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Representative Configurations of Unperturbed Poly(L-alanine) Chains

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ABSTRACT: Representative unperturbed poly(L-alanine) chains have been generated using Monte Carlo methods and the conformational energy surface obtained by Brant, Miller, and Flory (Brant, D. A.; Miller, W. G.; Flory, P. J. *J. Mol. Biol.* **1967**, *23*, 47–65). This conformational energy surface has previously been shown to reproduce unperturbed dimensions of several homopolypeptides and denatured proteins. Representative poly(L-alanine) chains have the overall character of a random coil. They contain no evidence whatsoever of α-helical character at the local level. Instead there are occasional stretches that resemble the conformation adopted in the pleated sheet. These stretches may extend over as many as ten residues. They are of a length comparable to strands in the pleated sheets found in globular proteins. Propagation of the minimum-energy configuration would result in a left-handed helix with three residues per turn. In the representative chains, however, sequences that approximate a left-handed helix with three residues per turn occur much less frequently and are considerably shorter than sequences containing about two residues per turn. This situation arises because most unperturbed L-alanyl residues adopt conformations that are distributed over a rather broad region of low conformational energy. At one corner of this low-energy region lie conformations that can propagate a left-handed helix with three residues per turn. A longer traverse through the broad region of low conformational energy is found for a contour line on which lie conformations that would propagate a helix with two residues per turn.

Characteristic ratios, C_∞, for polypeptides are conveniently defined as $\langle r^2\rangle_0/n_p l_p^2$, where $\langle r^2\rangle_0$ denotes the mean square unperturbed end-to-end distance for a chain containing n_p virtual bonds of length l_p.[1] Virtual bonds, of length 380 pm, link consecutive C^α atoms when standard peptide units are retained in the planar trans configuration. Due to the difficulty in finding Θ solvents for disordered homopolypeptides, experimental characteristic ratios are usually based on measurements of the mean square perturbed dimensions in a good solvent. An estimation of the expansion coefficient is used to obtain $\langle r^2\rangle_0$.[1-6] Experimental results have ranged from values as low as 2–3 for several sequential copolypeptides rich in glycyl residues[4] to values as large as 23 for poly(L-proline) in organic solvents at low temperature.[3] A much narrower range is obtained if attention is restricted to experimental results obtained with homopolypeptides hearing a CH_2R side chain in the L configuration, as is shown in Table I. Characteristic ratios obtained for five such homopolypeptides fall in the range 8.6–10.

Characteristic ratios collected in Table I are subject to rationalization using a conformational energy surface computed for an unperturbed amino acid residue in poly(L-alanine). By evaluation of nonbonded interactions, intrinsic torsional potentials, and the electrostatic interaction of neighboring peptide units, Brant et al.[8] obtained a conformational energy surface that leads to a theoretical estimate of 9.3 for the characteristic ratio. This theoretical characteristic ratio is clearly in harmony with experimental results summarized in Table I. The conformational energy surface used to obtain a characteristic ratio of 9.3 is redrawn in Figure 1. The NMR coupling constant between the NH and $C^\alpha H$ protons of several homopolypeptides is well reproduced with this energy surface.[9] It also satisfactorily accounts for dipole moments of 14 small alanine peptides when combined with a conformational energy surface for the D-alanyl residue, obtained by reflection through the origin.[10]

When used in conjunction with additional conformational energy surfaces required for polypeptides containing glycyl[8,11] or L-prolyl[11,12] residues, the conformational energy surface obtained by Brant et al.[8] permits calculation of unperturbed dimensions for denatured proteins. The dominant conformational energy surface for the residues of typical proteins low in glycyl and L-prolyl content is the one depicted in Figure 1. Results obtained in this manner have been quite impressive.[13-15] For example, light-scattering measurements conducted on the denatured, crosslinked tropomyosin dimer in 5 M guanidine hydrochloride[16] yield an unperturbed root-mean-square radius of gyration of 8.33 nm, which is in excellent agreement with the calculated value of 8.75 nm.[14] Bovine myelin basic protein in water is calculated to have an unperturbed root-mean-square radius of gyration of 4.64 nm,[15] while small-angle X-ray scattering yields an unperturbed root-mean-square radius of gyration of 4.56 nm.[17]

Since the conformational energy surface obtained by Brant et al.[8] has been shown to successfully capture many conformational characteristics of unperturbed amino acid residues bearing CH_2R side chains, it becomes of interest to examine representative chains generated with this surface. Representative chains are depicted and described

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Table I
Characteristic Ratios for Homopolypeptides with CH_2R Side Chains

amino acid residue	solvent	C^a	ref
β-benzyl-L-aspartyl	*m*-cresol	9.6	2
L-glutamyl	0.3 M sodium phosphate, pH 7.85	8.8	2
L-lysyl	1.0 M sodium bromide, pH 4.54	8.6	2
γ-benzyl-L-glutamyl	dichloroacetic acid	8.8	2, 7
(hydroxyethyl)-L-glutaminyl	water	10	4

[a] Typical uncertainty is ±10%.

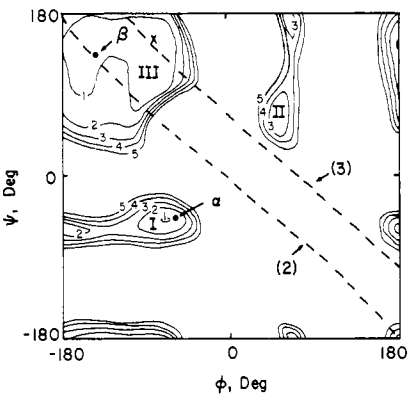

Figure 1. Conformational energy surfce for an L-alanyl residue (redrawn from ref 8). Contour lines are drawn at 1 kcal/mol intervals relative to the energy minimum, which occurs at the position denoted by ×. Dashed lines denote conformations that, if propagated throughout a long chain, yield a ribbon with two residues per turn (2) or a left-handed helix with three residues per turn (3). Conformations adopted by poly(L-alanine) in the helix and pleated sheet are denoted by α and β, respectively.

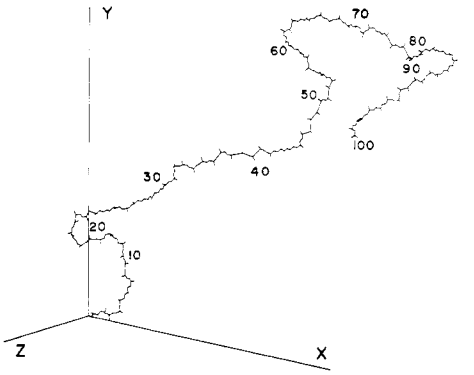

Figure 2. Representative poly(L-alanine) chain of 100 residues having a squared end-to-end distance near that obtained upon averaging over all chains. The *X,Y,Z* coordinates of the last atom are 4.48, 5.21, and −8.31 nm, respectively. For this chain $r^2/n_p l_p^2$ is 8.1.

in this paper. We also examine representative chains generated using portions of the conformational energy surface.

Methods

The polypeptide backbone geometry and conformational energy surface are those described by Brant et al.[8] The side chain is depicted as a single bond whose length has been exaggerated so that it is more readily visible in the representative configurations generated. Amino acid residues are assumed to behave independently. The residue configuration partition function, *z*, is defined as

$$z = \sum_{\phi}\sum_{\psi}\exp(-E_{\phi,\psi}/RT) \quad (1)$$

and the probability, $P_{\phi,\psi}$, for occupancy of a specified configuration is

$$P_{\phi,\psi} = z^{-1}\exp(-E_{\phi,\psi}/RT) \quad (2)$$

The conformational energy surface was sampled at 10° intervals for ϕ and ψ. Sampling excluded regions of the surface where the energy was more than 5 kcal/mol above the minimum. Additional portions of the surface were excluded in certain specified cases. The temperature was taken to be 300 K. Computer-generated plots were prepared for the configurations adopted by over 30 representative chains. The chain configurations selected for depiction here are among those in which, from the viewpoint adopted in the plotting routine, it proved relatively easy to follow the course of the polypeptide backbone.

Results and Discussion

Chains with Dimensions Close to $\langle r^2\rangle_0$. Long unperturbed poly(L-alanine) chains have a distribution of end-to-end distances because an appreciable portion of the conformational energy surface is accessible. An approximate indication of the form of this distribution was obtained from the squared end-to-end distances for 99 independently generated chains comprised of 200 residues each. The resulting distribution for $r^2/n_p l_p^2$ had a broad maximum near 10. Over 90% of the chains had $r^2/n_p l_p^2$ lying between 3 and 27.

Figure 2 depicts the configuration of a representative chain for which the dimensions are close to those found for the ensemble average. The conformation is representative of that expected for a random coil. This particular chain contains no residues from region II of the conformational energy surface in Figure 1. Seven residues (numbers 4, 14, 17, 34, 72, 79, and 85) adopt conformations that occur in region I. The remainder are from region III. This distribution is in reasonable accord with contributions each region makes to the residue configuration partition function. These contributions are 5.6% from region I, 1.0% from region II, and 93.4% from region III.[18]

It is of interest to examine the local structure of this chain for hints of the occurrence of three ordered structures. In the solid state, poly(L-alanine) is known to form a right-handed α helix, with $\phi,\psi = -57.4°, -47.5°$.[19] Since the representative chain depicted in Figure 2 does not have two or more consecutive residues occupying configurations from region I, it is not surprising that this chain shows no local evidence of an α-helical structure. The absence of any indication of local α-helical structure was common to all representative chains generated. This absence is easily rationalized. The local conformation of the α helix lies in a narrow region of low energy that must compete with the more numerous low-energy conformations found in region III. As a result of this competition, region I contributes only 5.6% of the residue configuration partition function.[18] That portion of the conformational energy surface within 5° of the α-helical configuration, i.e., the portion where $\phi = -57.4 \pm 5.0°$, $\psi = -47.5 \pm 5.0°$, contributes only a few tenths of the residue configuration partition function. Representative chains may contain several consecutive residues with the conformation found in an α helix if attractive interactions of longer range are operative.[20] The

Table II
Illustrative Small Pleated Sheets in Globular Proteins

protein	n^a	strands[b]	residues in each strand	ref
lysozyme, T4	164	3	3, 5, 4	23
lysozyme, hen	129	3	5, 5, 3	24
ribonuclease S	124	3	6, 7, 6	25
papain	212	3	6, 7, 7	26
plasma prealbumin	127	4	3, 9, 9, 9 9, 9, 7, 8	27
subtilisin	275	5	5, 5, 5, 6, 6	28
ferricytochrome b_5	87	5	3, 5, 5, 5, 5	29
adenylate kinase	194	5	5, 4, 5, 5, 5	30
thioredoxin-S_2	108	5	7, 8, 6, 5, 4	31
triosephosphate isomerase	247	8	7, 7, 4, 5, 8, 9, 5, 5	32
thermolysin	316	10	10, 10, 3, 2, 5, 6, 2, 6, 4, 4	33

[a] Number of amino acid residues in the polypeptide chain. [b] Number of strands in the pleated sheet (plasma prealbumin contains two sheets of four strands each).

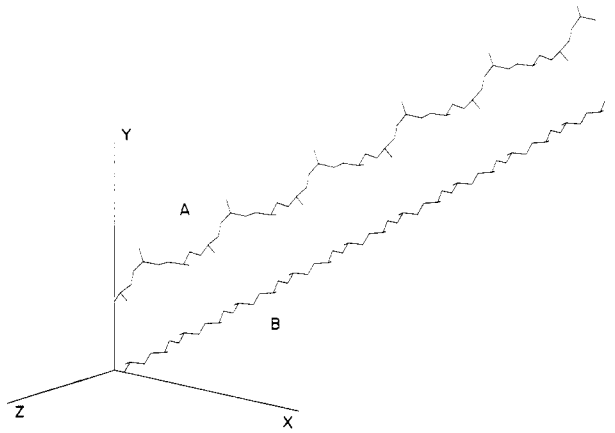

Figure 3. Poly(L-alanine) chain in which each residue has (A) ϕ,ψ = −80°, +150° (minimum-energy conformation, 17 residues) or (B) ϕ,ψ,ω = −138.8°, +134.7°, −178.5° (chain configuration adopted in the pleated sheet, 18 residues).

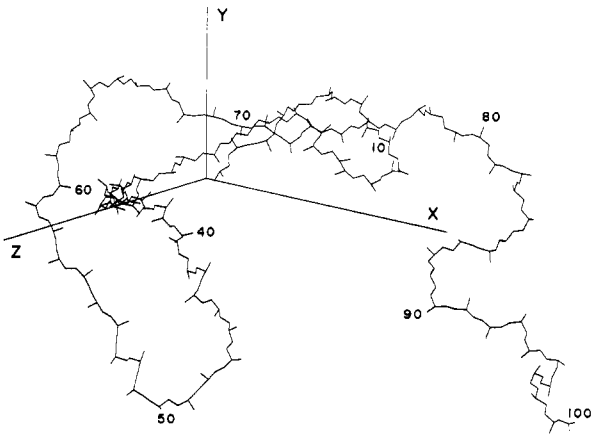

Figure 4. Representative poly(L-alanine) chain of 100 residues selected from the lower end of the distribution function for $r^2/n_p l_p^2$. The X,Y,Z coordinates of the last atom are 7.61, −1.24, and 2.25 nm, respectively. For this chain $r^2/n_p l_p^2$ is 4.5.

conformational energy surface for the unperturbed random coil (Figure 1) only includes interactions of peptide units i and $i + 1$, but the hydrogen bond involved in α helix formation occurs between peptide units i and $i + 3$. Interactions of at least this range are required to stabilize the α helix.

A second ordered structure adopted by poly(L-alanine) in the solid state is the pleated sheet. The L-alanyl residues have ϕ,ψ = −138.8°, 134.7°, and there is also a rotation of 1.5° about the peptide bond.[21] Figure 3B depicts a chain in which each residue adopts the conformation found in the poly(L-alanine) pleated sheet in the solid state. In the representative chains, local approximations to the pleated sheet configuration would appear as stretches where the chain is extended, with side chains i, $i + 2$, $i + 4$, etc. occurring on the same side of the main chain. The chain depicted in Figure 2 has several short sequences with these characteristics. These sequences may extend over as many as ten residues, as illustrated by residues 87–97 in the representative chain depicted in Figure 2. Thus representative unperturbed poly(L-alanine) chains contain local approximations to the conformation found in the pleated sheet, but there is no comparable evidence of a local tendency for α-helix formation.

It is of interest to compare the short approximations to the pleated sheet conformation that commonly occur in unperturbed poly(L-alanine) chains with the individual strands found in pleated sheets in globular proteins. While some globular proteins contain pleated sheets with strands longer than ten residues,[22] in many proteins, as shown in Table II, all strands contain fewer than ten residues. Precursors for many of these pleated sheets are of relatively common occurrence in the unperturbed poly(L-alanine) chain.

A third ordered structure of interest is that formed when all residues have ϕ,ψ = −80°, 150°. While this structure has not been observed with poly(L-alanine) in the solid state, it is the location of the energy minimum computed for the unperturbed L-alanyl residue. Propagation of the minimum-energy conformation produces a left-handed, nearly threefold helix, as shown in Figure 3A. Local approximations would appear as extended helices in which side chains i, $i + 3$, $i + 6$, etc. occur on the same side. Segments with these characteristics can be found, but they are not as common as approximations to the pleated sheet chain configuration. An example of an approximation to a threefold helix is provided by residues 4–7 in Figure 2.

The explanation for the relatively common occurrence of approximations to the chain configuration found in the pleated sheet and relatively rare occurrence of the helix that would arise from propagation of the minimum-energy configuration can be sought in contour lines that depict the number of residues per turn in polypeptide helices.[34] The contour line for helices with two residues per turn follows a nearly straight course from the upper left-hand corner to the lower right-hand corner of the conformational energy map (Figure 1). The contour line for left-handed helices with three residues per turn runs parallel to that for twofold helices, but it is displaced vertically by about 70° in ψ (Figure 1). Consequently it has a somewhat shorter traverse through region III. Therefore region III contains more conformations near the twofold helix contour than there are near the threefold left-handed helix contour.

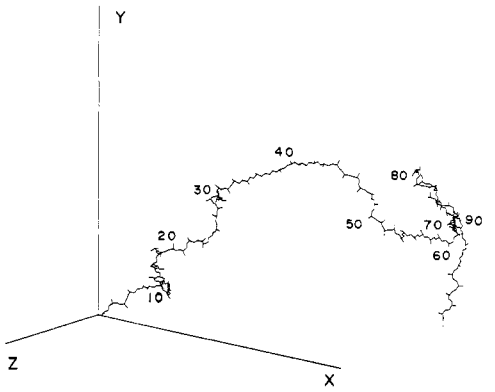

Figure 5. Representative poly(L-alanine) chain of 100 residues selected from the upper end of the distribution function for $r^2/n_p l_p^2$. The X,Y,Z coordinates of the last atom are 17.91, 4.06, and 5.76 nm, respectively. For this chain $r^2/n_p l_p^2$ is 25.9.

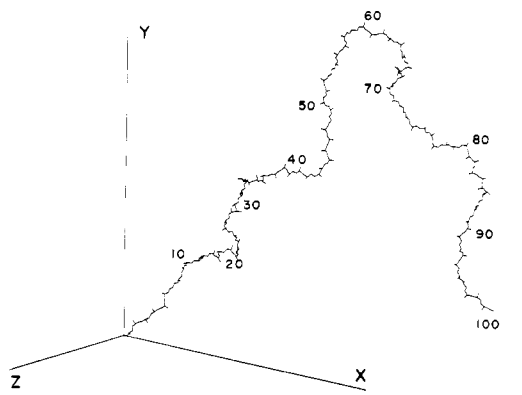

Figure 6. Representative poly(L-alanine) chain of 100 residues grown using only that portion of the conformational energy surface that lies in region III. The X,Y,Z coordinates of the last atom are 10.98, 1.80, and −4.93 nm, respectively. For this chain $r^2/n_p l_p^2$ is 10.3.

Chains with Small and Large Dimensions. Chain configurations depicted in Figures 4 and 5 have dimensions significantly smaller and larger, respectively, than the average for the ensemble. They occur in the wings of the approximate distribution function obtained from the 99 representative chains of 200 residues each. One factor leading to the differences in dimensions lies in the variability of the sampling of regions I and II by individual chains. The compact chain depicted in Figure 4 has 7 residues (18, 40, 46, 65, 85, 96, and 98) from region I and no residues from region II. In contrast, the comparatively extended chain depicted in Figure 5 has only two residues (22 and 84) from region I and one residue (33) from region II. Inspection of numerous other chain configurations reveals that there is a tendency for a correlation between small end-to-end distances and occupancy of regions I and II. This tendency should not be taken to be absolute, however, because individual chains can be found which have dimensions that are not in harmony with the general trend. A significant reduction in unperturbed dimensions is known to occur when the conformational energy surface depicted in Figure 1 is modified so that the energy minimum moves from region III to region I.[8,35] This behavior is in harmony with the general trend seen here with representative chain configurations.

Chains depicted in Figures 4 and 5 contain segments that approximate twofold helices (residues 51–59 and 67–77 in Figure 4, as well as residues 55–61 and 94–99 in Figure 5). Segments approximating threefold left-handed helices are less prevalent. Among the best examples are residues 61–64 in Figure 4 and residues 47–50 in Figure 5. Thus these two chains share with the one depicted in Figure 2 the features that local approximations to the pleated sheet chain configuration are more prevalent than are local approximations to a threefold left-handed helix.

Chains in Which Regions I and II Are Excluded. Region III makes the dominant contribution to the configuration partition function of the unperturbed L-alanyl residue. In order to emphasize the effect on representative chains from the occasional occupancy of a conformation from regions I and II, we now examine representative chains grown using only that portion of the conformational energy surface that lies within the 5 kcal/mol contour line for region III. A representative chain is depicted in Figure 6. It has the shape expected for a random coil. Short approximations to local twofold helices are present (for example, residues 1–6 and 79–85). Less obvious, but also present, are short sequences that approximate a threefold helix (residues 90–94). This representative chain consequently retains many of the features seen in representative chains obtained using the entire conformational energy surface. The major effect of the occasional occupancy of conformations from regions I and II is on the overall dimensions.[8,35] The local character of representative chains is much less affected by regions I and II.

Comparison with Representative Poly(L-proline) Chains. At 30 °C poly(L-proline) has a characteristic ratio of 14 in water and 18–20 in three organic solvents.[3] For this reason representative poly(L-proline) chain configurations[36] are more extended than are typical poly(L-alanine) chains. These two polypeptides also differ in their tendencies to adopt short segments of local helical structure. Poly(L-proline) chains do not contain segments whose conformation is that found in the pleated sheet. The necessary value of ϕ is incompatible with pyrrolidine ring closure. Representative poly(L-proline) chains do, however, contain short segments that approximate a left-handed helix with three residues per turn.[36] Thus the most easily identified approximation to an ordered structure differs in the two chains: in poly(L-alanine) it is an extended chain with two residues per turn, but for poly(L-proline) it is a left-handed helix with three residues per turn. In the solid state, poly(L-proline) forms a left-handed helix with three residues per turn if peptide bonds are in the trans configuration.[37]

Conclusion

Representative unperturbed poly(L-alanine) chains have an overall conformation typical of a random coil. Local chain conformations reminiscent of a right-handed α helix are absent. The local structure contains occasional stretches of as many as ten residues that are crude approximations to the chain conformation found in the pleated sheet. Conformations approximating a left-handed helix with three residues per turn are of much rarer occurrence.

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Registry No. Poly(L-alanine), 25191-17-7; (*S*)-poly[imino(1-methyl-2-oxo-1,2-ethanediyl)], 25213-34-7.

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Monte Carlo Study of Chain Folding in Melt-Crystallized Polymers

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ABSTRACT: The amorphous region between two crystalline lamellae is simulated with a set of chains on a simple cubic lattice. The model takes account of steric interactions between individual chains (no two chains occupying the same lattice site), has the correct density (no vacant lattice sites), and for properly chosen model parameters, exhibits a partially ordered layer between each crystalline lamella and the amorphous region. (Such a layer is considered important in determining the nature of chain folding.) An energy term destabilizing tight folds is also included. In the absence of this energy term a high degree of adjacent reentry, greater than about 50% or 60%, is observed, even in the presence of the above-mentioned partially ordered layer. When tight folds are destabilized, adjacent reentry can become much less important, but the combined adjacent and next-nearest-neighbor reentry never falls below about 50% in the examples considered. The model is compared to a simpler model, consisting of random walks on a simple cubic lattice between two absorbing barriers, and it is found that the random walk model gives a correct qualitative picture.

I. Introduction

The nature of chain folding in melt-crystallized polymers has been a controversial subject from the time that it was first recognized that such polymers crystallize in a lamellar habit. Two opposing opinions[1] have been presented: One holds that a high degree of regular or adjacent folding occurs, while the other, the "switchboard" model, holds that different polymer stems within the crystal are connected randomly by chains in the amorphous phase.

Steric arguments favoring a high degree of adjacent folding have been given.[2] Basically stated, these hold that the amorphous phase between two crystalline lamellae would have much too large a density if a large number of chains from the two crystals were permitted to enter the amorphous phase and perform random walks. For example, models[3,4] based on random walk statistics predict that each walk in the amorphous region would be on the average about three times too long. One way to compensate for this within the context of these models is to have about two-thirds of the chains turn abruptly about and reenter the crystal along an adjacent site, never entering the amorphous region. Such steric arguments have been countered by arguing that they apply only to cases where the loss of order upon passage from the crystal to the amorphous region is abrupt, while polymers actually exhibit an interfacial layer, on the order of 10 Å thick, between the crystal and the amorphous region that retains some of the order of the crystal.[5,6] Also, the random walk models suffer from the well-known fact that ideal chains are perturbed by the presence of boundaries,[2,7] so that random walks may not well characterize the chains in the amorphous region near the crystal.

It has also been argued that crystallization proceeds too rapidly for chains in the melt to disentangle and form crystals with a large degree of adjacent reentry.[8,9] This, as well as the fact that the radius of gyration does not

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