In Figure 11, the molecular weight dependence of J_{eN}^0 for the star polymer (open circles) is compared with that for the linear polymer (broken line). As is evident from this figure, J_{eN}^0 for the star polymer does not differ greatly from that of the linear polymer, in marked contrast to the case of J_e^0. The value of J_{eN}^0 for the star polymer is somewhat higher than that for the linear one at lower molecular weights, but approaches the latter as molecular weight increases. Correspondingly, M_e for the star polymer is somewhat higher than the average value of 18,000 for the linear polymer,[1] but decreases with increasing molecular weight. These results imply that the center of a star-shaped chain affects entanglements near this point, but that the effect fades as the molecular weight or length of the branches increases. For example, M_e for LB7 (M_w = 213,000) and LB18 (M_w = 580,000) are respectively 35,500 and 19,300.

A Comparison of the Effects of Molecular Weight Distribution and Branching. As was emphasized in the previous papers,[1,2] viscoelastic properties in the rubbery and flow or terminal zones are strongly affected by the molecular weight distribution and blending. On the other hand, they are also affected by branching, as has been described above. It is, therefore, very interesting to compare the effects of molecular weight distribution and branching. Such a comparison has been made using the following three samples of roughly equal M_w

Star LB15	$M_w = 2.48 \times 10^5$, $M_w/M_n = 1.18$
Narrow Distribution L15	$M_w = 2.15 \times 10^5$, $M_w/M_n = 1.00$
Broad Distribution PS7	$M_w = 3.03 \times 10^5$, $M_w/M_n = 1.57$

The last of these samples, PS7, was obtained by bulk polymerization.

Figure 12 shows the frequency dependence curves of G' for these samples. The three samples manifest the same G' in the transition zone, but the rubbery plateau of L15 alone is very flat and much longer than that of LB15. The G' curves for LB15 and PS7 are almost identical down to ω = 0.3, and decrease with decreasing frequency in the rubbery zone; but the curve for PS7 decreases more gradually even in the terminal zone. Similar characteristic features of these samples are also clearly seen in their relaxation spectra as determined by Tschoegl's equation[22] (Figure 13). L15 shows a clear peak in the rubbery flow transition region, and LB15 has a broader peak at a shorter relaxation time. PS7 shows no peak.

Notes

On the Conformation of a Segment of Carp Hemoglobin

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Chemical data on the primary structure of proteins being much more abundant than X-ray data, it seems desirable to develop indirect methods of investigation of tertiary structures.

Here we report computer calculations of the conformation of a small segment (residues 118–120, Phe–Pro–Pro) of the α chain of carp hemoglobin (Hb).[1,2]

In homologous proteins of known tertiary structure, horse Hb and whale sperm myoglobin, the corresponding segment is located at the beginning of the H helix[3] with the following sequences of amino acids: Phe–Thr–Pro (residues 117–119) and Phe–Gly–Ala (residues 123–125), respectively. Phenylalanine is the last residue of the nonhelical part GH.

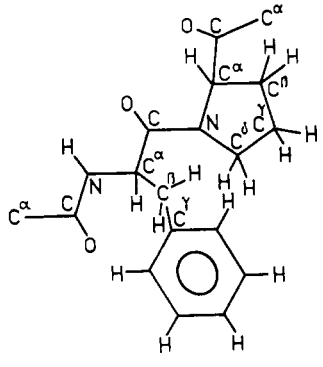

Figure 1. Schematic representation of sequence Phe–Pro.

The presence of the second proline should restrict the number of available conformations for this segment of carp Hb, since it is known that proline modifies the steric maps of the residue preceding it.

Steric maps for a prolyl[4] and an alanyl[5] preceding a prolyl residue in a peptide sequence have been calculated by Schimmel and Flory. New calculations for the alanyl–prolyl sequence were reported during the period of the present investigations by Damiani, De Santis, and Pizzi.[6]

It is to be expected that the steric map of an alanyl residue should be representative of any residue with a β-carbon atom, such as a phenylalanine. We have felt, however, that it was worthwhile to reconsider steric maps for phenylalanyl–prolyl and prolyl–prolyl sequences in order to get a consistent set of results for the potential functions used and also in order to determine the allowed positions of the side chain of phenylalanine.

The theroetical unit Phe–Pro is represented in Figure 1. The geometrical parameters[4,7] and the potential functions are those of Flory,[8] but with hydrogen and carbon treated as individual atoms.

(1) K. Hilse and G. Braunitzer, *Z. Physiol. Chem.*, **349**, 433 (1968).
(2) M. O. Dayhoff, "Atlas on Protein Sequence and Structure," Vol. IV, National Biomedical Research Foundation, Silver Spring, Md., 1969.
(3) M. F. Perutz, *J. Mol. Biol.*, **13**, 646 (1965).
(4) P. R. Schimmel and P. J. Flory, *Proc. Nat. Acad. Sci. U. S.*, **58**, 52 (1965).
(5) P. R. Schimmel and P. J. Flory, *J. Mol. Biol.*, **34**, 105 (1968).
(6) A. Damiani, P. De Santis, and A. Pizzi, *Nature (London)*, **226**, 542 (1970).
(7) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969, p 251.
(8) Reference 7, pp 256 and 257.

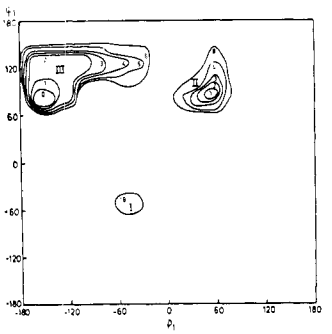

Figure 2. Phe–Pro lowest energy section ($\varphi_2 = -58°$, $\psi_2 = 140°$), in kcal/mol. Flory's potential functions, with all C and H as individual atoms. Angles of rotation of phenylalanyl side chain $\chi_1 = 240°$, $\chi_2 = 90°$.

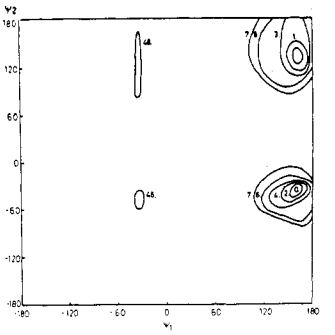

Figure 3. Pro–Pro lowest energy section ($\varphi_1 = \varphi_2 = -58°$), in kcal/mol. Flory's potential functions with all C and H as individual atoms.

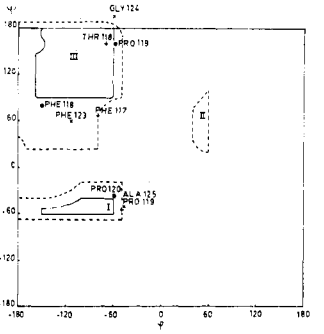

Figure 4. Ramachandran plot of the conformation of the segments Phe(117)–Thr(18)–Pro(119) (α chain of horse Hb) (+), Phe(123)–Gly(124)–Ala(125) (myoglobin) (×), Phe(118)–Pro(119)–Pro(120) (α chain of carp Hb) (●). The values for horse Hb and whale sperm myoglobin have been obtained from X-ray crystallography data (see ref 11, 12) and the values for carp Hb are those calculated in the present work.

The pyrrolidine[9] and phenyl rings[10] have been constructed according to the available X-ray data. The dihedral angle φ of proline has been thereby fixed at $-58°$. The atoms of the pyrrolidine ring and imide bond were assumed to be coplanar.

In the vicinity of the minima of steric maps, dihedral angles φ and ψ were varied by 10°, angles χ_1 and χ_2 by 40 and 20°, respectively. For phenylalanyl, minima of steric repulsion occur around 240 and 90° for χ_1 and χ_2, respectively.

For phenylalanyl–prolyl, two sets of calculations were performed, with the dihedral angle ψ_2 equal respectively to -60 and 140°. The two sets of results obtained were identical.

It can be seen from the steric maps in Figures 2 and 3 that region I is not accessible to either of the residues considered when followed by a proline. The distances between atoms responsible for steric repulsion are shown in Table I. The small section of low energy for Ala–Pro in region I (Ra) obtained by Damiani, De Santis, and Pizzi[6] is probably due to the "eso" geometry of the pyrrolidine ring, which in our calculations and in those of Schimmel and Flory[4,5] has been taken as planar. Minimization techniques in which all rotational and bond angles are allowed to relax would be desirable for more general results.

From the data available at present it appears that, in the absence of external constraints, there are only four possible conformations for the Phe–Pro–Pro, Phe (III or II)–Pro (III)–Pro(III or I), conformation II being disallowed for proline.

TABLE I
CRITICAL DISTANCES BETWEEN HYDROGEN ATOMS IN REGION I

Type of atoms		Distance,	Type of atoms		Distance,
Phe(1)	Pro(2)	Å	Pro(1)	Pro(2)	Å
H^{β}	H^{δ}	1.74	H^{β}	H^{δ}	1.68
H^{β}	H^{δ}	1.95	H^{γ}	H^{δ}	1.72
			H^{δ}	H^{δ}	1.67

In Figure 4, the conformation of the residues in the corresponding segments of horse Hb and myoglobin[11] are shown. The rotational angles in horse Hb have been computed from atomic coordinates.[12] Both these segments have the conformation III–III–I in spite of a large number of possibilities (12 and 27, respectively) in the absence of proline in the central position. The computed conformation III–III–I of carp Hb is also shown in this figure, and it is evident that this sequence of rotational angles strongly resembles that of the other two proteins.

It follows that the presence of two prolines in this part of carp Hb is compatible with the tertiary structure of related proteins and it seems very probable that the segment considered has an identical conformation.

(9) Y. C. Leung and R. E. Marsh, *Acta Crystallogr.*, **11**, 17 (1958).
(10) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 18, The Chemical Society, London, 1958, p M196.
(11) H. C. Watson, unpublished compilation on the stereochemistry of the protein myoglobin.
(12) H. Muirhead and M. F. Perutz, private communication concerning the atomic coordinates of horse hemoglobin, 2.8-Å resolution.