Conformational Characteristics of Isotactic Polypropylene

Alan E. Tonelli

Bell Laboratories, Murray Hill, New Jersey 07974. *Received May 12, 1972*

ABSTRACT: The increase in the conformational or intramolecular entropy accompanying the fusion process is calculated for isotactic polypropylene in the rotational isomeric state approximation. When the calculated change in the intramolecular entropy is compared to the experimental entropy of fusion, after correcting for the entropy resulting from the volume expansion of melting, good agreement is found, providing the rotational state statisical weight parameters τ and ω are both small. More precisely, the energy E_τ of the three-bond interaction between CH_3 and CH and the energy E_ω of the four-bond pentanelike interference in the $g^{\pm}g^{\mp}$ conformations must be at least 0.5 and 2.0 kcal/mol, respectively, in order to predict the small observed change of 0.85–1.05 eu/mol of backbone bonds in the conformational or intramolecular contribution to the entropy of fusion of isotactic polypropylene. Values for E_τ and E_ω of this magnitude have been found to be consistent with the dimensions and other properties measured in dilute solution for vinyl polymers and ethyl-branched polyethylene.

Fatou[1] has recently conducted and reported a study of the fusion process in carefully crystallized molecular weight fractions[2] of isotactic polypropylene. Extrapolation of the experimental relation between the temperatures of fusion and crystallization led to a melting temperature T_m of 208°. The enthalpy of fusion ΔH_u was found to be 1386 cal/mol of repeat unit when the apparent heats of fusion of the various fractions were plotted against their specific volumes and extrapolated to the specific volume of the crystalline unit cell. Thus, the total entropy of fusion ΔS_u ($\Delta S_u = \Delta H_u/T_m$) is 1.5 eu/mol of backbone bonds.

Fortune and Malcolm[4] have estimated the intermolecular or volume expansion contribution[5] ΔS_V to the total entropy of fusion through measurement of the thermal pressure coefficient γ of isotactic polypropylene melt.

$$\Delta S_V = (\partial P/\partial T)_V \Delta V_u = \gamma \Delta V_u = \frac{\alpha}{\beta} \Delta V_u \qquad (1)$$

where α, β, and ΔV_u are the thermal expansion coefficient, the compressibility, and the volume change on melting, respectively. They find[4] $\Delta S_V \approx$ 0.44–0.65 eu/mol of backbone bonds. By difference, then, the intramolecular or conformational contribution[5] $(\Delta S_u)_V = \Delta S_{conf}$ to the total entropy of fusion must be in the range 0.85–1.06 eu/mol of backbone bonds, or about half the value (1.8) for linear polyethylene.[6,7]

Recent demonstrations[8,9] of the validity of separating the total entropy of fusion ΔS_u into the two independent contributions ΔS_V (intermolecular or volume expansion) and $(\Delta S_u)_V$ (intramolecular or conformational), together with the rotational isomeric state model[10,11] of polymer chains, permit a comparison to be made between the calculated and observed changes in the intramolecular or conformational contribution to the entropy of fusion of isotactic polypropylene. Since the calculated conformational entropy is dependent solely upon the number and energy of the backbone bond rotational states (see below), this comparison affords a check on the statistical weight parameters crucial to the description of the conformational characteristics of vinyl polymers which is independent of chain geometry (valence angles, bond lengths, exact location of the rotational states, etc.) and estimates of the chain stereoregularity. Such a comparison, which has not been possible using chain dimensions and other geometry-dependent properties, is the purpose of the present conformational entropy calculations performed on isotactic polypropylene.

Description of Calculations

The intramolecular contribution[8] $(\Delta S_u)_V$ to the total entropy of fusion is just the difference between the configurational entropy of a polymer chain in the molten amorphous and crystalline states

$$(\Delta S_u)_V = \Delta S_{conf} = S_a - S_c \qquad (2)$$

where in the first approximation we assume the crystalline polymer to possess perfect conformational order ($S_c = 0$). From the partition function Z, which describes the configurational characteristics of the chain, the configurational entropy of a single isolated unperturbed chain may be obtained.[12]

$$S_a = R\left[\ln Z + \left(\frac{T}{Z}\right)(\mathrm{d}Z/\mathrm{d}T)\right] \qquad (3)$$

Similarly, the conformational energy change accompanying fusion can be calculated[9,12] from

$$\Delta E_{conf} = E_a - E_c = (RT^2/Z)\left(\frac{\mathrm{d}Z}{\mathrm{d}T}\right) \qquad (4)$$

where the energy of the crystalline conformation E_c is taken as zero, and by analogy[9]

$$\Delta H_u \approx \Delta E_u = \Delta E_{conf} + \Delta E_V \qquad (5)$$

Adoption of the rotational isomeric state model[10,11] of polymers (each polymer backbone bond is only able to reside in a small number of rotational states) and the mathematical

---

(1) J. G. Fatou, *Eur. Polym. J.*, **7**, 1057 (1971).

(2) (a) Mandelkern[2b] has stressed the importance of utilizing molecular weight fractions in studying the melting behavior of crystalline polymers. None of the previous melting studies[3] of isotactic polypropylene has utilized the approach described by Mandelkern[2b] and employed by Fatou,[1] resulting in a wide range of reported[3] values for the heat of fusion of isotactic polypropylene. (b) L. Mandelkern, *J. Phys. Chem.*, **75**, 3909 (1971).

(3) I. Kirshenbaum, Z. W. Wilskinsky, and B. Groten, *J. Appl. Polym. Sci.*, **8**, 2723 (1964).

(4) G. C. Fortune and G. N. Malcolm, *J. Phys. Chem.*, **71**, 876 (1967).

(5) L. Mandelkern, "Crystallization of Polymers," McGraw-Hill, New York, N. Y., 1964, Chapter 5.

(6) F. A. Quinn, Jr., and L. Mandelkern, *J. Amer. Chem. Soc.*, **80**, 3187 (1958).

(7) H. W. Starkweather, Jr., and R. H. Boyd, *J. Phys. Chem.*, **64**, 410 (1960).

(8) A. E. Tonelli, *J. Chem. Phys.*, **52**, 4749 (1971).

(9) A. E. Tonelli, *ibid.*, **54**, 4633 (1971).

(10) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," (English translation), Interscience, New York, N. Y., 1963, Chapter 3.

(11) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969, Chapters I–VI.

(12) T. L. Hill, "Introduction to Statistical Thermodynamics," Addison-Wesley, Reading, Mass., 1960, Chapter I.

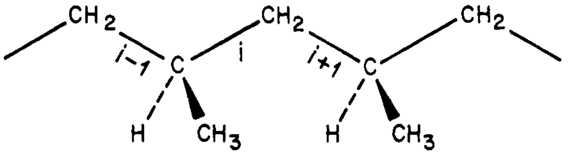

Figure 1. A schematic drawing of a portion of an isotactic polypropylene chain in the all-trans or planar-zigzag conformation.

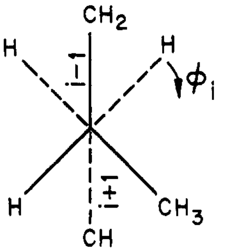

Figure 2. Diagram illustrating the nonbonded interactions between groups separated by three bonds in the isotactic polypropylene chain which depend on the single skeletal rotation angle φ_i.

matrix methods of Flory and Jernigan[11,13,14] allows the evaluation of both Z and $(\mathrm{d}Z/\mathrm{d}T)$ required in eq 3 and 4. For a polymer chain of n backbone bonds

$$Z = J^*\left(\prod_{i=2}^{n-1} U_i\right)J \tag{6}$$

where J^* and J are the $1 \times \nu$ and $\nu \times 1$ row and column vectors

$$J^* = [1000\ldots0];\quad J = \begin{bmatrix}1\\1\\\cdot\\\cdot\\\cdot\\1\end{bmatrix} \tag{7}$$

and

$$\mathrm{d}Z/\mathrm{d}T = G^*\left(\prod_{i=2}^{n-1} \hat{U}_{T,i}\right)G \tag{8}$$

where G^* and G are the $1 \times 2\nu$ and $2\nu \times 1$ row and column vectors

$$G^* = [J^*00\ldots0];\quad G = \begin{bmatrix}0\\0\\\cdot\\\cdot\\\cdot\\0\\J\end{bmatrix} \tag{9}$$

The $\nu \times \nu$ statistical weight matrices U_i consist of the ν^2 statistical weights, or Boltzmann factors, corresponding to the rotational states of bonds $i - 1$ and i. The rows of U_i are indexed by the rotational states of bond $i - 1$ and its columns by the rotational states of bond i. The $2\nu \times 2\nu$ matrices $\hat{U}_{T,i}$ are given by

$$\hat{U}_{T,i} = \begin{bmatrix}U_i & U'_{T,i}\\0 & U_i\end{bmatrix} \tag{10}$$

where

$$U'_{T,i} = \mathrm{d}U_i/\mathrm{d}T \tag{11}$$

It is clear from eq 2–11 that the calculation of the conformational or intramolecular contribution to the entropy and energy of fusion depends solely upon knowledge of the statistical weight matrices U_i. A brief outline of the formulation of such statistical weight matrices for isotactic polypropylene follows. (See ref 11 and 15 for the complete details of the formulation of such statistical weight matrices.)

In Figure 1 a portion of an isotactic polypropylene chain in the all-trans or planar-zigzag conformation is presented. Following the treatments of Flory, *et al.*,[11,15] we initially confine our attention to those interactions between groups or atoms separated by three bonds which depend upon the rotation about only one backbone bond.

The three-bond interactions dependent upon rotations φ_i about bond i (see Figure 1) are illustrated schematically in Figure 2. In the trans (t) conformation shown in Figure 2, the CH and CH_3 groups are close together and interact. This interaction is assigned a statistical weight $\sigma\eta$. Clockwise rotation of $\approx 120°$ about bond i results in the g^+ state, where the CH and CH_2 groups interact with the statistical weight σ. In the g^- state ($\varphi_i \approx 120°$) the CH group is close to both the CH_3 and CH_2 groups. The three-bond interactions in this state (g^-) receive the statistical weight $\tau\sigma$. If we normalize to a weight of unity for the g^+ state, then the statistical weights of the three-bond interactions dependent upon φ_i can be conveniently incorporated into the diagonal matrix

$$D' = \begin{bmatrix}\eta & 0 & 0\\0 & 1 & 0\\0 & 0 & \tau\end{bmatrix} \tag{12}$$

The interactions between groups separated by four bonds which depend on a pair of adjacent backbone rotation angles are termed four-bond interactions. The four-bond interactions associated with the pair of rotation angles φ_{i-1} and φ_i (see Figure 1) may be assigned the statistical weights contained in the matrix

$$V' = \begin{array}{c|ccc} & \mathrm{t} & \mathrm{g}^+ & \mathrm{g}^- \\ \hline \mathrm{t} & 1 & 1 & 1\\ \mathrm{g}^+ & 1 & 1 & \omega\\ \mathrm{g}^- & 1 & \omega & 1\end{array} \tag{13}$$

where the steric overlap corresponding to the $g^{\pm}g^{\mp}$ conformation of n-pentane[16] is assigned the relative statistical weight ω.

Since interactions dependent upon more than a pair of adjacent skeletal rotation angles are negligible,[11,15] the statistical weight matrix for bonds of the type i in Figure 1 may be generated from D' and V' according to

$$U' = V'D' = \begin{array}{c|ccc} & \mathrm{t} & \mathrm{g}^+ & \mathrm{g}^- \\ \hline \mathrm{t} & \eta & 1 & \tau\\ \mathrm{g}^+ & \eta & 1 & \tau\omega\\ \mathrm{g}^- & \eta & \omega & \tau\end{array} \tag{14}$$

Similarly, for bonds of the type $i + 1$

$$U'' = \begin{array}{c|ccc} & \mathrm{t} & \mathrm{g}^+ & \mathrm{g}^- \\ \hline \mathrm{t} & \eta\omega & \tau\omega & 1\\ \mathrm{g}^+ & \eta & \tau\omega & \omega\\ \mathrm{g}^- & \eta\omega & 0 & \omega\end{array} \tag{15}$$

---

[13] P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3509 (1965).

[14] R. L. Jernigan, Ph.D. dissertation, Stanford University, 1967.

[15] P. J. Flory, J. E. Mark, and A. Abe, *J. Amer. Chem. Soc.*, **88**, 639 (1966).

[16] A. Abe, R. L. Jernigan, and P. J. Flory, *ibid.*, **88**, 631 (1966).

where the g^-g^+ element corresponds to the statistical weight ω^2 as a result of two pentane interferences between CH_2 and CH_3 groups occurring in the g^-g^+ rotational state.

The configurational partition function Z and its temperature coefficient dZ/dT are calculated according to eq 6–11 using the statistical weight matrices (eq 14 and 15) formulated and presented above for isotactic polypropylene. Calculations are performed on chains of 500 bonds[17] at $T = T_m = 208°$ with the statistical weight $\tau = \exp[-E_\tau/RT]$ and $\omega = \exp[-E_\omega/RT]$ treated as parameters. $\eta = 1.0$ is adopted throughout, because the three-bond interactions between CH_3 and CH in the trans state *and between* CH_2 and CH in the g^+ state should be similar.

Results and Discussion

The conformational contributions to the entropy and energy of fusion of isotactic polypropylene calculated as a function of E_τ and E_ω are presented in Table I. It is clear that $E_\tau \geq 0.5$ and $E_\omega \geq 2.0$ kcal/mol are required to obtain calculated entropies which agree with the experimentally determined intramolecular or conformational contribution of 0.85–1.06 eu/mol of backbone bonds.

Other quantities, which agree with experiment when calculated with $E_\tau \geq 0.5$ and $E_\omega \geq 2.0$ kcal/mol are the dimensions (mean-square end-to-end distance) of ethyl-branched polyethylene[18] and linear polyethylene[11,16] (only E_ω is relevant), the depolarized scattering of light from 2,4-dimethylpentane,[19] and the dimensions[11,16,20] and optical rotatory properties[21] of highly isotactic vinyl polymers (5–10% racemic placements of repeat unit dyads). However, only the intramolecular or conformational contribution to the entropy of fusion calculated here is totally independent of chain geometry and/or estimates of stereoregularity.

The arguments advanced by Abe and Flory, *et al.*,[15,16,20–22] favoring a small value of ω ($E_\omega \geq 2.0$ kcal/mol) for vinyl polymers including polypropylene are further supported by the present comparison of calculated and measured conformational entropies. In fact, if $E_\tau \sim 500$ cal/mol is adopted, as suggested[23] by the analysis of heat of formation data, then E_ω must approach 3.0 kcal/mol to achieve agreement between the calculated change in conformational and the measured constant volume entropies of fusion. Consequently, in agreement with these authors we conclude that to date no one has successfully synthesized a vinyl polymer with more than *ca.* 90–95% meso dyad placements.

The calculated and measured conformational contribution to the entropy of fusion of isotactic polypropylene leads to the conclusion that isotactic polypropylene is less flexible (smaller conformational entropy) than linear polyethylene. The decrease in the flexibility of isotactic polypropylene relative to linear polyethylene results from the increase in the incidence of four-bond pentane interferences[16] in vinyl polymers.

Throughout the preceding treatment of the melting entropy of isotactic polypropylene, it was assumed that the intramolecular or constant-volume contribution to the entropy of fusion can be attributed exclusively to the increase in the number of conformations available to an isolated chain in the melt. However, as noted by Flory[24] in his lattice treatment of flexible chain molecules, when isolated chains are constrained to occupy the same region of space, spatial overlaps must be avoided. The lattice theory[24] for a chain of X segments yields a term $(1/e)^X$ in the configurational partition function resulting from the mutual exclusion of segments. Thus, the entropic contribution made by the exclusion of segments from different chains is $-R$ eu/mol of segments. If N is defined as the number of backbone bonds in a segment or the segment length, *i.e.*, $N = n/X$, then this contribution becomes $-R/N$ eu/mol of backbone bonds.

TABLE I
THE CONFORMATIONAL CONTRIBUTION TO THE ENTROPY AND ENERGY OF FUSION OF ISOTACTIC POLYPROPYLENE CALCULATED AS A FUNCTION OF E_τ AND E_ω

E_ω, cal/mol	E_τ, cal/mol	ΔS_{conf},[a] eu/mol of backbone bonds	ΔE_{conf},[b] cal/mol of backbone bonds
2000	500	1.42	371
	1000	1.30	348
	1500	1.21	321
	2000	1.13	297
	2500	1.07	277
2500	500	1.21	346
	1000	1.11	320
	1500	1.03	295
	2000	0.96	273
	2500	0.91	255
3000	500	1.03	311
	1000	0.94	286
	1500	0.87	263
	2000	0.81	245
	2500	0.78	232

[a] The calculated entropies are virtually independent of the statistical weight parameter η in the range $0.6 \leq \eta \leq 1.0$. [b] ΔE_{conf} for linear polyethylene is 220 cal/mol of backbone bonds.

Since the lattice model[24] treats the polymer chain as a collinear succession of isodimensional segments, the number of backbone bonds which gives a unit ratio of the length to the breadth of the corresponding portion of the chain is by definition the segment length N. The breadth of a polypropylene chain is crudely estimated to be *ca.* 4 Å, if a van der Waals radius of 2 Å is assigned to the CH_2 and CH_3 groups. From the work of Fujiwara and Flory,[25] who have calculated the mean-square end-to-end distance of isotactic polypropylene as a function of E_ω, E_τ, and chain length, it appears that a five-bond portion of isotactic polypropylene has a mean end-to-end distance $(\langle r^2\rangle_0)^{1/2}$ of 4–5 Å. Hence, a reasonable estimate of the segment length N would be $\sim$5 for isotactic polypropylene, and the corresponding entropy contribution due to the lattice packing of molten chains would be *ca.* -0.4 eu/mol of backbone bonds.

On the other hand, Starkweather and Boyd[7] considered an additional contribution to the constant-volume entropy of fusion which they suggested originates in the appearance of long-range disorder in all liquids. Based on the calculations performed by Oriani[26] on several metals, Starkweather and Boyd propose a value on the order of $R/2$–R eu/mol of backbone bonds for the long-range disorder contribution.

(17) The quantities $(\ln Z)/n$ and $(1/n)(d \ln Z/dT)$ both reach their asymptotic limits for isotactic polypropylene at chain lengths well below $n = 500$ bonds.

(18) A. E. Tonelli, *J. Amer. Chem. Soc.*, **94**, 2972 (1972).

(19) A. E. Tonelli, Y. Abe, and P. J. Flory, *Macromolecules*, **3**, 303 (1970).

(20) A. Abe, *Polym. J.*, **1**, 232 (1970).

(21) A. Abe, *J. Amer. Chem. Soc.*, **90**, 2205 (1968).

(22) (a) P. J. Flory, *Macromolecules*, **3**, 613 (1970); (b) P. J. Flory, J. E. Mark, and A. Abe, *J. Polym. Sci., Part C*, No. 3, 973 (1965).

(23) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

(24) P. J. Flory, *Proc. Roy. Soc., Ser. A*, **234**, 60 (1956).

(25) Y. Fujiwara and P. J. Flory, *Macromolecules*, **3**, 280 (1970).

(26) R. A. Oriani, *J. Chem. Phys.*, **19**, 93 (1951).

If both of these contributions to the constant volume entropy of fusion are accounted for, then the entries in the third column of Table I, which should now be labeled $(\Delta S_{\text{u}})_{\text{V}}$ instead of ΔS_{conf}, must each be increased by 0.6 to 1.6 eu/mol of backbone bonds. Since the total entropy of fusion of isotactic polypropylene is 1.5 eu/mol of backbone bonds, addition of 1.6 eu to the calculated conformational entropies in Table I leads to constant-volume entropies of fusion in excess of the total entropy of fusion. Even inclusion of the lower estimate (0.6 eu) of the combination of lattice exclusion and long-range disorder entropies to the conformational entropies results in constant volume entropies of fusion which exceed the experimental value (0.85–1.06 eu) for all values of E_τ and E_ω less than *ca.* 4.0–5.0 kcal/mol.

Hence, it appears that either the calculated segment length (five backbone bonds) is an overestimate and/or Starkweather and Boyd's[7] proposal of $R/2$–R eu/mol of backbone bonds for the magnitude of the long-range disorder contribution is excessive. More likely, we believe, is the possibility that both contributions tend to largely cancel each other, resulting in the validity of eq 2 and 3, which means in words that the constant-volume entropy of fusion is given by the gain in conformational entropy upon melting calculated for an isolated polymer chain. This belief is supported by the general agreement found[8] between the experimental constant volume entropies of fusion and the calculated changes in isolated chain conformational entropies for several polymers with widely differing chemical structures.

Consequently, the previously drawn conclusions that for isotactic polypropylene $E_\tau \geq 0.5$ and $E_\omega \geq 2.0$ kcal/mol, that isotactic vinyl polymers including polypropylene contain several per cent of racemic dyad placements, and that isotactic polypropylene is less flexible than polyethylene most probably remain valid.[27]

Acknowledgment. The author is grateful to the referees of this paper for their helpful comments and suggestions.

---

(27) NOTE ADDED IN PROOF. After completion of the present manuscript, papers by Heatley [F. Heatley, *Polymer* **13**, 218 (1972)] and Boyd and Breitling [R. H. Boyd and S. M. Breitling, *Macromolecules*, **5**, 279 (1972)], which modify the usual[11,15] three rotational isomeric state model of isotactic polypropylene, have appeared. This modification was achieved by employing semiempirical potential functions to locate the rotational minima and estimate their energies. Both Heatley and Boyd and Breitling conclude that for reasonable values of E_τ and E_{w} the dimensions and their temperature coefficient calculated from their models of isotactic polypropylene are in agreement with the experimental values, thus rendering unnecessary the contention[11,15,19-21] that all isotactic polypropylenes studied to date contain several per cent of racemic dyad placements. Heatley presents E_τ = 1250 ± 500 cal/mol and E_{w} = 1950 ± 100 cal/mol as the appropriate energies to be used with his model. When these energies, together with Heatley's statistical weight matrix, are used to calculate the conformational or intramolecular contribution to the entropy and energy of melting, the following results are obtained: ΔS_{conf} = 1.43–1.66 eu/mol of backbone bonds and ΔE_{conf} = 366–407 cal/mol of backbone bonds. On the other hand, Boyd and Breitling conclude, as appropriate for isotactic polypropylene, E_τ = 600 cal/mol and E_{w} = 1300 cal/mol. These energies lead to ΔS_{conf} = 1.80 eu/mol of backbone bonds when inserted as Boltzmann factors into the statistical weight matrices developed by them. Both rotational isomeric state models lead to calculated intramolecular or conformational contributions to the entropy of fusion which equal or exceed the value of 1.5 eu/mol of backbone bonds measured[1] for the total entropy of fusion. In fact, the intramolecular or conformational contribution to the energy of fusion calculated from Boyd and Breitling's model exceeds the total measured[1] enthalpy of fusion (700 cal/mol of backbone bonds). Thus, we conclude that both of these rotational isomeric state models are incompatible with or fail to adequately describe the conformational characteristics of isotactic polypropylene as deduced from its fusion behavior.

The Poly(hydroxy-L-proline) Ring Conformation Determined by Proton Magnetic Resonance

D. A. Torchia*

Bell Laboratories, Murray Hill, New Jersey 07974. *Received March 10, 1971*

ABSTRACT: From a computer simulation of the 220-MHz spectrum of poly(hydroxy-L-proline), all ring vicinal couplings have been obtained. Using these couplings and a Karplus-type equation to estimate ring dihedral angles, it is found that the ring maintains a single nonplanar conformation in aqueous solution. This puckered conformation, having C_γ exo, is described by the angles $\chi_1 \approx -\chi_4 \approx -25°$, $\chi_2 \approx -\chi_3 \approx 45°$, $\varphi \approx 120°$. Prolyl and hydroxyprolyl conformations obtained previously are compared to this conformation, and discussion is provided of a possible interaction of the peptide backbone with the OH moiety, in a C_γ-exo Hyp ring.

Recently, prolyl ring conformations of cyclo(tri-Pro)[1,2] and poly(Pro)[3] have been obtained using Karplus-type equations[4-6] to relate ring dihedral angles to vicinal couplings, the latter determined by computer simulating nmr spectra obtained by 220 MHz. In the case of poly(Pro), the nmr analysis indicated that several conformations were in rapid equilibrium (on the nmr time scale), and it was concluded, on the basis of the nmr results, X-ray data,[7] and energy calculations,[8] that two C_γ puckered ring conformations (C_γ exo or endo

---

* Address correspondence to the author at the U. S. Department of Commerce, National Bureau of Standards, Polymers Division, Washington, D. C. 20234.

(1) The following abbreviations are used in this paper: Pro for L-prolyl, Hyp for hydroxy-L-prolyl, Gly for glycyl, poly(Pro) and poly(Hyp) for the helical forms of these polymers having trans peptide bonds, X for any amino acid residue except Pro or Hyp, $|\varphi|$ for absolute value of φ, DP for degree of polymerization.

(2) C. M. Deber, D. A. Torchia, and E. R. Blout, *J. Amer. Chem. Soc.*, **93**, 4893 (1971).

(3) D. A. Torchia, *Macromolecules*, **4**, 440 (1971).

(4) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *ibid.*, **33**, 1842 (1960).

(5) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(6) M. Barfield and M. Karplus, *ibid.*, **91**, 1 (1969).

(7) R. Balasubramanian, A. V. Lakshminarayanan, M. N. Sabesan, G. Tegoni, K. Venkatesan, and G. N. Ramachandran, *Int. J. Protein Res.*, **2**, 303 (1970).

(8) G. N. Ramachandran, A. V. Lakshminarayanan, R. Balasubramanian, and G. Tegoni, *Biochim. Biophys. Acta*, **221**, 165 (1971).