of view, offers interesting perspectives for the elucidation not only of the relative amounts of the different conformations but, perhaps, of their sequence as well, as described in section 4.2.

4.2. Glycine oligomers

Given the importance of the conformational sequence, especially in polyglycine chains with α-helix and β-sheet conformations, in the calculated values of the properties considered we undertook a study of short chains of glycine, the results of which are presented here. The number of residues in the chain is denoted by x. If $x = 2$, there are three dipeptides that are denoted by c, α and β which means that the conformation of the second unit of glycine with respect to the first is random coil, α-helix or β-sheet, respectively. Three sets of tripeptides are allowed when $x = 3$, yielding nine possibilities for the joining of three repeat units which are represented by adding a new symbol (c, α or β), corresponding to the conformation of the third repeat unit, to the notation of dipeptides. If $x = 4$, there are 27 tetrapeptides with different sequence conformation considered,

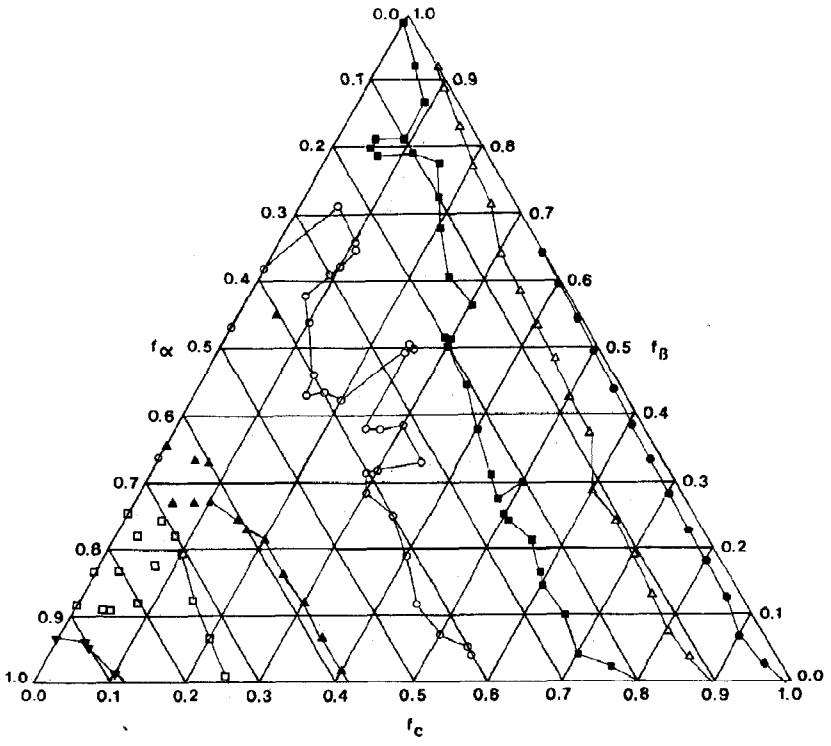

Fig. 5. Dependence of ln K_x on chain conformation (see legend to fig. 2). ln $K_x = 13.0$ (▼), ln $K_x = 11.0$ (□), ln $K_x = 10.0$ (▲), ln $K_x = 9.0$ (○), ln $K_x = 8.0$ (■), ln $K_x = 7.0$ (△), ln $K_x = 6.0$ (●).

and the notation is extended by adding a new symbol for the conformation of the fourth unit. Through all the calculations we have used the geometry of the units in the required conformation, with the sole purpose of studying influence of the sequence on the magnitudes without taking into account the actual possibility of having a few isolated units of a chain in a rigid conformation such as β-sheet or α-helix.

In the case of dipeptides, the calculated results for the end-to-end vector and for C_x are those expected, since the β-sheet conformation is the most extended and for $x = 2$ the asymptotic limit of C_x has not been reached. Thus, the highest value of C_x is found for dipeptide β ($C_x = 1.43$) and the lowest for α ($C_x = 0.99$). In a similar way, the presence of β-sheet in tripeptides contributes to a more extended chain (i.e., $C_x = 2.24$ for $\beta\beta$; $C_x = 0.61$ for $\alpha\alpha$) but the effect of the sequence for rigid conformations begins to increase. Thus it is worth pointing out the different dimensions obtained for $\alpha\beta$ and $\beta\alpha$ for which r has the values 0.6 and 0.9 nm, respectively, corresponding to C_x values of 0.82 and 1.86, respectively. This same behavior is encountered in tetrapeptides for which the greatest dimensions are for chains starting with $\beta\beta$, namely, $\beta\beta\beta$ ($C_x = 2.85$), $\beta\beta\alpha$ ($C_x = 2.35$) and $\beta\beta$c ($C_x = 2.38$), whereas the smallest dimensions calculated are for chains commencing with $\alpha\alpha$, namely, $\alpha\alpha$c ($C_x = 0.73$), $\alpha\alpha\alpha$ ($C_x = 0.76$) and $\alpha\alpha\beta$ ($C_x = 0.70$). The sequence effect is noted not only for those chains with rigid conformations such as α-helix or β-sheet, but also for those composed of rigid conformations and random coil ones. The presence of β-sheet at the beginning of the chain is decisive in obtaining more extended chains. These facts can be explained by taking into account the effect of an interruption by one unit in a different conformation which causes the chains to fold [2]. This effect is much more pro-

nounced in extended chains, hence the value obtained for $\beta\alpha\beta$ ($C_x = 1.48$) is much smaller than those stated above for $\beta\beta\ldots$ tripeptides.

The values calculated for D_x can be easily explained by taking into account the fact that the α-helix is the conformation with the highest dipole moment and the β-sheet that with the lowest. Thus, the highest values are for α ($D_x = 1.77$), $\alpha\alpha$ ($D_x = 2.46$) and $\alpha\alpha\alpha$ ($D_x = 3.26$) for di-, tri- and tetrapeptides, respectively, the lowest being for β ($D_x = 0.004$), $\beta\beta$ ($D_x = 0.34$) and $\beta\beta\beta$ ($D_x = 0.01$). Besides this fact, there is a significant difference between the results obtained for C_x and D_x; in the last case, the same values are obtained for reverse oligomers (i.e., XY and YX; XYZ and ZYX) and the sequence effect is only observed if the conformational sequence is permuted (i.e., XYZ and YZX).

The results obtained for optical anisotropy G_x show that this magnitude is the least sensitive to both the sequence and value of x. The values of G_x for the dipeptides are very close, 3.20, 3.20 and 3.45 (in units of 10^{-6} nm^6) for c, α and β, respectively, and taking into account that G_x for c structure approaches a limit and G_x increases for α and β in a similar way, the effect of sequence is not very pronounced. However, this effect for rigid conformations can be observed in different values obtained for $\alpha\beta$ and $\beta\alpha$ tripeptides, $\alpha\beta\beta$, $\beta\beta\alpha$ and $\beta\alpha\beta$ tetrapeptides, etc. The highest values for tetrapeptides are for $\beta\beta\beta$ ($G_x = 6.89 \times 10^{-6}$ nm^6), $\alpha\beta\beta$ ($G_x = 6.15 \times 10^{-6}$ nm^6), $\alpha\alpha\alpha$ ($G_x = 5.99 \times 10^{-6}$ nm^6) and $\beta\alpha\alpha$ ($G_x = 5.41 \times 10^{-6}$ nm^6); the lowest are obtained for sequences with two c conformations or one c in the middle position such as ccα ($G_x = 3.10 \times 10^{-6}$ nm^6) and $\alpha c\alpha$ ($G_x = 2.97 \times 10^{-6}$ nm^6). The low dependence on optical anisotropy of the glycine oligomers of x for $x = 2$–4 which had been reported previously [21] is easily seen for peptides containing the coil structure. Thus, the values obtained for c, cc and ccc are 3.20, 3.31 and 3.26×10^{-6} nm^6, respectively, and for α, αc and αcc 3.20, 3.34 and 3.34×10^{-6} nm^6, respectively.

In the results calculated for the Kerr constant the striking sensitivity of this magnitude becomes readily apparent. Its values for tetrapeptides range from $K_x = -672$ for $\alpha\beta\alpha$ to 2.9×10^4 for $\alpha\alpha\alpha$ in units of 10^{-27} m^5 V^{-2} mol^{-1}. The behavior for the different sequences is similar to D_x, due, as stated above, to the strong influence of the dipole moment term in the total value. Thus, reverse oligomers (such as XY and YX, XYY and YYX, XYZ and ZYX, etc.) have similar values of K_x whereas if the order is permuted, K_x changes drastically, i.e., K_x ($\alpha\alpha\beta$) $\simeq K_x(\beta\alpha\alpha) = 5.5 \times 10^3 \neq K_x(\alpha\beta\alpha = -672$ in units of 10^{-27} m^5 V^{-2} mol^{-1}. This strong sensitivity to conformation makes the Kerr constant a particularly attractive property for studying polypeptides and proteins, although the other magnitudes, especially the dimensions, would complement such studies. In the literature [21] there are experimental data for the Kerr constant of aqueous solutions of di-, tri- and tetraglycine, expressed as values of $B = \Delta n/\lambda E^2$ without indicating units. In order to compare these data with our results we have calculated the corresponding values of K_x supposing the units were StatV^{-2} cm, giving values of $K_x = 190$, 256 and 251×10^{-27} m^5 V^{-2} mol^{-1} for di-, tri- and tetraglycine, respectively. Comparison of experimental results with our calculated values is not very easy, since we have not calculated the values of K_x for oligomers of glycine in their more stable conformations, but the values for rigid conformations (α and β) in which it is very improbable that such short chains of glycine will be found and for the random coil conformation. With respect to the random coil the values calculated ($K_x = 718$, 816 and 601×10^{-27} m^5 V^{-2} mol^{-1} units for c, cc and ccc, respectively) are of the same order of magnitude but greater than the experimental results. Although the discrepancy is not great if we take into account the enormous variation of K_x as stated above, we cannot state that the oligomers of glycine are in the random coil or in a different preferred conformation.

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