Conformational characteristics of poly(*N*-vinyl pyrrolidone)

A. E. Tonelli
Bell Laboratories, Murray Hill, New Jersey 07974, *USA*

(*Received* 9 *July* 1981; *revised* 26 *August* 1981)

Conformational energies are calculated for poly(*N*-vinyl pyrrolidone) (PVP) chains as a function of stereosequence using semiempirical potential functions appropriate to peptides and n-alkanes. The planar pyrrolidone side groups are permitted to adopt both conformations which result in an eclipsed arrangement of the pyrrolidone N–CH$_2$ or N–(C=O) and the C$^\alpha$–H$^\alpha$ bonds. Solvent interactions were considered in the manner used to treat other vinyl polymers bearing planar side groups. Dimensions and dipole moments were calculated using the RIS model developed for PVP from the conformational energies considering both the effects of stereosequence and temperature. Dipole moments were measured for three PVP samples with molecular weight ranging from 10 000 to 360 000. The dimensions and dipole moments calculated for atactic PVP chains agree with the dimensions reported in the literature and the dipole moments measured here.

Keywords Conformations; stereo sequences; RIS model; dimension; dipole moments; poly(*N*-vinyl pyrrolidone)

INTRODUCTION

Poly(*N*-vinyl pyrrolidone) (PVP) is an example of a vinyl polymer possessing planar side groups. Previous studies of such vinyl polymers, i.e., poly(methyl methacrylate)[1,2], poly(methyl acrylate)[3], poly(vinyl acetate)[4], polystyrene[5], poly(α-methyl styrene)[6], and poly(*N*-vinylcarbazole)[7], led to the observation that the planarity of the side groups severely limits the conformations (φ_1, φ_2), available to the pair of backbone bonds flanked by the side groups (see *Figure 1a*).

In addition to being planar, the side groups of PVP are highly polar due to the incorporation of a peptide bond in the five-membered pyrrolidone ring. Access of solvent molecules to the PVP backbone is limited in the *tt* conformation of a meso dyad illustrated in *Figure 1a*. Also, possible interactions between the polar peptide groups in neighbouring pyrrolidone rings are probably maximal in the same *tt* conformation, or in the *tg*$-$ conformation of a racemic dyad, resulting in the dependence of PVP conformations not only on stereosequence, but on solvent interactions and side group orientations.

We have performed conformational energy calculations on PVP chains using semiempirical potential functions appropriate to vinyl polymers and polypeptides. Solvent interaction energies are approximated, and the side groups are permitted to adopt different orientations. PVP chains of different stereoregularity are treated, and a rotational isomeric state (RIS) model is derived from the conformational energies. Unperturbed mean square end-to-end distances and dipole moments are calculated as a function of stereoregularity from the RIS model derived for PVP and compared to dilute solution dimensions reported in the literature and dipole moments measured here for three PVP samples of different molecular weight.

CONFORMATIONAL ENERGIES

Methods of calculation

The crystal structures[8] of L-5-iodomethyl-pyrrolid-2-one and L-pyrrolid-2-one-5-carboxamide and consistent force field calculations[9] performed on 2-pyrrolidone indicate that the five-membered pyrrolidone ring is planar. From the crystal structures[8] of these two pyrrolidone derivatives, we obtain the planar PVP side group geometry indicated in *Figure 1c*. Backbone $\langle$C$^\alpha$–CH$_2$–C$^\alpha$ and $\langle$CH$_2$–C$^\alpha$–CH$_2$ angles of 114° and 112° are adopted, and $\langle$H–C–H $= \langle$H–C$^\alpha$–N $= 110°$ are assumed. All backbone C–C bonds are set at 1.54 Å and C–H bonds of 1.10 Å are used.

A threefold intrinsic torsional potential with a barrier height of 2.8 kcal mol^{-1} was assigned[10] to each backbone C–C bond. The C$^\alpha$–N backbone to side chain bond was by analogy to the treatment of polypeptides also assigned a threefold intrinsic torsional potential, but with a barrier height[10–12] of 1.5 kcal mol^{-1}. The Lennard-Jones 6–12 potential together with a coulombic term were used to evaluate the van der Waals and electrostatic interactions between nonbonded atoms and groups. The methylene groups belonging to the pyrrolidone side chains were each treated as a united atom with the van der Waals radius of a methyl group. The parameters of the 6–12 potential and the partial atomic charges (see *Figure 1b*) were taken from the Brant, Miller and Flory potential for polypeptides[12]. A dielectric constant of 3.5 was assumed to mediate the electrostatic interactions.

In vinyl polymers with large side chain substituents, the proximity of the side chains in a meso dyad when in the *tt* conformation (see *Figure 1a*) prevents the solvent molecules from gaining access to the backbone[5]. However, in the *tg*$-$ conformation the side chains are no longer close enough to interact and prevent the access of

0032-3861/82/050676–05$03.00

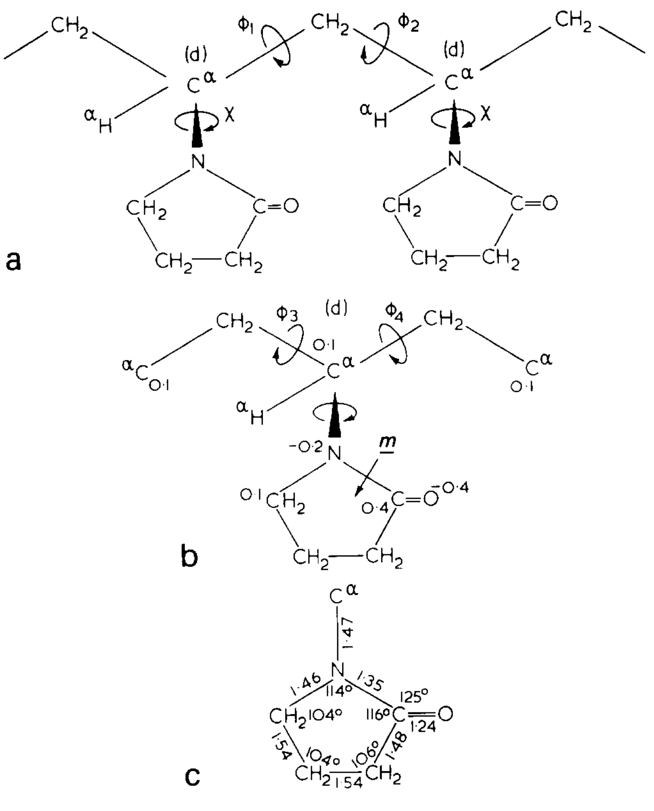


Figure 1 (a) A meso (*dd*) dyad in the *tt* conformation ($\phi_1 = \phi_2 = 0°$) along the PVP chain. (b) Portion of a PVP chain whose conformation depends on rotations ϕ_3 and ϕ_4 flanking a C^α carbon. The location of the group dipole moment $\underline{m}$ and the partial atomic charges are also indicated. (c) Geometry of the pyrrolidone side chain

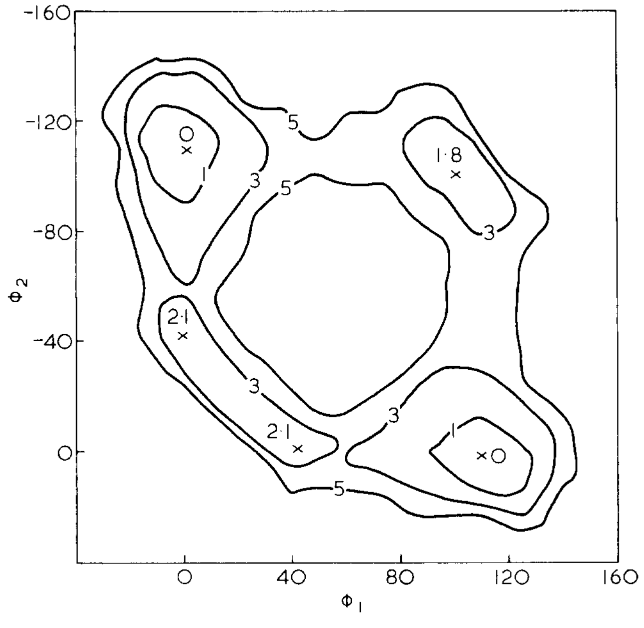


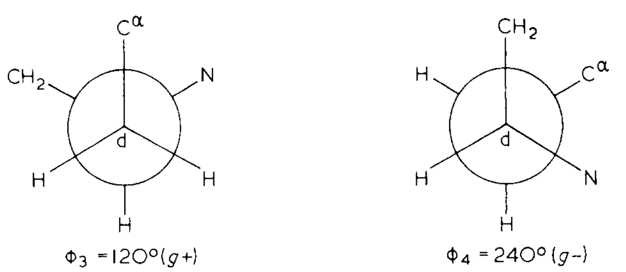
Figure 2 Conformational energy map for a meso (*dd*) PVP dyad calculated with σ = 5.0 Å. X indicates the location of local minima and the contours are drawn in units of kcal mol^{-1} relative to the lowest energy conformations at ϕ_1, ϕ_2 = 0°, 110° (*t*, *g*+) and 110°, 0° (*g*+, *t*)

solvent. Yoon *et al.*[5] devised a procedure to allow for the conformational dependence of solvent interactions. Side chain–side chain interactions are replaced by side chain–solvent interactions when the distance r between side chains becomes sufficiently great ($r=\sigma$), and the energy should level off at this distance σ. Thus we require the calculated conformational energy to remain constant at its value for $r=\sigma$ for distances greater than σ. σ = 4–5 Å seems to be a reasonable value judging from previous results[1–7]. In our calculations, σ = 4 Å, 5 Å, and ∞ (no solvent–polymer interactions considered) were utilized.

Backbone rotation angles (see *Figures 1a* and *b*) were stepped in increments of 10° and two orientations (χ) of the pyrrolidone ring (see *Figure 1b*) were permitted; $\chi = 0°$ where N–CH_2 and C^α–H^α are eclipsed and $\chi = 180°$ where N–C(=O) and C^α–H^α are eclipsed. For reasons previously discussed[13,14], each of the permitted side chain conformations has the plane of the pyrrolidone ring bisecting the valence angle ($\measuredangle CH_2$–$C^\alpha H$–CH_2) defined by the backbone bonds flanking the C^α carbon to which it is attached.

Results

In *Figures 2* and *3* the conformational energy maps for meso (*dd*) and racemic (*dl*) dyads (see *Figure 1a*) are presented. *Figure 4* presents the conformational energy calculated as a function of the rotation angles flanking a dC^α carbon (see *Figure 1b*). It is apparent from these conformational energy maps that backbone conformations which result in the simultaneous *gauche* arrangements of C^α, CH_2, and the pyrrolidone side chain such as:



are precluded. Thus, each of the backbone bonds in PVP is limited to just two rotational states. A similar conclusion was reached in the conformational studies of

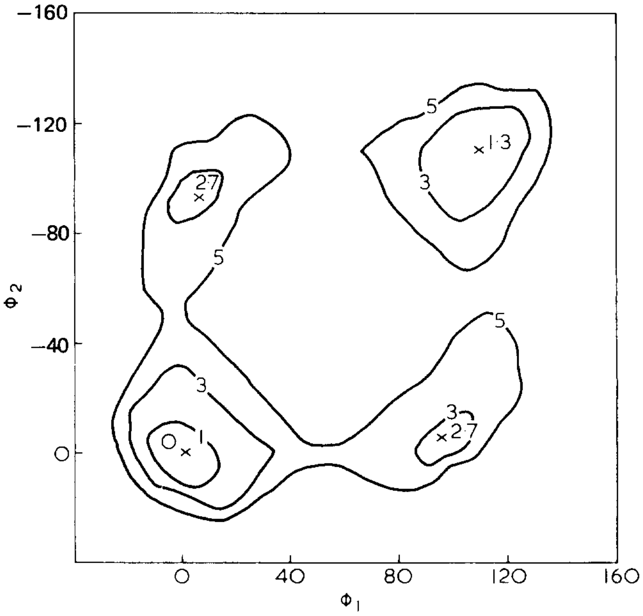


Figure 3 Same as *Figure 2* except replace meso (*dd*) with racemic (*dl*) and ϕ_1, ϕ_2 = 0°, 110° (*t*, *g*+) and 110°, 0° (*g*+, *t*) with ϕ_1, ϕ_2 = 0°, 0° (*t*, *t*)

other vinyl polymers[1-7] with bulky side groups, such as polystyrene[5].

Although the relative energies of the allowed backbone conformations depend on the value of σ used to approximate the solvent–polymer interactions, restriction of each backbone bond to just two rotational states was found to be independent of σ. In our derivation of an RIS model for PVP we will therefore limit our consideration to just two rotational states for each backbone bond leading to 2×2 statistical weight matrices.

RIS MODEL

Statistical weight matrices appropriate to bond pairs flanking and between substituted C^{α} carbons, respectively, may be written[5] as:

$$U'=\begin{bmatrix}1 & 1\\ 1 & 0\end{bmatrix} \text{and } U''=\begin{bmatrix}Z_{tt} & Z_{tg\pm}\\ Z_{g\pm t} & Z_{g\pm g\pm} \text{ or } Z_{g\pm g\mp}\end{bmatrix} \qquad (1)$$

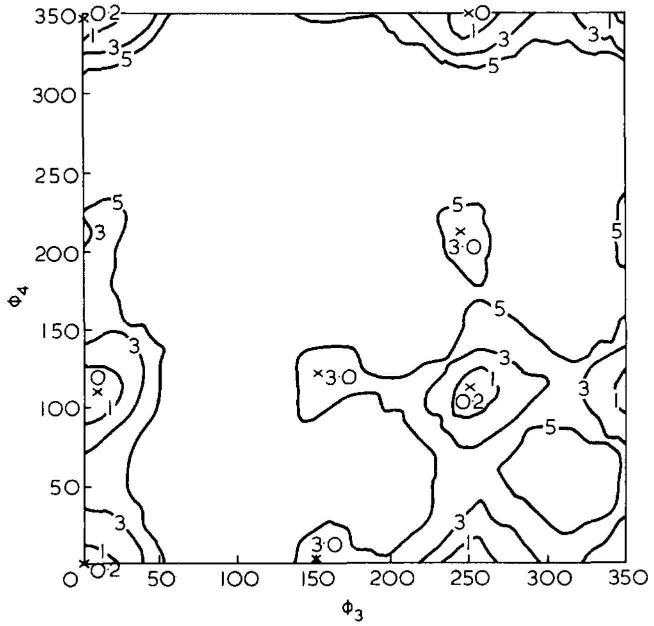


Figure 4 Conformational energy map for the PVP chain fragment shown in *Figure 1b* calculated with σ = 5.0 Å. X indicates the location of the local minima and the contours are drawn in units of kcal mol^{-1} relative to the lowest energy conformations at ϕ_3, ϕ_4 = 10°, 110° (t, $g+$) and 250°, 350° ($g-$, t)

The partition functions Z_s of the low energy conformation domains found in the dyad energy maps constitute the elements of U'' and may be evaluated[5] from the energy maps according to $Z_s=\alpha_s\exp[-\langle E_s\rangle/RT]$, where α_s and $\langle E_s\rangle$ are the pre-exponential factor and average energy of each conformational domain s. Such an evaluation is presented in *Table 1* for the *dd*-meso and *dl*-racemic dyads, where the racemic *tt* domain is assigned a zero average energy.

Expression of the statistical weight matrices in terms of the first- and second-order interactions[10] dependent upon a single or a pair of rotations leads to[5,15]:

$$U'_d=\begin{array}{c|cc} & t & g^+\\ \hline t & 1 & 1\\ g^- & 1 & 0\end{array} \quad U'_l=\begin{array}{c|cc} & t & g^-\\ \hline t & 1 & 1\\ g^+ & 1 & 0\end{array} \qquad (2)$$

$$U''_{dd}=\begin{array}{c|cc} & t & g^-\\ \hline t & \omega'' & \frac{1}{\eta}\\ g^+ & \frac{1}{\eta} & \frac{\omega}{\eta^2}\end{array} \qquad U'_{ll}=\begin{array}{c|cc} & t & g^+\\ \hline t & \omega'' & \frac{1}{\eta}\\ g^- & \frac{1}{\eta} & \frac{\omega}{\eta^2}\end{array} \qquad (3)$$

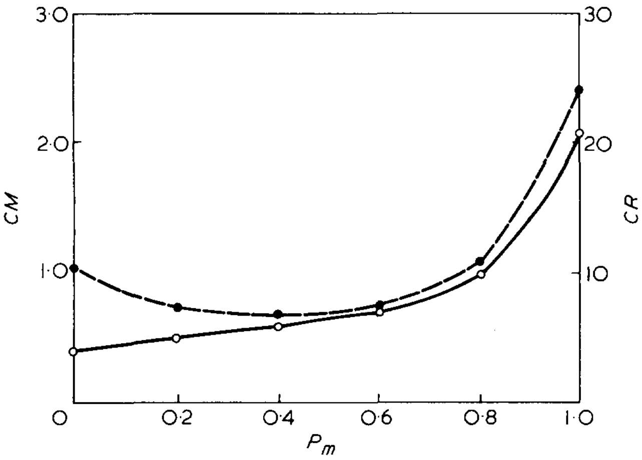


Figure 5 (———), CM = $\langle\mu^2\rangle_0/(n/2)m^2$ and (— — —), CR = $\langle r^2\rangle_0/nl^2$ calculated at 25°C for n = 400 bond PVP chains of varying stereoregularity P_m. The following statistical weights were used: ω = 0.69 exp(−600/T), ω' = 1.5 exp(−850/T), ω'' = 1.3 exp(−1160/T), η = 0.73 exp(−50/T)

Table 1 Partition functions (Z_s), average energies ($\langle E_s\rangle$), and pre-exponential factors (α_s) for the various low-energy dyad conformations as obtained from the energy maps

	Z_s*			$\langle E_s\rangle$, (kcal mol^{-1})			α_s		
State(s)	a	b	c	a	b	c	a	b	c
dd; tt	0.007	0.066	0.088	2.52	1.95	1.86	0.49	1.77	2.03
dd; tg−	1.414	0.357	0.295	−0.02	0.82	0.87	1.37	1.42	1.28
dd; g+t	1.414	0.357	0.295	−0.02	0.82	0.87	1.37	1.42	1.28
dd; g+g	0.175	0.017	0.006	1.23	2.57	3.05	1.39	1.29	1.04
dl, tt	1.0	1.0	1.0	0.0	0.0	0.0	1.0	1.0	1.0
dl; tg+	0.102	0.021	0.014	1.55	2.50	2.63	1.39	1.42	1.18
dl; g+t	0.102	0.021	0.014	1.55	2.50	2.63	1.39	1.42	1.18
dl; g+g+	0.909	0.146	0.057	0.24	1.31	1.75	1.36	1.33	1.09

* $Z_s=\alpha_s\exp[-\langle E_s\rangle/RT]$, T = 25°C
(a) σ = 4.0Å
(b) σ = 5.0Å
(c) σ = ∞

Table 2 Measured dipole moments of PVP

Molecular weight	$\frac{\langle\mu^2\rangle_0}{(n/2)}$* (D²)
10 000	8.2
40 000	6.7
360 000	8.0

* Estimated uncertainty is ±5% and *n* is the number of bonds in the PVP chain

$$U''_{dl}=\begin{array}{c|cc} & t & g^+ \\ \hline t & 1 & \frac{\omega'}{\eta} \\ g^+ & \frac{\omega'}{\eta} & \frac{1}{\eta^2} \end{array} \qquad U''_{ld}=\begin{array}{c|cc} & t & g^- \\ \hline t & 1 & \frac{\omega'}{\eta} \\ g^- & \frac{\omega'}{\eta} & \frac{1}{\eta^2} \end{array} \tag{4}$$

where the racemic *tt* state is given a statistical weight of unity. Using the results of the conformational energy maps summarized in *Table 1* leads to the following solutions for the first- and second-order statistical weights:

$$\omega=0.69\exp\left[-\frac{600}{T}\right]$$

$$\omega'=1.5\exp\left[-\frac{850}{T}\right]$$

$$\omega''=1.3\exp[-E_{\omega''}/RT],\quad E_{\omega''}=1.9\text{–}2.5\ \text{kcal mol}^{-1}$$

$$\eta=0.73\exp[-E_\eta/RT],\quad -0.9\leqslant E_\eta\leqslant 0.1\ \text{kcal mol}^{-1}$$

A range of values is possible for $E_{\omega''}$ and E_η, because the meso and racemic *tt* conformations bear the statistical weights $\eta^2\omega''$ and η^2 respectively, before normalization (see equations (3) and (4)) and have neighbouring pyrrolidone rings in close contact. Thus, $E_{\omega''}$ and E_η are sensitive to σ, while E_ω and $E_{\omega'}$ are not.

DIPOLE MOMENTS AND DIMENSIONS

Measurement of PVP dipole moments

Dielectric constants were measured with a WTW Dipolmeter DM01 using a DFL-1 dielectric cell thermostatically controlled at 25°C. A Bausch and Lomb Abbe type refractometer was used to obtain refractive indices.

Three samples of PVP with molecular weights of 10 000, 40 000, and 360 000 obtained from Aldrich Chemical Co. were dissolved in *p*-dioxane dried over 4 Å molecular sieves to form solutions of weight fractions $W_2=0.5\text{–}2\%$. The measured dielectric constant ε and refractive index *n* exhibited a linear dependence on W_2 and were fitted to the following equations.

$$\varepsilon=\varepsilon_1(1+\alpha W_2) \tag{5}$$

$$n=n_1(1+\gamma W_2) \tag{6}$$

1 and 2 denote the solvent and solute, respectively.

Mean-square dipole moments $\langle\mu^2\rangle$ were obtained from the equation of Smith and Guggenheim[16]

$$\langle\mu^2\rangle=\frac{27kTM}{4\pi N_A d_1(\varepsilon_1+2)^2}(\alpha\varepsilon_1-2n_1^2\gamma) \tag{7}$$

where *M* is the molecular weight of the PVP solute, $d_1=1.0337$, $\varepsilon_1=2.209$, and $n_1=1.4204$ are the density, dielectric constant, and refractive index of *p*-dioxane, and N_A is Avogadro's number. The observed $\langle\mu^2\rangle$ are presented in *Table 2*.

CALCULATED DIPOLE MOMENTS AND DIMENSIONS

Matrix multiplication techniques[10] were utilized to calculate the mean-square dipole moments $\langle\mu^2\rangle_0$ and dimensions $\langle r^2\rangle_0$ of PVP chains consisting of 400 bonds and possessing different stereosequences. Monte Carlo generation of chains a repeat unit at a time permitted the entire range of stereosequence to be considered. Rotations of 0° and ±120° were assigned the *t* and $g\pm$ rotational states and the calculations were performed at $T=25°$ and 100°C.

A group dipole moment $\underline{m}$ of 3.70 D was assigned to the pyrrolidone rings in PVP based on the dipole moment measured[17] for 2-pyrrolidone. The dipole moment was located (see *Figure 1b*) in the same position as the peptide group dipole moment placed by Brant and Flory[11] in their calculations on polypeptides. The group's moment was transformed from the pyrrolidone ring to the usual coordinate system[10] along the C^α–CH_2 backbone bond to the right of the C^α carbon to which it is attached, such as the $C^\alpha \overset{\varphi_4}{\text{—}} CH_2$ bond in *Figure 1b*.

In order to achieve this transformation the orientation χ of the pyrrolidone ring with respect to the backbone must be specified. From the conformational energy calculations it was determined that at 25°C (100°C) the probabilities of $\chi=0°$ and $\chi=180°$ orientations were 0.85 (0.80) and 0.15 (0.20), with only a minor dependence on stereosequence. This results in

$$\underline{m}=\begin{bmatrix}-1.566\\ 2.321\\ \pm 0.197d,l\end{bmatrix}\quad(25°\text{C}) \tag{8}$$

and

$$\underline{m}=\begin{bmatrix}-1.423\\ 2.109\\ \pm 0.030d,l\end{bmatrix}\quad(100°\text{C}) \tag{9}$$

expressed in the reference frame along the backbone C^α–CH_2 bond.

In *Table 3* we present the ratios $\text{CM}=\frac{\langle\mu^2\rangle_0}{(n/2)m^2}$ and $\text{CR}=\frac{\langle r^2\rangle_0}{nl^2}$ calculated at $T=25°$ and 100°C, for $E_{\omega''}=2.2\pm0.3$ kcal mol⁻¹ and $E_\eta=0.1$ kcal mol⁻¹ as a function of stereosequence (P_m), where $m^2=(3.7)^2$, $l^2=(1.54)^2$, and *n* is the chain length (400 bonds). It was assumed that the polymerization statistics of PVP are described by Bernoullian statistics with the probability of meso (*m*) dyads given by P_m.

From *Table 2* the experimental CM = 0.49–0.60 are in good agreement with the calculated values presented in *Table 3* for atactic PVP chains with $P_m=0.2\text{–}0.6$.

For $E_\eta<0.100$ kcal mol⁻¹ all calculated dipole

Table 3 CM = $\langle\mu^2\rangle_0/(n/2)m^2$ and CR = $\langle r^2\rangle_0/nl^2$ for 400 bond PVP chains with Bernoullian probability P_m* for meso dyad addition. $E_{\omega''}$ = 2.2 ± 0.3 kcal mol^{-1} and E_η = 0.100 kcal mol^{-1}

	CM		CR	
P_m	25°C	100°C	25°C	100°C
0.0	0.39	0.37	10.3	10.4
0.2	0.49	0.44	7.08	7.53
0.4	0.59	0.51	6.65	6.78
0.6	0.70	0.60	7.41	7.65
0.8	0.98	0.77	10.8	9.96
1.0	2.07	1.22	24.4	17.2

* For P_m = 0.2–0.8 ten Monte Carlo chains were generated and CM and CR were averaged over this ensemble

moments exceeded the observed values. Dimensions (CR) calculated with $E_{\omega''}=2.2\pm0.3$ kcal mol^{-1} and $E_\eta=0.100$ for atactic PVP chains are in agreement with those reported in the literature[18] (CR = 5–11) and which were also presumably measured for predominantly atactic samples.

The temperature coefficients d ln $\langle\mu^2\rangle_0/\mathrm{d}T$ and d ln $\langle r_2\rangle_0/\mathrm{d}T$ calculated for PVP chains as a function of stereosequence are presented in *Table 4*. For atactic chains (P_m = 0.4–0.6) $\langle\mu^2\rangle_0$ and $\langle r^2\rangle_0$ are predicted to have relatively large negative and small positive temperature coefficients, respectively.

DISCUSSION

We have developed a RIS model for the conformational characteristics of PVP which is successful in predicting the dipole moments and dimensions observed for atactic chains. This RIS model is characterized by the following statistical weights

$$\omega=0.69\exp\left(-\frac{600}{T}\right),\ \omega'=1.5\exp\left(-\frac{850}{T}\right),$$

$$\omega''=1.3\exp\left(\frac{-1100\pm150}{T}\right)\ \text{and}\ \eta=0.73\exp\left(-\frac{50}{T}\right).$$

Each backbone bond may adopt only two rotational states due to steric interactions involving the planar pyrrolidone side groups. Each of the pyrrolidone rings can assume two different orientations with respect to the backbone characterized by $\chi=0°$ and 180°, with the former orientation favoured by a factor of 4 or 5.

Table 4 d ln$\langle\mu^2\rangle_0$/dT and d ln$\langle r^2\rangle_0$/dT calculated for 400 bond PVP chains as a function of stereosequence P_m

P_m	d ln$\langle\mu^2\rangle_0$/dT	d ln$\langle r^2\rangle_0$/dT
0.0	−0.0007	0.0002
0.2	−0.0014	0.0008
0.4	−0.0019	0.0003
0.6	−0.0021	0.0004
0.8	−0.0031	−0.0011
1.0	−0.0069	−0.0046

As a means to test the validity of our RIS model further we are currently measuring Kerr constants of PVP chains as obtained in electrical birefringence experiments[19]. Comparison of the observed Kerr constants with those calculated using our RIS model for PVP should provide an additional sensitive test[20–23] of its validity.

REFERENCES

1 Sundararajan, P. R. and Flory, P. J. *J. Am. Chem. Soc.* 1974, **96**, 5025
2 Sundararajan, P. R. *J. Polym. Sci., Polym. Lett. Edn.* 1977, **15**, 699
3 Yoon, P. Y., Suter, U. W., Sundararajan, P. R. and Flory, P. J. *Macromolecules* 1975, **8**, 784
4 Sundararajan, P. R. *Macromolecules* 1978, **11**, 256
5 Yoon, D. Y., Sundararajan, P. R. and Flory, P. J. *Macromolecules* 1975, **8**, 776
6 Sundararajan, P. R. *Macromolecules* 1977, **10**, 623
7 Sundararajan, P. R. *Macromolecules* 1980, **13**, 512
8 Molin-Case, J. A., Fleischer, E. and Urry, D. W. *J. Am. Chem. Soc.* 1970, **92**, 4728
9 Warshel, A., Levitt, M. and Lifson, S. *J. Mol. Spectr.* 1970, **33**, 84
10 Flory, P. J. 'Statistical Mechanics of Chain-Molecules', Interscience, New York, 1969, Ch. I–VI
11 Brant, D. A. and Flory, P. J. *J. Am. Chem. Soc.* 1965, **87**, 2791
12 Brant, D. A., Miller, W. G. and Flory, P. J. *J. Mol. Biol.* 1967, **23**, 47
13 Abe, Y., Tonelli, A. E. and Flory, P. J. *Macromolecules* 1970, **3**, 294
14 Tonelli, A. E. *Macromolecules* 1973, **6**, 682
15 Suter, U. W. and Flory, P. J. *Macromolecules* 1975, **8**, 765
16 Bottcher, C. J. F. and Bordewijk, P. 'Theory of Dielectric Polarization', Elsevier, Amsterdam, 1978, Vol. II, Ch. 14
17 McClellan, A. L. 'Tables of Experimental Dipole Moments', W. H. Freeman, San Francisco, 1963, Vol. I
18 Meza, R. and Gargallo, L. *Eur. Polym. J.* 1977, **13**, 235
19 Le Fevre, C. G. and Le Fevre, R. J. W. in 'Techniques of Chemistry', (Ed. A. Weissberger), Wiley-Interscience, New York, 1972, Vol. I, Part IIIc, Ch. VI
20 Tonelli, A. E. *Macromolecules* 1977, **10**, 153
21 Saiz, E., Suter, U. W. and Flory, P. J. *J. Chem. Soc. Faraday Trans. II*, 1977, **73**, 1538
22 Khanarian, G. and Tonelli, A. E. *J. Chem. Phys.* 1981, **75**, 5031
23 Khanarian, G. and Tonelli, A. E. *Polym. Prepr.* 1981, **22(2)**, 409