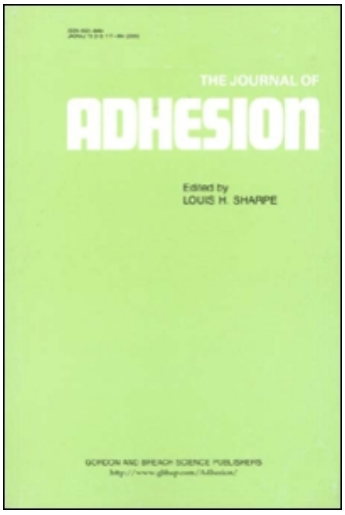

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Slightly Bizarre Protein Chemistry: Urea-Formaldehyde Resin from a Biochemical Perspective†

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A linear urea-formaldehyde polymer and a glycine polypeptide have a significant degree of chemical similarity. The low solubility of fibrous proteins, the planarity of the peptide bond, the existence of hydrogen-bonded structures such as α-helices and β-sheets when considered together, suggest new possibilities for interpreting the structure of the urea-formaldehyde polymer. These new possibilities could provide a chemical explanation for urea-formaldehyde solids based on colloidal substructure as has been proposed recently. X-ray diffraction patterns from urea-formaldehyde resins, reported here for the first time, as well as laser Raman spectra, lend support to the proposal that UF resins may contain protein-like colloidal regions of semicrystalline nature.

KEYWORDS: Alpha-helix, Beta-sheet, Biochemical perspective, Colloidal structure, Protein-like structure, Urea-formaldehyde polymer

INTRODUCTION

The formation of solid material following the polymerization of urea and formaldehyde in aqueous solutions has been considered to be the result of the formation of high molecular weight polymers[1,2] just as has been observed for other common polymerization processes such as

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phenol-formaldehyde or melamine-formaldehyde condensate. However, recent work has led to alternative theories.

Pratt, *et al.*[3] have pointed out that the kinetics of the "cure" of a urea-formaldehyde (UF) resin, dilute solution properties, and light-scattering qualities seem to be explained more readily as the coalescence of a colloidal dispersion rather than the completion of a condensation reaction (for a review of the colloidal behavior see Ref. 4). Electron micrographs of cured UF resins show aggregates of colloid-sized particles[3] rather than the smooth surfaces expected for highly cross-linked, high molecular-weight polymers. Considering that the greatest use of UF resins today is for the manufacture of particleboard where the UF mole ratios are surprisingly low, and at least one major producer is supplying a resin at a U:F mole ratio of 1:1.05, it is hard to imagine exactly how a highly cross-linked network of primary chemical bonds could form. Thus, several observations point to a cure process based on the aggregation of colloidal particles. In this paper aspects of the chemistry of UF polymers were considered which lead to the conclusion that solid UF polymers are formations of colloidal aggregates held together by noncovalent bonding.

The formation of high-molecular weight, noncovalently linked aggregates from lower molecular weight precursors is a common event in protein chemistry. Furthermore, a variety of evidence suggests that the basic principles of protein structure are fairly well understood.[5] These considerations as well as the chemical similarity of the linear UF polymer and the glycine polypeptide led us to consider whether the known properties of protein structure could provide rationalization for the putatively colloidal nature of the solid UF resins.

The possible relevance to UF chemistry of several principles of protein chemistry were explored, namely:

1. The importance of interactions with water for maintaining solubility;
2. The reduced conformational entropy of the backbone due to the planarity of the peptide group;
3. The steric hindrance of the peptide group leading to a rather small range of possible structures;
4. The possibility of forming stable structures based on internal hydrogen bonding.

All of these features, which are well established for proteins, were

found to support the possibility that UF oligomers could form colloids of limited solubility.

Extending the principles of protein structure even further, models were constructed which revealed that rather low molecular weight UF oligomers could form protein-like hydrogen-bonded structures. Without the hydrophilic side chains found in proteins, such hydrogen-bonded structures would be expected to be highly insoluble in water, thus rationalizing the possibility of a colloidal basis for the structure of solid UF material.

If these principles of protein chemistry are the underlying basis for the formation of colloidal structures by UF oligomers, then the solid UF material would be devoid of water and would be highly organized due to the extensive formation of the hydrogen bonds found in our model structures. To test these predictions, X-ray diffraction and laser Raman studies of the UF solid material were conducted. The resulting crystalline X-ray reflections support the suggestion that UF solids are composed of micro-crystalline colloids held together by regular hydrogen bonding although, at this early stage in these studies, other possible explanations cannot be ruled out. The Raman spectra showed the solid material to contain no measurable water which agrees with the supposition that the formation of UF solid comes about from the precipitation of low molecular weight, hydrophobic molecules.

MATERIALS AND METHODS

Formation of UF Resins

Resins used for the X-ray phase of this research[6] were prepared using urea-formaldehyde concentrate (UFC), a common material of commerce. UFC, as supplied by Borden Chemical, is an 85% solids clear solution of urea and formaldehyde at a mole ratio of 1:4.8 (U:F). Analysis *via* ^{13}C NMR showed virtually all of the urea present as trimethylol urea in mixture with free formaldehyde present in aqueous solution as methylene glycol along with low molecular-weight forms of paraformaldehyde.

To make a typical resin, 300 grams of UFC was charged into reaction kettle with sufficient water to yield a final product of approximately 65% solids. Heating and agitation were begun and solid urea was added to reduce the mole ratio to 1:2.2. The reaction mixture was heated to 80°C and the pH adjusted to 8.0 and held for 30 minutes. After this alkaline

hold, the pH was adjusted to 5.0. The resin was allowed to advance to a target viscosity of approximately 800 cps. The mixture was then neutralized and more urea was added to reduce the mole ratio to the final target of 1 : 1.1. The resin was cooled to room temperature by immersing the resin kettle in cold water.

All pH adjustments were completed with 1N NaOH or H_2SO_4. Temperature and pH were monitored continuously and adjusted as necessary to maintain 80° C and the desired pH.

To prepare the solid resin sample, liquid resin was diluted to approximately 5% solids with distilled water and the mixture vigorously agitated. Flocculations occurred with or without the addition of acid catalyst, although the addition of acid accelerated the process. No differences were observed in X-ray diffraction patterns based on whether an acid catalyst was or was not used.

X-ray Diffraction

X-ray diffraction patterns were obtained at room temperature using a Debyl-Scherrer camera (114.6 mm diameter) and nickel filtered CuK_2 X-radiation. Powder samples were placed in 1.0 mm glass capillary tubes. Three hour exposures were used.

Calculation of Allowed Conformations

Conformational calculations were carried out using the methods described by Hopfinger[7] incorporated in the computer program described previously.[8] The method, in brief, starts with the atomic coordinates of one repeat unit of the polymer chain in the all-trans (planar) conformation determined graphically or geometrically. The program replicates the repeat unit to build a polymer chain of prescribed length, and then causes bond rotations in the required sequence to form a particular conformation. Next, the distances between every pair of atoms in the polymer chain are computed and compared to a set of standard "contact distances", normally a distance on the order of the sum of the van der Wall's radii of the two atoms being scrutinized. This process is repeated for each conformation as specified by a pair of ϕ, ψ angles (replicated down the polymer chain) (Figures 4 and 5). Only ϕ, ψ pairs having no pairwise contacts less than the standard contact distances are considered acceptable (or likely) and are so indicated in Ramachandran plots of ϕ versus ψ (Figure 6). For the computations

used in this report, the repeat unit was held fixed in the trans-trans configuration of the urea moiety.

Laser Raman Spectra

UF solids were prepared by methods described above, collected by settling and agglomeration at room temperature, and then transferred to a standard melting point capillary for Raman spectral analysis. The powdery samples were illuminated with the 5145 A line of Spectra Physics model 169 argon ion laser. The power focused on the sample was about 100 mW and the Raman scattering was collected at an angle of 90°. Spectral dispersion and stray light rejection were achieved with a computer controlled Jobin-Yvon Ramanor HG 2S monochrometer equipped with two 1 meter holographic gratings and with photon counting electronics. Spectra were collected at a scan rate of 1 cm^{-1}/sec and stored on floppy disks. Repetitive scans were digitally added to achieve the desired signal to noise ratio (6–10 scans for the spectra shown).

RESULTS

Comparison of polyglycine and UF Polymers

A glycine polypeptide contains methylene groups alternating with peptide bonds. A linear UF polymer contains methylene groups alternating with the substituted urea moiety (Figure 1). To facilitate the comparison of polyglycine and UF polymers, the possibility of branching and the potential formation of methylol ether linkages in the UF polymer were ignored. These assumptions seem reasonable in light of the mole ratio (1 : 1.1) of the resins made and the results of ^{13}C NMR analysis completed by one of the authors (Rammon[6]) which showed the rather minimal amount of methylene ether linkages present in the final resin.

Splitting Out Water Lowers Solubility

If the cure of a UF resin were to depend on the precipitation of colloidal particles, then it would be necessary that the formation of the UF polymer be accompanied by a decrease in solubility. Urea-formaldehyde resins do not form stable aqueous solutions. Virtually all commonly supplied liquid UF resins are milky or cloudy suggesting that

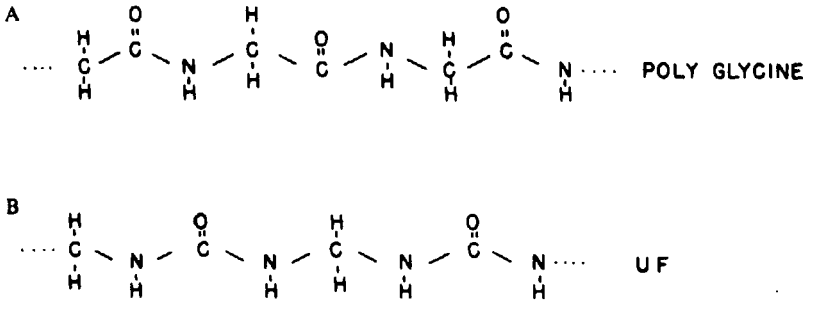
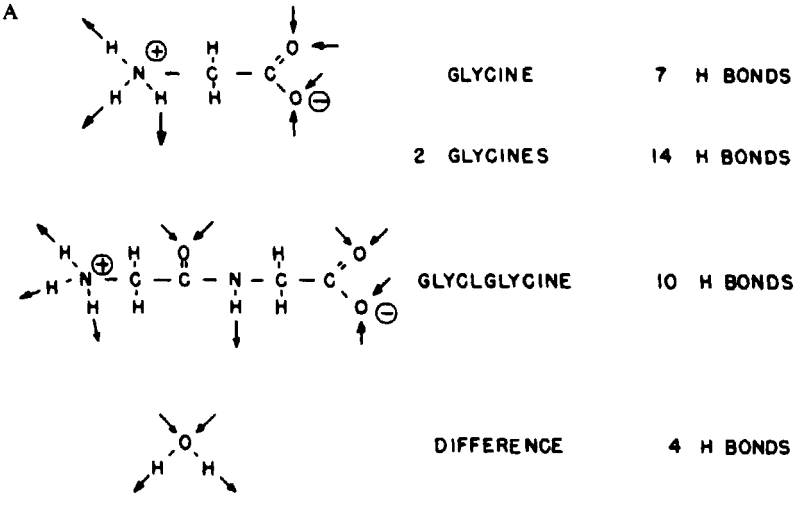


FIGURE 1 Comparison of polyglycine and linear UF polymer. Polyglycine (a) and linear UF polymer (b) are drawn schematically.

they are near their solubility limit. Since these resins are so near their solubility limit it seems reasonable that a drop in solubility by a factor of 10 during polymerization would be sufficient to convert most of the polymer into an insoluble mass.

The solubility of many molecules in water is greatly influenced by the ability to form hydrogen bonds with the solvent. During the formation of polyglycine, one water moleucle is split out for each peptide bond (Figure 2), which is accompanied by the loss of four potential hydrogen



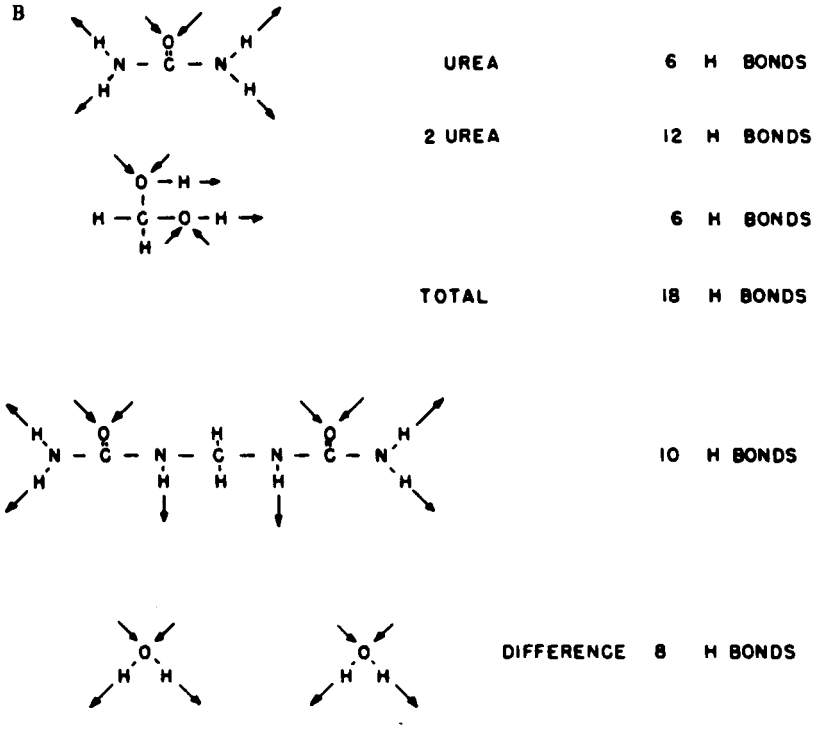


FIGURE 2 Hydrogen bonding between solute and solvent. The potential hydrogen bonds between glycine monomers and water and the potential hydrogen bonds between polyglycine and water are compared in (a). Note the loss of 4 potential hydrogen bonds between the solute and the solvent as the one water molecule is split out.

The potential hydrogen bonds between the urea and formaldehyde monomers and the solvent and the potential hydrogen bonds between UF polymer and the solvent are compared in (b). Note the loss of eight potential hydrogren bonds between the solute and the solvent as the two water molecules are split out.

bonds between the solute and the solvent. Even without considering the change in charge as glycine polymerizes, the loss of the potential for hydrogen bonding would lead to a considerable decrease in solubility as the glycine monomer converts to a polymer.

During the formation of a UF oligomer, the formation of each repeating unit is accompanied by the loss of two water molecules, which is accompanied by the loss of eight potential bonds between the solute and the solvent. This loss of eight potential hydrogen bonds should bring about a large decrease in solubility of the UF polymer as compared to the monomer constitutents. Thus, as for proteins, the poly-

merization process should be accompanied by a large decrease in solubility.

Past research[5] has indicated that the strength of a hydrogen bond ranges from about 1.5 to 5 kcal/mol. To make our calculations for this paper conservative, the hydrogen bond strength was considered to be only 1 kcal/mol. If only the enthalpic contributions to solubility were considered, then the loss of eight potential hydrogen bonds would decrease the solubility of the polymer as compared to the monomers by an amount corresponding to 8×1 or by 8 kcal/mol. In addition to enthalpic contributions, changes in entropy could also change the solubility of the polymer as compared to the monomer precursors; calculations based on the entropy of mixing showed the entropic contributions would be small, about 2 kcal/mol. Thus, even using a most conservative value for the hydrogen bond energy, the net change in free energy of solubilization would be about 6 kcal/mol as the monomer precursors convert to the polymer.

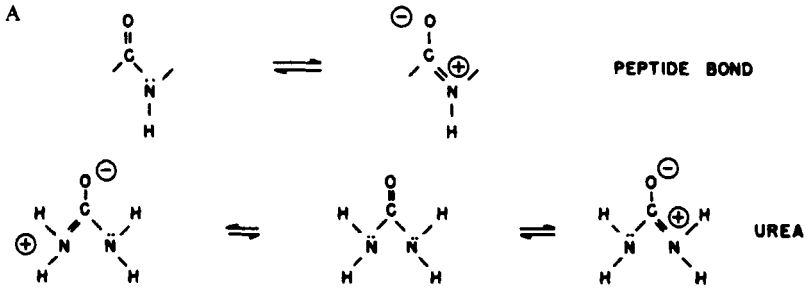
By the equation $\Delta G = -RT \ln[K]$, a 6 kcal increase in the free energy of solubilization leads to a 10^4 fold decrease in solubility of the polymer as compared to the monomer. Thus, simply considering the hydrogen bonding between solute and solvent led to the suggestion that formation of UF oligomers caused a large decrease in solubility. As suggested above, since the monomers were near their solubility limit in typical resin formulations, such a decrease in solubility would lead to the precipitation of the polymer as it forms.

Planarity of the Peptide Bond and Urea Moiety

A well-known feature of the peptide bond is its planarity due to the resonance of the pair of nitrogen electrons with the carbonyl π electrons.[2,4] In addition to the planarity, a second measurable result of the resonance is the large dipole moment of about 3.7 D for the peptide bond.

For the UF polymer, resonance should lead to planar urea moieties. This supposition was supported by the observed planarity of the urea molecule in urea crystals[6] and by the high dipole moment of about 4.6 D for the urea molecule in solution.

The resonance of the nitrogen electrons with the carbonyl electrons provides a rotational energy barrier of about 15–20 kcal/mol.[2,4] Therefore, the peptide can exist in either a *cis* or a *trans* conformation (Figure



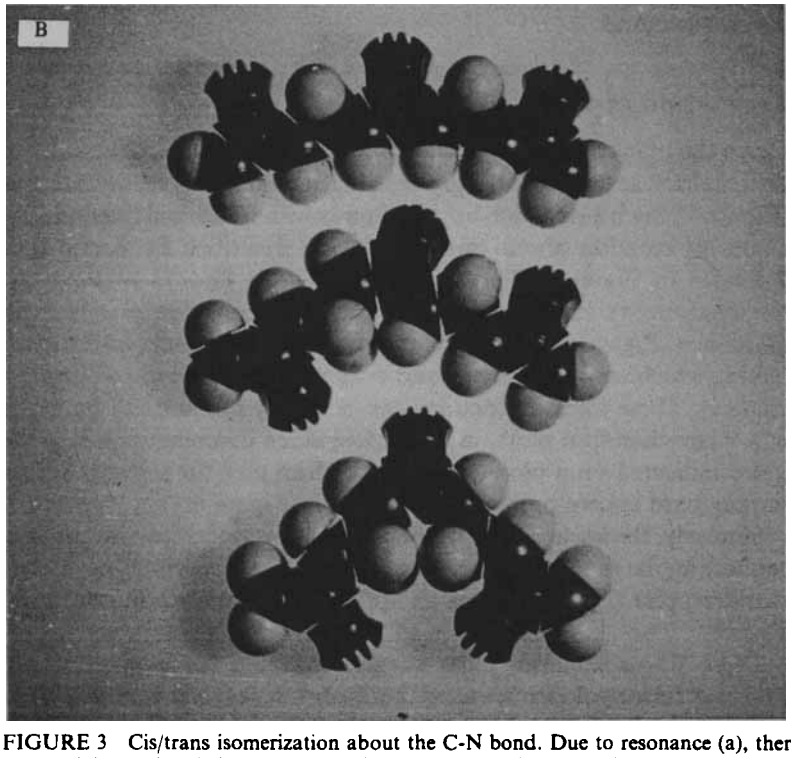


FIGURE 3 Cis/trans isomerization about the C-N bond. Due to resonance (a), there is partial double-bond character to the C-N amide bond in both polypeptides and linear UF polymers. For proteins, there are just two possibilities, cis and trans. for UF polymers (b), there are three possibilities, trans/trans (upper model) trans/cis (or trans/cis; middle model) and cis/cis (lower model).

3). Due to steric factors, however, the trans conformation is about 3–4 kcal/mol lower energy than the *cis* and so the *trans* conformation is the predominant form found in proteins.[2,4]

Since the urea moiety has two amide bonds, there are two partial double bonds in this structure. Compared to normal protein chemistry, this is slightly bizarre. In theory, there are three possible conformations about the urea moiety: *trans-trans*; *trans-cis* (or *cis-trans*, which is equivalent); and *cis-cis* (Figure 3). Visual inspection of the space filling models suggests that the *trans* conformation should be favored over the *cis* conformation for steric reasons, just as has been found for the peptide bond. In the discussions that follow, we will consider only the *trans-trans* structure, although in future, more detailed studies, it would certainly be worthwhile to consider the possible implications of the *trans-cis* or *cis-cis* structures.

Estimation of Steric Hindrance

Given the planarity of the peptide bond, the polyglycine molecule can be visualized as two large flat groups hinged together by methylene units (Figure 4). Such a structure has two bonds with rotational freedom. The angles of rotation about these bonds are described by ϕ and ψ as indicated in Figure 4. Furthermore, particular choices of these two torsional angles lead to structures that are forbidden due to steric hindrance (Figure 5). The steric restrictions can be mapped by determining which choices of the ϕ and ψ angles lead to unallowable steric contacts. These steric restrictions can be neatly summarized by means of a Ramachandran plot[2], in which forbidden combinations of ϕ and ψ are indicated on a plot. A Ramachandran plot for polyglycine, assuming hard sphere potentials, is shown in Figure 6.

Similarly, the linear UF polymer can be visualized as methylene units connecting large planar moieties (Figure 7). The resulting Ramachandran plot (Figure 8) gives an appearance similar to that for polyglycine.

These Ramachandran plots suggest that the conformational entropies of linear polypeptides and the linear UF polymer would be much smaller than expected for a polymer with free rotation about all of the bonds. The low conformational entropy of the backbone means that there is a smaller than expected unfavorable entropy decrease as the polymer converts from a disordered to an ordered structure.

Possible Hydrogen Bonded Structures

For proteins it is found that certain combinations of the ϕ and ψ

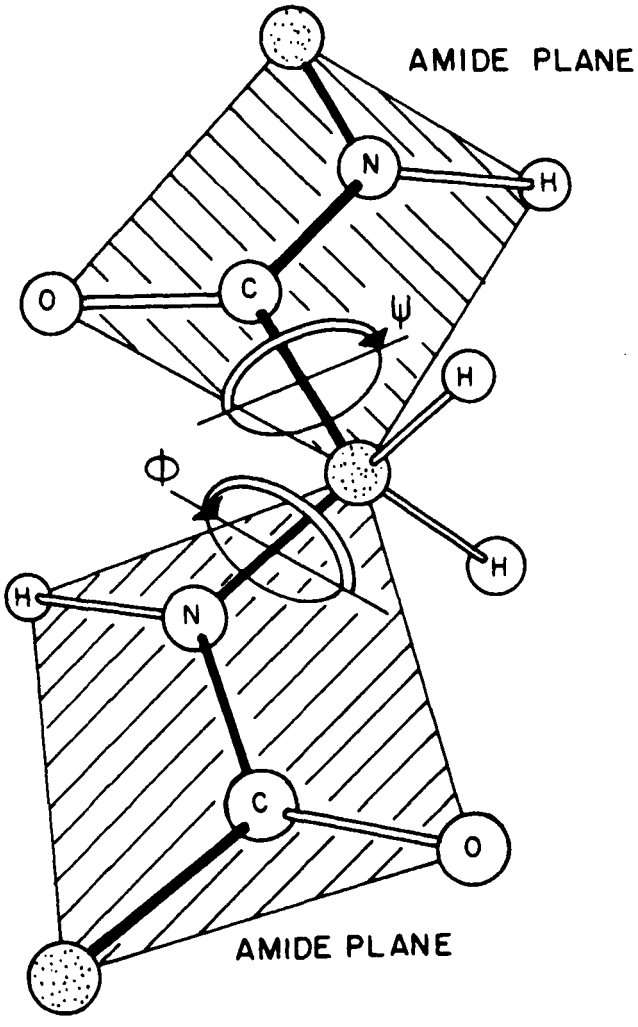


FIGURE 4 Definition of the ϕ and ψ angles are as shown.

angles, if repeated over and over, lead to regular structures with repeated hydrogen bonds. Two such structures are the α-helix and the β-sheet, shown schematically in Figure 9. In the α-helix, the hydrogen bonds are within a single strand of the polymer and, in the β-sheet, the hydrogen bonds are between two strands of the polymer. The relevance of the steric hindrance discussed above is that the steric constraints lower the

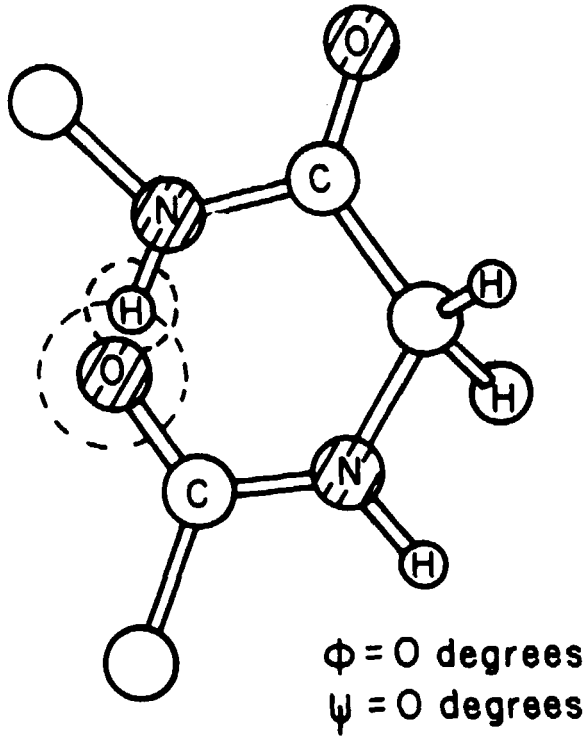


FIGURE 5 Steric hindrance. Certain combinations of the φ and ψ angles are not allowed due to steric hindrance. The particular structure shown corresponds to $\phi = 0$ and $\psi = 0$, which is a strongly forbidden combination.

conformational entropy of the random form, thus making it less costly to form the ordered structures. An equivalent statement is that the steric constraints tend to guide the polymer into one of these hydrogen-bonded structures.

Model building studies confirm that the UF linear polymer can likewise form hydrogen-bonded structures (Figure 10). We have constructed the analogue of the α-helix, but due to the larger size of the urea moiety as compared to the peptide bond, it is not possible to turn the chain as tightly as it is turned in the α-helix. The hypothetical UF structure exhibits a closer resemblance to another protein helix, called the π-helix; hence the name given in Figure 10.

In addition to the helical analogue with the hydrogen bonding within a single polymer, we have found it possible to construct an analogue of

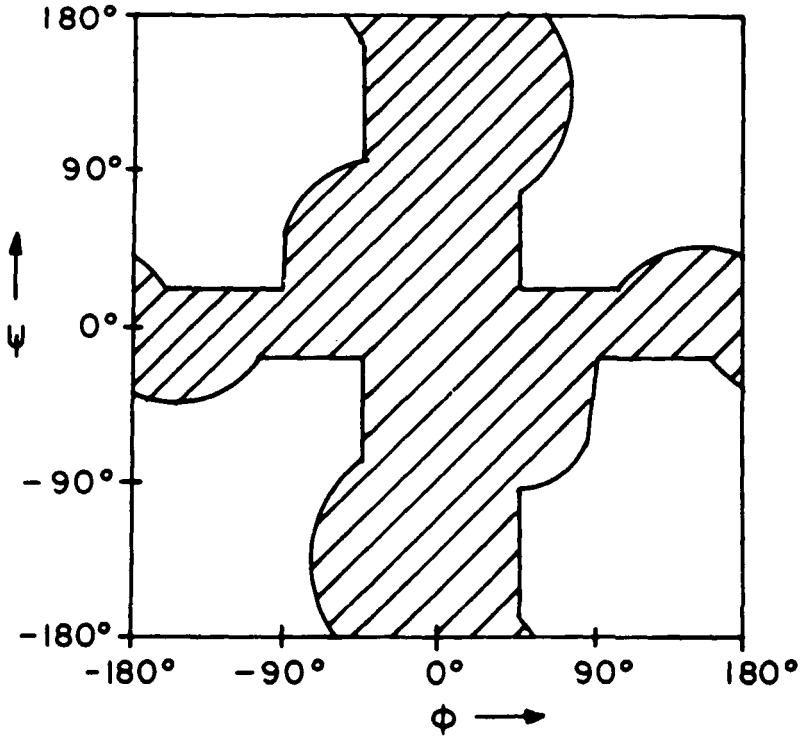


FIGURE 6 Ramachandran Plot of polyglycine. Assuming hard sphere potentials as described in materials and methods, the various combinations of ϕ and ψ leading to steric repulsion were determined. The unallowed regions are shaded.

the β-sheet, with hydrogen bonds between adjacent strands of the UF polymer. In the protein β-sheet, any two adjacent carbonyl groups along the protein backbone point in opposite directions. In the UF model, the two adjacent carbonyl groups point in the same direction, which is a local arrangement more similar to that observed in the α-helix. For this reason we named the potential UF sheet structure an α-sheet.

Folding of Proteins and Possible Folding of UF Polymers

The process of changing from a random polypeptide chain in solution to an ordered structure such as an α-helix or a β-sheet is called protein folding. The net free energy of folding is the result of the difference between the free energies of those factors favoring the folded state and

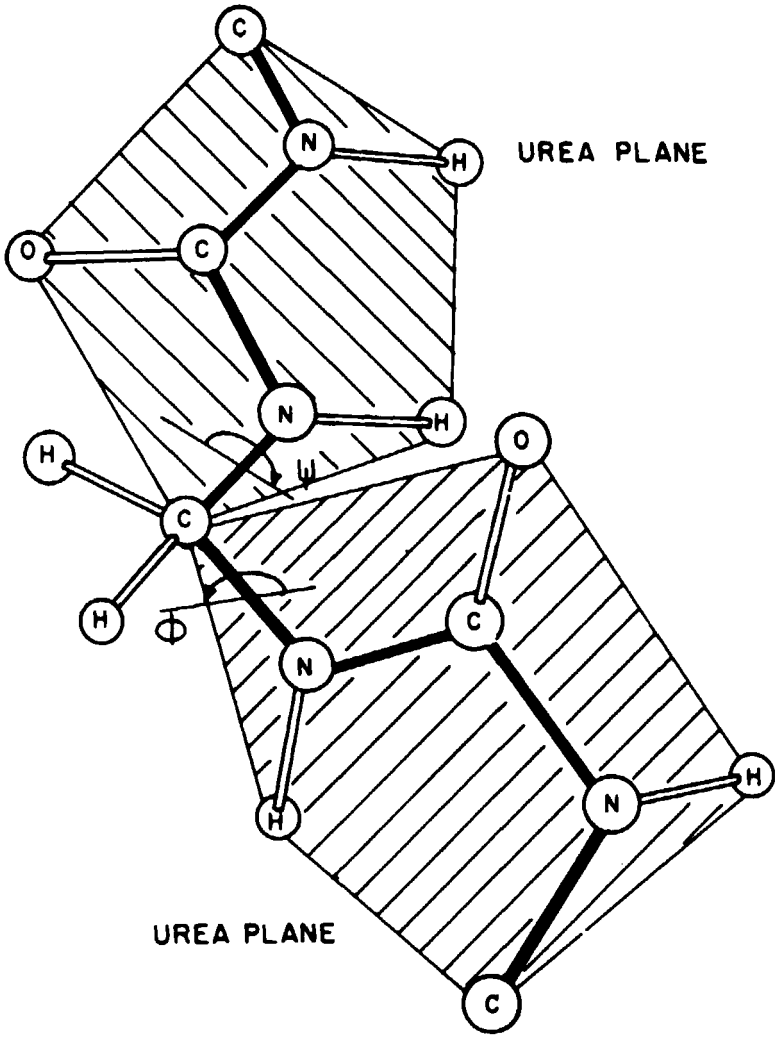


FIGURE 7 Definition of ϕ and ψ angles for the UF polymer. By analogy to the polyglycine molecule, the ϕ and ψ angles are defined as shown.

those favoring the unfolded state. It is generally agreed that the free energies for folding and for unfolding are both on the order of 100–200 kcal/mol for typical-sized proteins. For an entire protein, the net difference between the folding and unfolding energies is only a few kcal out of 100–200. Thus, even small errors in estimating the free energy of

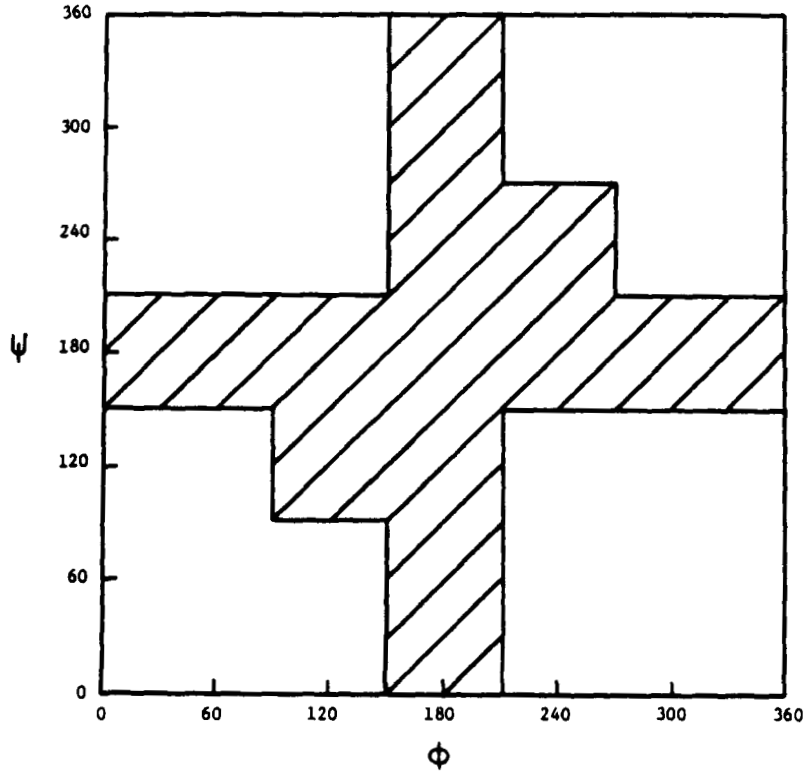


FIGURE 8 Ramachandran Plot of UF polymer. Assuming hard sphere potentials as described in the materials and methods, steric repulsion was estimated for the UF polymer. The unallowed regions are shaded.

the folding and unfolding process can change the sign of the net free energy for the overall folding reaction. Since the free energies for the folding and unfolding processes cannot be estimated precisely at our current level of understanding, it is presently impossible to calculate, even for the simplest polypeptides, whether the folded or unfolded state is favored (for an excellent review, see Finney, *et al.*[10]). Thus, it is unlikely that it would be possible to determine from first principles whether UF is more stable in an unfolded or folded state. Nevertheless, it is useful to compare polypeptides and UF polymers with regard to those factors favoring folding and those favoring unfolding. Such a comparison would indicate whether the folded forms of a UF polymer would be more or less likely than the comparable structures in proteins.

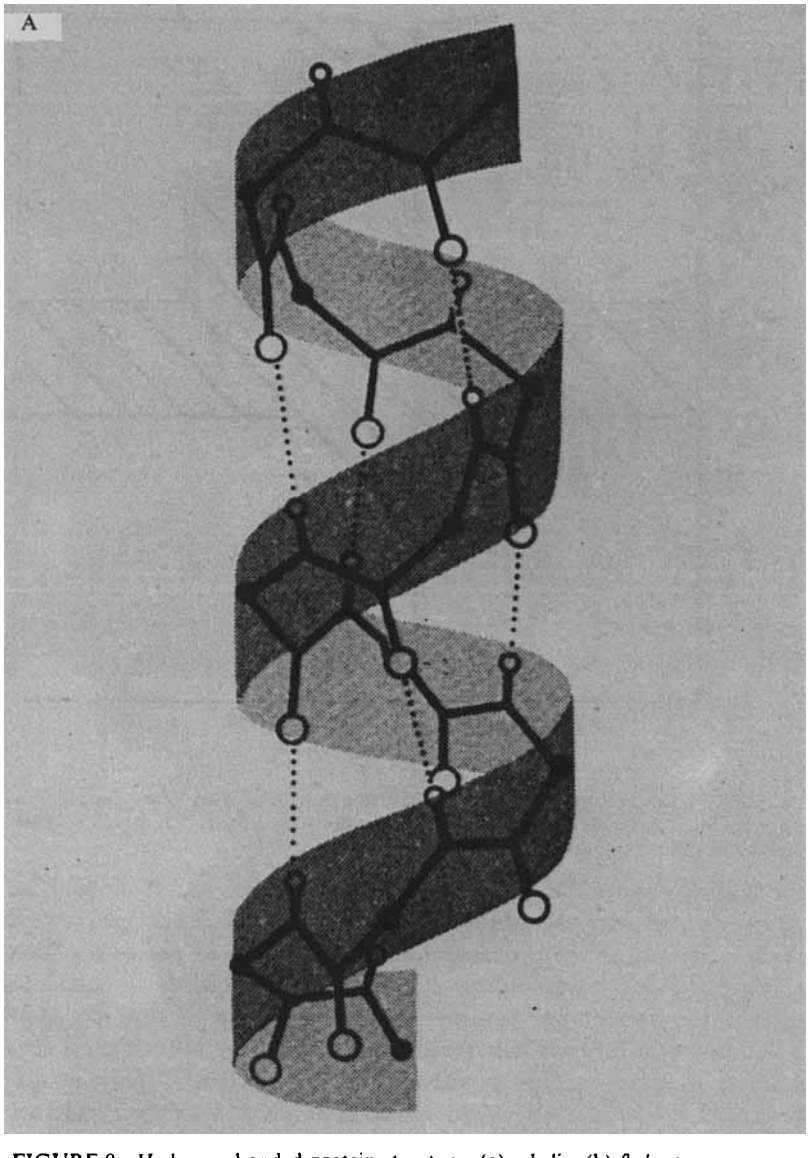
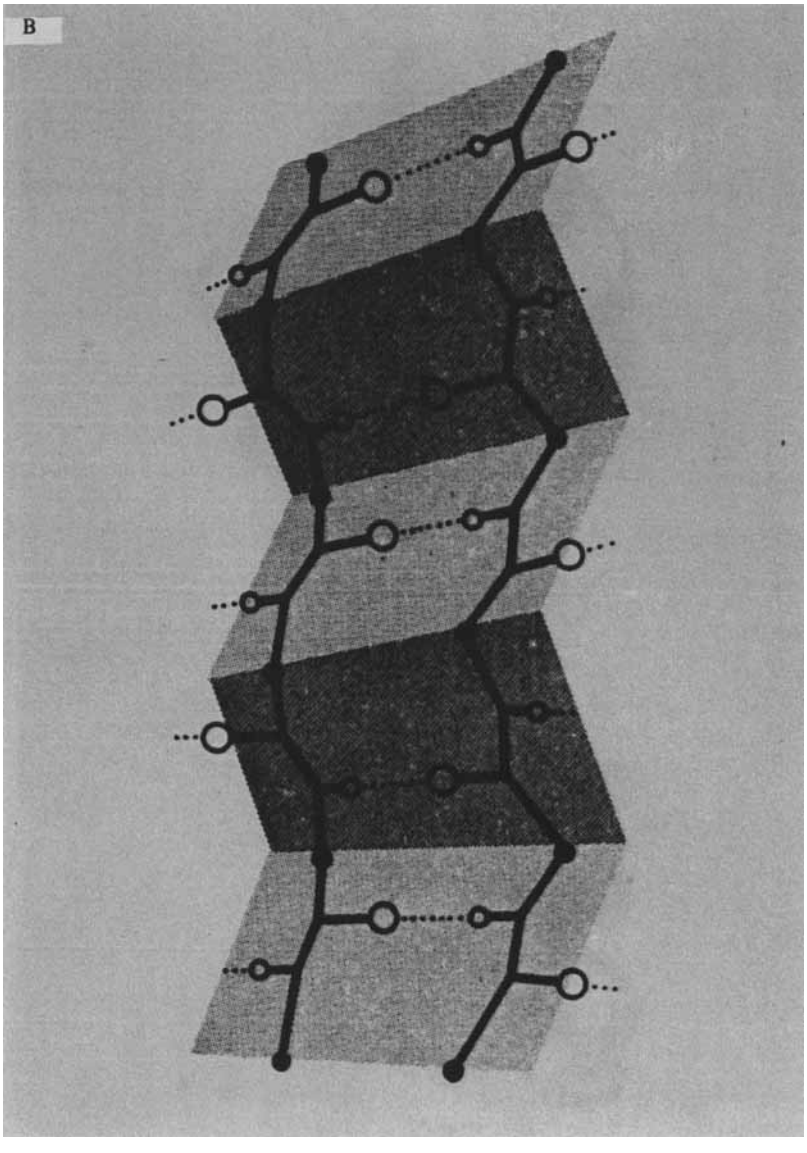
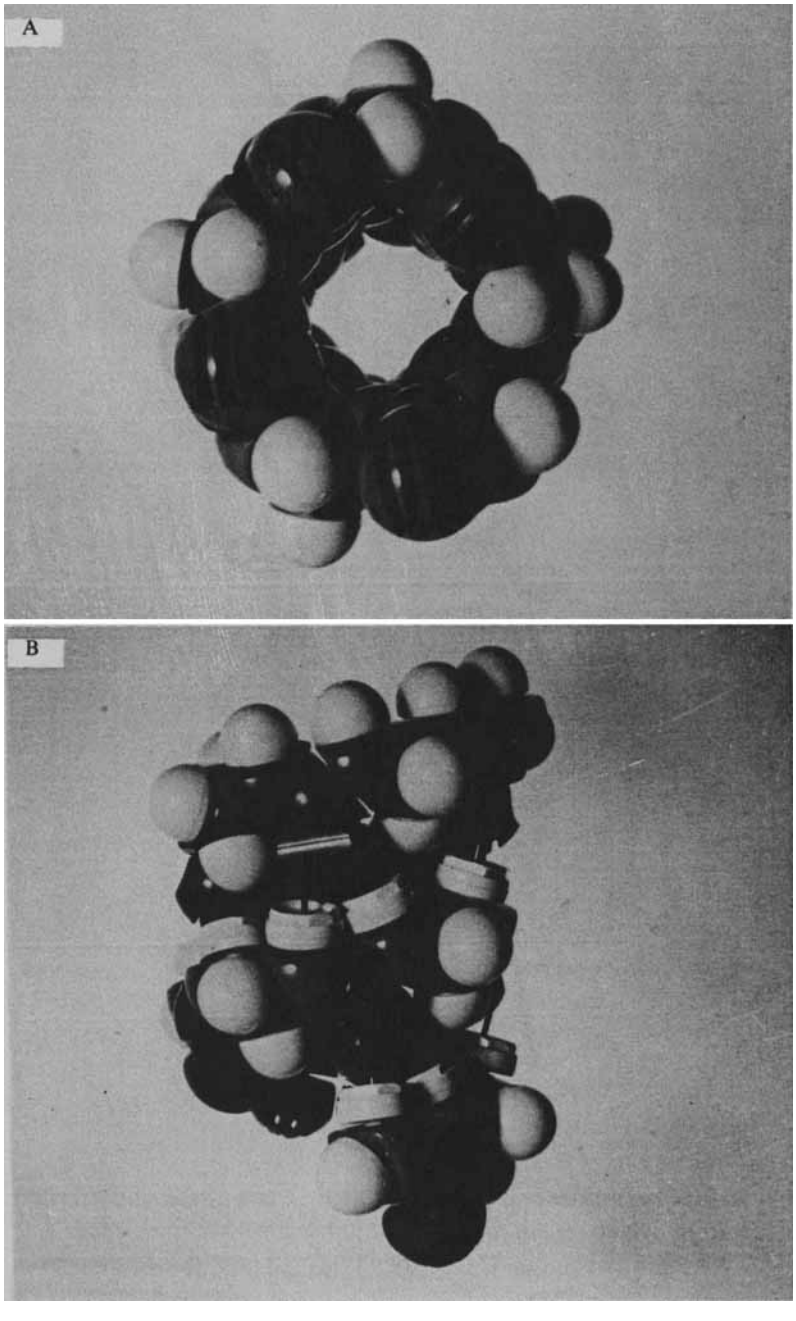


FIGURE 9 Hydrogen bonded protein structures (a) α-helix, (b) β-sheet.

It is generally agreed that the major factor favoring the unfolded form is the increase in conformational entropy of the backbone as the polypeptide converts from the folded to the unfolded or random state. Given



that both polypeptides and UF resins have just two angles with freedom of rotation which result in very similar Ramachandran plots (*e.g.* Figures 4–8), it is very likely that the UF polymer and the polypeptide



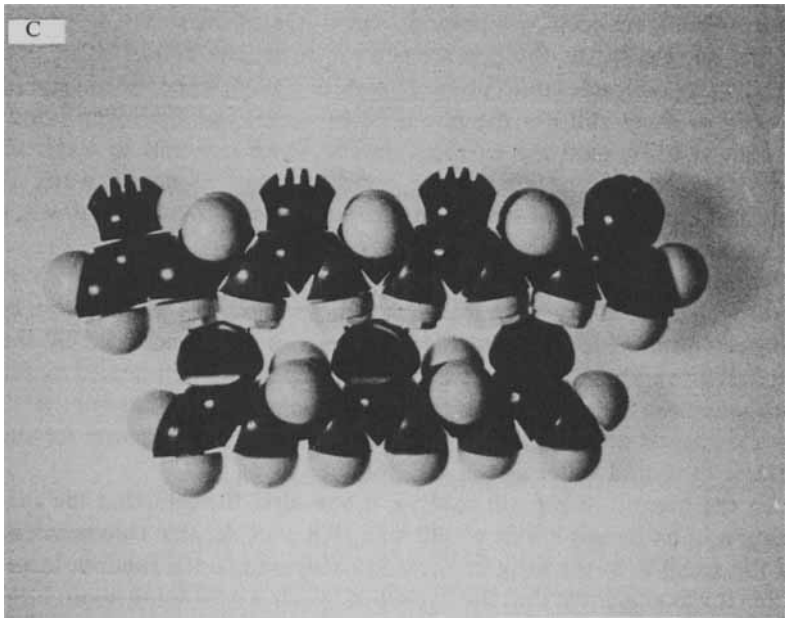


FIGURE 10 Possible hydrogen bonded structures. CPK space filling models were used to search for possible structures with self-satisfying hydrogen bonds. Two views of a model with hydrogen bonds within one strand, a structure we are calling the π-helix, are shown in (a) and (b). A model with hydrogen bonds between two strands, a structure we are calling the α-sheet, is shown in (c).

have very similar overall values for their conformational entropy. Since the urea moiety is slightly larger than the peptide group, the UF polymer exhibits more steric hindrance and hence, fewer allowed choices for the values of the ϕ and ψ angles. The UF polymer would exhibit a slightly smaller value for the conformational entropy change during polymer unfolding. Thus, a range of values for the conformational energy ($T\Delta S$) of the UF polymer would be somewhat smaller than the 0.6 to 1.5 kcal/residue indicated previously[10] for polypeptides.

If side chain contributions are ignored, which is appropriate for polyglycine and UF polymers, then there are two main factors favoring the folded state. The first factor is the release of bound water (which brings about an increase in entropy) as the polymer folds while the second is an increase in overall bond strength (*e.g.* a decrease in the enthalpy) as the polymer folds.

A peptide moiety in an unfolded polypeptide would be expected to be hydrogen-bonded to three water molecules. As the polymer converts

to a folded state such as a helix or sheet, two of the water molecules would be released as the peptide-peptide hydrogen bonds form. The third water molecule could possibly remain bound, since the oxygen in a helix or sheet still has the potential to accept one hydrogen bond. Finney *et al.*[10], used the entropy change as ice converts to water to provide a rough estimate for the energy change as bound water is released, and their (conservative) estimate was about 0.4 kcal/water molecule released, or about 0.8 kcal/residue.

A urea moiety in an unfolded UF polymer would be expected to be hydrogen bonded to about four water molecules. As the UF polymer converts to a folded state such as the helix or sheet indicated by the models given above, all four water molecules would be released as the two urea-urea hydrogen bonds form. The conjectures of Finney *et al.*[10], would suggest an energy change of about 1.6 kcal/urea moiety for the release of bound water as the UF polymer folds.

In the history of protein folding, it was first thought that the formation of hydrogen bonds would lead to a considerable enhancement of the stability of the helix or sheet as compared to the random form. Then it was suggested that the hydrogen bonds would bring about little or no net stability because the overall reaction was not the formation of peptide-peptide hydrogen bonds, but rather was merely an exchange of water-peptide hydrogen bonds for peptide-peptide and water-water hydrogen bonds. However, recent calculations of hydrogen-bond strengths have returned to the original suggestion that there is a net decrease in enthalpy as a protein folds. This postulated decrease in enthalpy comes about because the peptide-peptide hydrogen bonds are estimated to be about 25% stronger than the water-water or peptide-water hydrogen bonds due to the pairing of the large dipole moments of the peptide groups. From these considerations, Finney *et al.*[10], estimated that the increase in hydrogen bond strength results in a stabilizing enthalpy of about 0.5 to 0.8 kcal/residue.

Because the dipole moment of urea is much larger than the dipole moment of the peptide bond, about 4.6 as compared to 3.7 D, we would expect the decrease in enthalpy during folding to be much larger for UF polymers as compared to polypeptides. However, even if this effect were ignored, our UF model suggests that the folding of a UF polymer would be accompanied by the formation of two hydrogen bonds (compared to one for the folding of a protein), which would give a value of about 1.0 to 1.6 kcal/urea moiety for the enthalpy contribution favoring folding.

Overall, the energy balance for the folding of simple polymers such

as polyglycine is about 0.6 to 1.5 kcal/residue favoring the unfolded state and about 0.4 + (0.5 to 0.8) = 0.9 to 1.2 kcal/mol favoring the folded state. It is evident, as suggested above, that the values for folding and unfolding are comparable and that the uncertainties prevent a prediction as to whether the folded or unfolded state would be the more stable.

Comparing the UF structure with the protein structure suggests that the overall energy balance for the folding of UF polymer is something less than the 1.5 kcal/urea moiety favoring the unfolded state and about 1.6 + (1.0 to 1.6) = 2.6 to 3.2 kcal/mol favoring the folded state. These approximate calculations suggest that the UF polymer would very likely assume a folded form.

Note that the formation of hydrogen-bonded structures such as the helix or sheet would remove the last hydrogen bonds between the UF polymer and the solvent. This would make the structured UF polymer even more hydrophobic than the structured polyglycine polymer. That is, the structured polyglycine can potentially form one hydrogen bond between each peptide moiety and the solvent, whereas the structured UF polymer uses all its hydrogen bonding potential in the internal hydrogen bonds and thus cannot form any hydrogen bonds with the solvent.

X-ray diffraction studies

One prediction arising from these structural studies is that UF solid material should have local regions with a high degree of order due to the hydrogen bonding and, therefore, should exhibit X-ray diffraction patterns characteristic of such order.

We have carried out X-ray studies on UF solids and urea (Figure 11). It is evident that UF solid material contains some highly ordered, crystalline material that is distinct from crystalline urea as evidenced by the very different pattern of relative intensities of the various reflections. It is also evident that the UF solid material has some spacings that are similar or identical to several of the spacings observed in urea crystals. This suggests that at least some of the dimensions of the crystalline material are specified by the size of the urea moiety. Another point of interest is the relative intensity of the reflections shown in Figure 11. The urea crystals yield a much sharper powder pattern than the UF resin solid. This implies that the UF polymer forms much smaller crystal volume units than the urea. This suggests that the amount of UF polymer actually involved in the crystalline region is quite small.

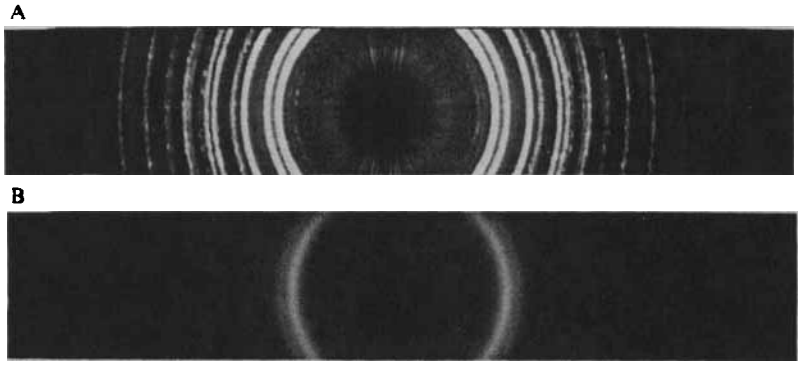


FIGURE 11 X-ray diffraction of UF resins. X-ray powder diffraction patterns of urea (a) and typical UF resin (b).

Although these results support our models for the structure of UF polymer, it is difficult to rule out other possible origins for the diffracted intensity. For example, the crystalline reflections could arise from the crystallization of some minority component of the UF resin mixture or the presence of urons or other ring structures.

Results of laser Raman analysis

A second prediction resulting from our model of the structure of the UF solid as a material with a self-satisfying internal bonding arrangement, would be the lack of water within the UF solid structure. Cellulose, for example, is a highly organized hydrogen bonded system which can incorporate water within the secondary bonding system with relative ease; cellulose is known to shrink and swell with changes in atmospheric humidity. If the UF solid structures we are discussing are in fact precipitates from an aqueous system due to lack of hydrophilicity, then we might expect the absence of water in solid UF. Figure 12 shows a typical laser Raman spectrum of an uncured, dilute solution precipitate of a UF resin and, for comparative purposes, a Raman spectrum of water. Water vapour exhibits three peaks due to the H-O-H bend at 1630 cm^{-1}, the O-H antisymmetric stretch at 3200 cm^{-1}, and the symmetrical stretch at 3500 cm^{-1}.

Liquid water also exhibits three peaks in similar positions, but the interpretation of the stretching vibrations is complex due to water/water hydrogen bonding interactions. These water peaks are not observed in the UF solid material; the only peaks in these spectral regions are due to the urea group. From the lack of water peaks we can estimate an upper

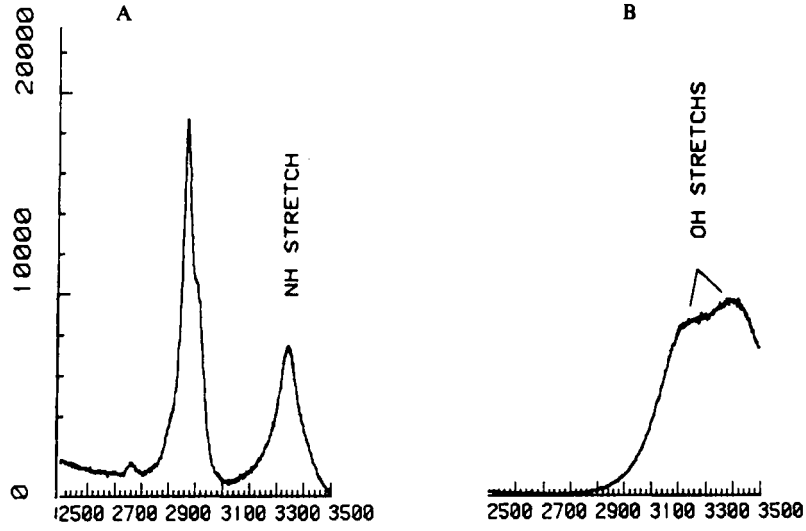


FIGURE 12 Laser Raman spectrum of UF resin. Raman spectrum of a typical UF resin is shown in (a). For comparative purposes, the Raman spectrum of water is shown in (b), but the two spectra are not necessarily to the same scale. We find no Raman evidence for water in the UF resin material.

limit of about 5% water in the solid material. This result suggests that the formation of UF solid material is accompanied by an exclusion of water from the vicinity of the UF molecules.

DISCUSSION

Application of several of the principles of protein chemistry to the UF polymer leads to the hypothesis that UF polymers could have a high degree of local order arising from the formation of hydrogen bonds. It should be emphasized that the model building studies to date have been cursory. Thus, we do not know whether there are other, more likely hydrogen bonded structures. Also, we have not yet carried out energy minimization calculations on the structures that we have constructed, and so we are not certain whether there should be important modifications in the particular models that we have built.

Even with the limitations mentioned above, we believe the model building to be significant in pointing out previously unconsidered possibilities for the UF polymers. Our models suggest that hydrogen bonding could become manifest in rather small oligomers of urea and formaldehyde. Thus, it seems possible that the loss of solubility in water

is due to the loss of water (of condensation) from the urea and formaldehyde monomers coupled with the formation of intra- or intermolecular hydrogen bonds. Together, these two effects would lead to a complete loss of hydrogen bonds between the UF molecule and the surrounding water. Total loss of hydrogen bonding would be expected to result in an abrupt drop in solubility after only a few molecules become linked together. In this view, the loss of solubility causes the low molecular weight UF oligomers to aggregate into colloidal structures supporting the arguments of Pratt *et al.*[3] Precipitation of these insoluble colloidal structures then leads to the formation of the solid UF materials.

This comparison of UF and protein chemistry had led to the suggestion that the lack of hydrophilic side chains such as those in proteins leads to insolubility of the UF oligomer. This suggestion provides a rationalization for the growing body of evidence that UF resins have colloidal properties.

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