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Chain Dimensions and Intrinsic Viscosities of Polypeptides in the Helix-Coil Transition Region

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An equation is derived which correlates the unperturbed dimensions $\langle r^2 \rangle_0$ of polypeptides with the helical contents in the helix-coil transition region by using a simple model of a polypeptide chain. The model is a chain of connected balls which represent the repeating units, -CO-NH-CHR-, based on the fact that the repeating unit has a plane structure. The changing trend of the expansion factor α_n in the transition region is connected with the helical content f_H . The intrinsic viscosities $[\eta]$ of polypeptides are calculated from the unperturbed dimensions and the α_n factors.

The above calculated results concerning $\langle r^2 \rangle_0$ and $[\eta]$ are compared with other authors' theoretical and experimental results. From the comparison, we concluded that our theory explains better the chain dimensional behavior of polypeptides in the helix-coil transition region than others.

Introduction

The helical structure of polypeptides was studied early by Pauling *et al.*,¹ the structure was an α -helical structure which includes 3.6 residues or repeating units per turn. Doty *et al.*² discovered that polypeptide chains in solution perform a reversible transition between the randomly coiled and the α -helical forms according to the solution conditions. From that time down to this day, experimental researches about the helix-coil transition in polypeptides have been actively under way. For example, there are researches for the effects of solvents,³ pH⁴ and the concentration of a surfactant ion in the solution,⁵ and the effects of the temperature and the length of side-chains⁶ attached to the polypeptides were also studied. Many researches have been conducted on the conformation of polypeptide molecules by using various kinds of analytical instruments.^{7,8}

In theoretical studies, Zimm and Bragg,⁹ Lifson and Roig¹⁰

and many others¹¹ set up the statistical mechanical models for polypeptide molecules. The transformation matrices were individually taken for the three chain elements in one repeating unit -(CO-NH-CHR)-, and then the mean behaviors per three repeating units were calculated. They calculated the helical contents, the sensitivity parameter of the transition and other properties of polypeptides, *e. g.*, electric moments, relaxation times, *etc.*, But not so many studies were conducted for calculating the chain dimensions in the helix-coil transition region. Nagai^{11,12} studied the chain dimensions by applying the Zimm-Bragg theory,⁹ But his theoretical results cannot explain the chain dimensional behavior of polypeptides in the transition region, and do not agree with the experimental results even qualitatively.

In order to solve the above difficulty, we set up a new model that is more simple and conclusive than other models. The excluded volume effect on the chain dimensions in the transition region was also studied in this paper, this kind of

studies has never been appeared in the literature. The detailed results and discussions will be reported in the text.

Theory

(1) Model

Polypeptides, being polyamides, have a planarity^{13,14} in each repeating units as shown in Figure 1. Consequently, our model that treats the bond-rotation angle ϕ (see Figure 1 where the *trans*-form was taken as $\phi=0^\circ$) per repeating unit should be more simple and reasonable than the model treating separately the bond-rotation angles appearing in the repeating unit.

The bond angles and the bond lengths in a chain are generally limited within narrow ranges, so we can take the mean value¹⁵ as if they are fixed. Then, in the helix-coil transition, the bond rotation angle ϕ is the only one variable in the unperturbed dimension of a polypeptide. The polymer connected by the broken lines (in Figure 1) exhibits chain dimensional behaviors of the polypeptide. Accordingly, the polypeptide chain is represented by a simple model as shown in Figure 2 where each repeating unit is represented by a ball. Thus the behavior of the ball expresses that of the repeating unit. The bond angle θ and the bond length l are defined in Figure 2.

In our theory, a random-coil is defined by a freely rotating chain in which ϕ changes since the freely rotating chain is closer to real chain state than the freely jointed chain in which ϕ as well as θ change, and since it is also more often used for defining the random-coil.¹⁶ The α -helix and the intermediates in the transition region are both defined as the rotation-hindered chain states because of the intramolecular hydrogen bonds, the hindrance in the former being complete.

(2) Unperturbed Dimension

We consider a simple polymer chain, *i.e.*, polymethylene, which becomes identical to our model if the ball (in Figure 2) expresses $-\text{CH}_2-$. If the bond rotational potential is independent on its neighbors and symmetric, the unperturbed mean-square end-to-end distance $\langle r^2 \rangle_0$ can be expressed by the following well-known equation:¹⁷

$$\langle r^2 \rangle_0 = nl^2 \left(\frac{1 + \cos \theta}{1 - \cos \theta} \right) \left(\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right) \quad (1)$$

where l , θ and ϕ were already defined, and chain length n is assumed to be very large. For the freely rotating chain,¹⁸ $\langle \cos \phi \rangle = 0$. Hence from Eq. (1)

$$\langle r^2 \rangle_{0c} = nl^2 \left(\frac{1 + \cos \theta}{1 - \cos \theta} \right) \quad (2)$$

If Eq. (1) is divided by Eq. (2), it gives the ratio of the unperturbed dimension of the α -helix or intermediates to that of the random-coil $\langle r^2 \rangle_{0c}$, *i. e.*,

$$\frac{\langle r^2 \rangle_0}{\langle r^2 \rangle_{0c}} = \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \quad (3)$$

The subscript *c* denotes the randomly coiled states. Since the formation of a polypeptide helix is due to the intramolecular hydrogen bonds, the fluctuation in the mean bond-rotation

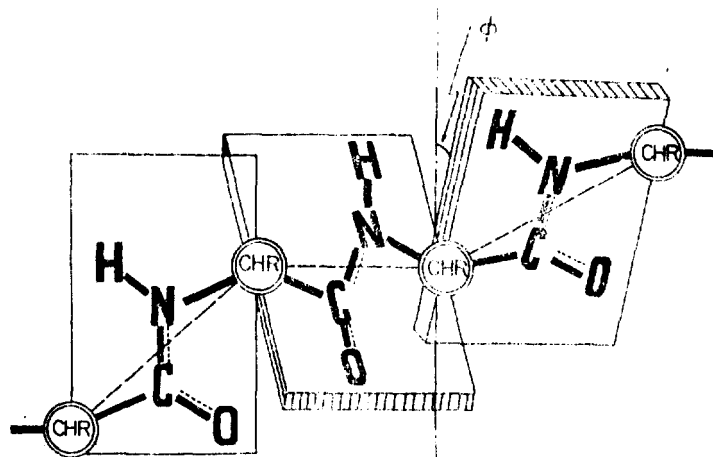


Figure 1. The plane structure of the repeating unit in a polypeptide chain.

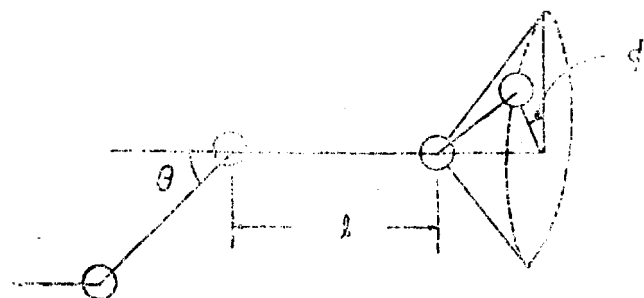


Figure 2. Simple model for a polypeptide molecule. Circle represents the repeating unit $-\text{CO}-\text{NH}-\text{CHR}-$. The quantities, ϕ , θ and l are defined in the figure.

angle per repeating unit or residue should be negligible. We define $\langle \cos \phi \rangle \equiv \cos X$, where X is the mean bond-rotation angle per residue for a polypeptide helix which is fastened tightly by the hydrogen bonds.

(i) α -Helix. The polypeptide helix is an α -helix,¹ *i. e.*, 3.6 residues per turn of the helix; thus, the mean bond-rotation angle per residue is $100^\circ (=360^\circ/3.6, \text{cis-convention})$. Since ϕ is defined as shown in Figures 1 and 2, it is given by $\phi=180^\circ$ bond-rotation angle, and since $\langle \cos \phi \rangle$ is defined as $\cos X$ (X , *trans*-convention) we obtain $X_H=80^\circ (=180^\circ - 100^\circ)$ where the subscript *H* denotes the α -helical state.

(ii) *Random-Coil*. The preceding procedure is applied to a general helix. Then we obtain an equation which relates X with the residue number per turn N , *i. e.*,

$$X = 180^\circ - \frac{360^\circ}{N} \quad (4)$$

Since a random-coil is defined by a freely rotating chain, the X satisfies $\cos X \equiv \langle \cos \phi \rangle = 0$, thus X_c is $90^\circ, 270^\circ, \dots$. If Eq. (4) can be applied to a random-coil, then N ($=N_c$) becomes 4 since $X_c=90^\circ$. Since N_c can not be negative, the angles 270° , etc. are discarded.

(iii) *Intermediates in the Transition*. If Eq. (4) can be applied to intermediates, the N lies between $N=3.6$ and $N=4$, *i. e.*, the intermediates are a kind of helix of $3.6 < N < 4$. If f_H represents the fraction of the α -helical residues in an intermediate, $1-f_H$ corresponds to the fraction of the rand-

only coiled residues. If these two kinds of residues are randomly distributed in the chain (since it is in the unperturbed state), the residue number per turn N can be written as following

$$\begin{aligned} N &= N_H f_H + N_c(1-f_H) \\ &= 3.6 f_H + 4(1-f_H) \end{aligned} \quad (5)$$

Now, using Eq. (4) and Eq. (5), we can obtain X at a certain f_H . By using the definition of X , Eq. (3) is rewritten as

$$\frac{\langle r^2 \rangle_0}{\langle r^2 \rangle_{0c}} = \frac{1 + \cos X}{1 - \cos X} \quad (6)$$

the X being calculated from Eqs. (4) and (5) at a given f_H , the ratio $\langle r^2 \rangle_0 / \langle r^2 \rangle_{0c}$ at the f_H is thus obtainable from Eq. (6).

Thus far, we treated only the case where the chain length n is very large. If it is not the case, for a freely rotating chain, the following equation holds:¹⁹

$$\frac{\langle r^2 \rangle_{0c}}{nl^2} = \frac{1 + \cos \theta}{1 - \cos \theta} - \frac{2 \cos \theta}{n} \left(\frac{1 - \cos^n \theta}{(1 - \cos \theta)^2} \right) \quad (7)$$

And, for a rotation hindered chain,²⁰

$$\begin{aligned} \frac{\langle r^2 \rangle_0}{nl^2} &= \left(\frac{1 + \cos \theta}{1 - \cos \theta} \right) \left(\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right) \\ &\quad - \left(\frac{\cos \theta \langle \cos \phi \rangle + \lambda_1}{\lambda_1 - \lambda_2} \right) p_1 + \left(\frac{\cos \theta \langle \cos \phi \rangle + \lambda_2}{\lambda_1 - \lambda_2} \right) p_2 \end{aligned} \quad (8)$$

where

$$p_k = (2\lambda_k/n) (1 - \lambda_k^n) / (1 - \lambda_k)^2, \quad k=1,2 \quad (8a)$$

and

$$\begin{aligned} \lambda_{1,2} &= \frac{1}{2} [\cos \theta (1 - \langle \cos \phi \rangle) \\ &\quad \pm \{ \cos^2 \theta (1 - \langle \cos \phi \rangle)^2 + 4 \langle \cos \phi \rangle \}^{1/2}] \end{aligned} \quad (8b)$$

where $\lambda_{1,2}$ indicates λ_1 or λ_2 , and λ_1 takes the positive sign whereas λ_2 takes the negative in the double \pm signs. The division of Eq. (8) by (7) yields

$$\begin{aligned} \frac{\langle r^2 \rangle_0}{\langle r^2 \rangle_{0c}} &= \left(\frac{1 + \cos X}{1 - \cos X} \right) \\ &\quad \times \left[1 - \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right) \left(\frac{1 - \cos X}{1 + \cos X} \right) \right. \\ &\quad \left. \left\{ \left(\frac{\cos \theta \cos X + \lambda_1}{\lambda_1 - \lambda_2} \right) p_1 - \left(\frac{\cos \theta \cos X + \lambda_2}{\lambda_1 - \lambda_2} \right) p_2 \right\} \right] \\ &\quad \times \left[1 - \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right) \left\{ \frac{2 \cos \theta}{n} \left(\frac{1 - \cos^n \theta}{(1 - \cos \theta)^2} \right) \right\} \right]^{-1} \end{aligned} \quad (9)$$

The second factor multiplied by the third on the right of Eq. (9) is expressed as $[E(X, \theta, n)]^2$ for simplicity. This factor represents the dependence of $\langle r^2 \rangle_0 / \langle r^2 \rangle_{0c}$ on the chain length n . Since θ is almost constant and X is determined by f_H , we can rewrite Eq. (9) as

$$\left(\frac{\langle r^2 \rangle_0}{\langle r^2 \rangle_{0c}} \right)^{1/2} = \left(\frac{1 + \cos X}{1 - \cos X} \right)^{1/2} E(n, f_H) \quad (10)$$

Results and Discussion

(1) Estimation of the $E(n, f_H)$ Factor

To examine the dependence of the unperturbed dimension ratio $\langle r^2 \rangle_0 / \langle r^2 \rangle_{0c}$ on n , the value of $E(n, f_H)$ factor in Eq. (10) should be known. First of all, the θ must be known since the $E(n, f_H)$ factor in Eq. (9) contains $\cos \theta$ as a constant. The characteristic ratio, $C_\infty \equiv \langle r^2 \rangle_{0c} / nl^2 = 10.3$, is obtained²¹ for a high-molecular-weight PBLG (poly- γ -benzyl-L-glutamate) in DCA (dichloroacetic acid) which is a coil solvent. Thus, we can obtain the value of $\cos \theta$ from Eq. (2), the θ value being 34.6° . Then the mean bond angle per residue is 145.4° which corresponds to a hypothetical bond angle since the random-coil of polypeptides is not exactly identical with the freely rotating chain.

The $E(n, f_H)$ factors are calculable by using Eq. (9), where X is calculated from Eqs. (4) and (5) at a given f_H , and $\lambda_{1,2}$ and $P_{1,2}$ are calculated from Eqs. (8a) and (8b) at a given n by using the X . The results obtained at $f_H=1$ are tabulated in Table 1. From Table 1, one notes that over a wide range of n , the values of $E(n, 1)$ is almost unity, and also that $E(n, 1)$ increases with n reaching asymptotically unity at $n=\infty$ where Eq. (10) becomes Eq. (6) which holds only at $n=\infty$. We next calculate the $E(n, f_H)$ factors at various f_H for $n=200$ which is a somewhat small chain length. The results are shown in Table 2. From the latter, one notes that the values of $E(200, f_H)$ lie between unity (at $f_H=0$, random-coil) and 0.993470 (at $f_H=1$, α -helix). See Table 2. Also one notes from Table 1 and 2, that the values of $E(n, f_H)$ are nearly equal to unity, thus we set $E(n, f_H)=1$. Since $E(n, f_H) \approx 1$ in Eq. (10), it is concluded that $\langle r^2 \rangle_0 / \langle r^2 \rangle_{0c}$ is nearly independent of chain length n .

(2) Excluded Volume Effect

The expansion factor α that represents that the excluded volume effect or the long range interaction is defined as

$$\alpha^2 \equiv \langle r^2 \rangle / \langle r^2 \rangle_0 \quad (11)$$

For general polymers, several theories about α have been presented.²² The theories, however, cannot be applied to the changeable α in the helix-coil transition region. In order to evaluate α by experiment, first of all, $\langle r^2 \rangle$ in a certain condition must be obtained by light scattering, etc., and also $\langle r^2 \rangle_0$ should be obtained in the θ -condition, but the two quantities must be for the same conformation. Polypeptides perform the helix-coil transition so that α cannot be obtained by the above procedure since the conformations change completely different from the original conformation. Therefore, in order to know $\langle r^2 \rangle$ we must obtain separately $\langle r^2 \rangle_0$ and α corresponding to each conformation in the transition region.

According to Nagai,¹¹ the long range interaction (or α) does not seem to be affected strongly by a small change in the atmosphere of the helix-coil transition system. Currently existing theories^{9,10} of the helix-coil transition all neglect the excluded volume effect. Neves and Soctt,²³ however, concluded that the existing theories are not capable of correctly predicting the dimension of the polypeptide undergoing a helix-coil transition, since the long range interaction was not taken into account whereas it is important.

TABLE 1: Dependence of $E(n, f_H)$ on the Chain Length n at $f_H=1$

n	$E(n, 1)$
150	0.991207
200	0.993470
350	0.996316
500	0.997434
750	0.998296
1000	0.998724
1500	0.999151
2000	0.999364
3000	0.999576
4000	0.999682
5000	0.999746
∞	1.000000

TABLE 2: Dependence of $E(n, f_H)$ on the Helical Content f_H at $n=200$

f_H	$E(200, f_H)$
0	1.000000
0.1	0.999488
0.2	0.998954
0.3	0.998389
0.4	0.997796
0.5	0.997172
0.6	0.996513
0.7	0.995817
0.8	0.995008
0.9	0.994300
1.0	0.993470

At a constant temperature, when polypeptides perform the transition according to the change of the solvent composition, the expansion factor for viscosity α_η , which is related with the hydrodynamic volume of a polymer in solution, may be expressed by the following equation:

$$\alpha_\eta = \alpha_{\eta H}x + \alpha_{\eta c}(1-x) \quad (12)$$

where x is the fraction of the helical solvent in a helical-coil mixed solvent, $\alpha_{\eta H}$ and $\alpha_{\eta c}$ are the α_η factor in a pure helical and pure coil solvent, respectively, the interaction between the helical and the coil solvents being neglected. Teramoto *et al.*,²¹ measured the optical rotation at 20–30°C for the PBLG of $\bar{N}_n=800$ (number-average degree of polymerization) in a mixed solvent composed of the helical solvent [ethylenedichloride (EDC)] and the coil solvent [dichloroacetic acid (DCA)]. We converted the optical rotations into the helical contents f_H by using Teramoto *et al.*'s expression,²¹ and constructed a graph of the EDC fraction x (by volume) vs. f_H (Figure 3) where x is directly connected to α_η through Eq. (12). In Figure 3, there is no perceptible change in the EDC fraction x between $f_H=0$ and 0.9, and it increases suddenly almost linearly after $f_H=0.9$. From Eq. (12), one obtains,

$$\alpha_\eta/\alpha_{\eta c} = 1 + [(\alpha_{\eta H}/\alpha_{\eta c}) - 1]x \quad (12a)$$

where x has the relation with f_H shown in Figure 3, *i.e.*, x is about constant over the range of $f_H=0$ to 0.9, thus in this range, $\alpha_\eta/\alpha_{\eta c}$ is about constant since $x \sim \text{constant}$ according to Eq. (12a). But, at $f_H > 0.9$, the x increases suddenly as

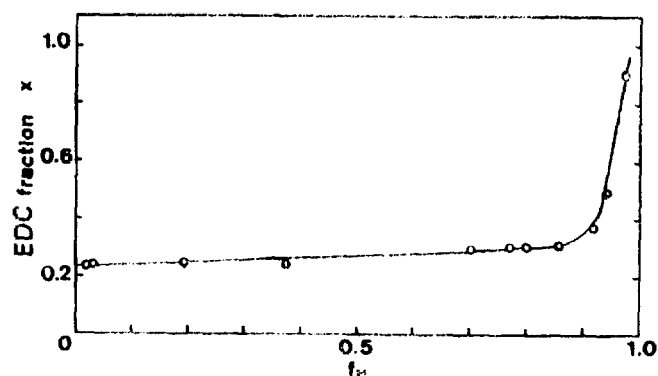


Figure 3. Dependence of the helical content f_H on the composition (by volume) of the DCA-EDC mixed solvent for the PBLG sample ($\bar{N}_n=800$) at 20–30°C. The DCA and EDC are the coil and helical solvents, respectively. Thus the EDC fraction x is related with f_H . The x vs. f_H was calculated from Teramoto *et al.*'s optical rotation vs. x data.²⁴

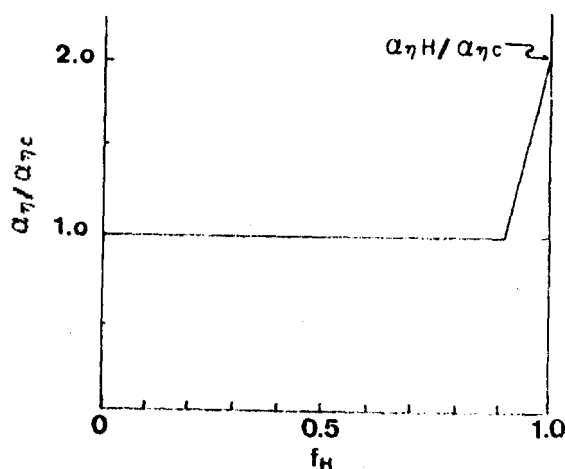


Figure 4. Schematic representation for the dependence of the expansion factor ratio $\alpha_\eta/\alpha_{\eta c}$ on the helical content f_H .

shown in Figure 3, thus, the $\alpha_\eta/\alpha_{\eta c}$ also increases in a similar way. Thus the behavior of $\alpha_\eta/\alpha_{\eta c}$ over the whole range of f_H is schematically as shown in Figure 4.

The reason for this trend (shown in Figure 4) is explained in the following way: the random-coil sections in fairly long chain act as flexible joints, thus, over the range of $f_H=0$ and 0.9 the chain of the polypeptide acts as if it were a random-coil; but in the range of $f_H=0.9$ and 1, the polypeptide chain acts a stiff chain because of the lack of the flexible joints (random-coil sections). The trend shown in Figure 3 and 4 will appear in all PBLG whose chain length are sufficiently large in the mixed solvent system (EDC and DCA). We should not expect, however, this trend will occur for other polypeptide-solvent systems since it may depend on the cooperativity parameter or the helix-initiation parameter σ .¹¹

(3) Intrinsic Viscosity

The Flory intrinsic viscosity equation²⁵ is written as

$$[\eta] = \phi \frac{\langle r^2 \rangle^{3/2}}{M} = \phi_0 \frac{\langle r^2 \rangle_0^{3/2}}{M} \alpha_\eta^3 \quad (13)$$

where $[\eta]$ is the intrinsic viscosity or the limiting viscosity number, M is the molecular weight of polymer, ϕ_0 is the

Flory viscosity constant which is a universal constant independent of the nature of the polymer, and ϕ is viscosity constant which depends on the excluded volume effect.

Norisuye²⁶ measured $[\eta]$ and $\langle r^2 \rangle$ for two high-molecular-weight samples of PBLG in a DCA-cyclohexanol mixed solvent at various stages of their thermal helix-coil transitions, and computed ϕ from Eq. (13). The resulting values of ϕ are almost constant in the transition region, and decrease sharply at the region of nearly $f_H=1$. Generally ϕ decreases with increasing expansion factor,^{22b} this fact is in agreement with the trend (shown in Figure 4) of expansion factor.

By using the 2nd equality of Eq. (13), one may write $[\eta]_c$ as

$$[\eta]_c = \phi_0 \frac{(\langle r^2 \rangle_{0c})^{3/2}}{M} \alpha_{\eta c}^3 \quad (13a)$$

Taking the $[\eta]$ and $[\eta]_c$ given by Eqs. (13) and (13a), respectively, and by using Eq. (6), we obtain,

$$\frac{[\eta]}{[\eta]_c} = \left(\frac{\alpha_{\eta}}{\alpha_{\eta c}} \right)^3 \left(\frac{1 + \cos X}{1 - \cos X} \right)^{3/2} \quad (14)$$

And, using Eq. (14), $\alpha_{\eta H}/\alpha_{\eta c}$ is given by

$$\frac{\alpha_{\eta H}}{\alpha_{\eta c}} = \left(\frac{[\eta]_H}{[\eta]_c} \times \frac{1}{1.69262} \right)^{1/3} \quad (15)$$

where $[(1 + \cos X)/(1 - \cos X)]^{3/2} = 1.69262$ at $f_H=1$ since $X=80^\circ$. The quantities $[\eta]_H$ and $[\eta]_c$ can be easily obtained by experiment.

Teramoto *et al.*²¹ measured the helical contents and the intrinsic viscosities for several samples of PBLG in EDC-DCA mixed solvents of various compositions in the transition region. Their experimental $[\eta]$ values for $\bar{N}_n=800$ and 600 vs. f_H are shown in Figures 5 and 6, respectively. We calculate $[\eta]/[\eta]_c$ from Eq. (14) according to the following scheme: (i) the term $[(1 + \cos X)/(1 - \cos X)]^{3/2}$ in Eq. (14) is calculated as a function f_H by using Eqs. (4) and (5); (ii) the term $(\alpha_{\eta}/\alpha_{\eta c})^3 \approx 1$ over the range of $f_H=0$ to 0.9; but increases sharply if $f_H > 0.9$ (refer to Fig. 4) and reaches the value of $(\alpha_{\eta}/\alpha_{\eta c})_{f_H=1}$, the latter being obtained from Eq. (15). (iii) the product of the above two terms becomes as shown by the full curves in Figs. 5 and 6, the values of $[\eta]_c$ being equal to 1.49 and 1.01 d l/g for $\bar{N}_n=800$ and 600, respectively.

The experimental $[\eta]$ values are compared with our theoretical values in Figure 5 and 6. Our results are in a good agreement with experiment. Nagai's theoretical results¹² on $\langle r^2 \rangle / \langle r^2 \rangle_c$ vs. f_H of similar chain length have a minimum in the transition region, this is not true experimentally (refer to the experimental points in Figures 5 and 6). Norisuye²⁶ performed the same kind of experiment for PBLG samples independently from Teramoto *et al.*²¹ The Norisuye's data exhibit almost the same behavior of $[\eta]$ vs. f_H as in Teramoto *et al.*'s work.

In the region between $f_H=0$ and 0.9 where the change of the excluded volume effect (expansion factor) is negligible as previously mentioned (*i. e.*, $\alpha_{\eta}/\alpha_{\eta c} \approx 1$), the unperturbed dimensions $\langle r^2 \rangle_0 / \langle r^2 \rangle_{0c}$ are directly related with the intrinsic viscosities $[\eta]/[\eta]_c$ (refer to Eqs. (14) and (6)). Judg-

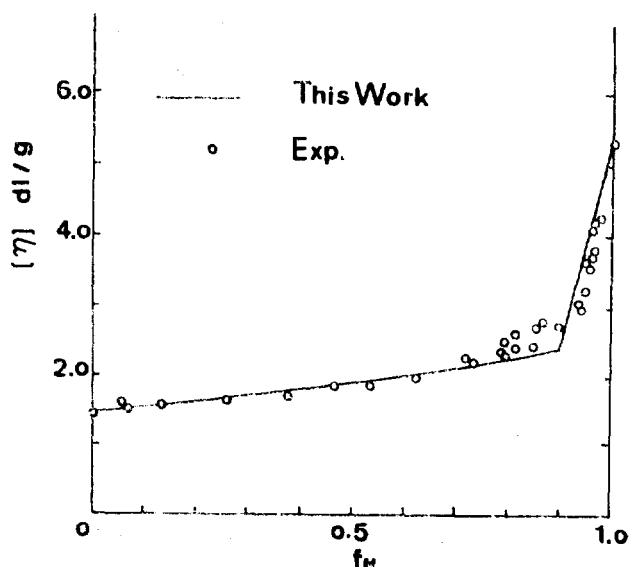


Figure 5. Variation of $[\eta]$ with the helical content. The experimental points²⁴ are for PBLG ($\bar{N}_n=800$) in DCA-EDC mixtures; at $f_H=1$ the DMF solvent was used.

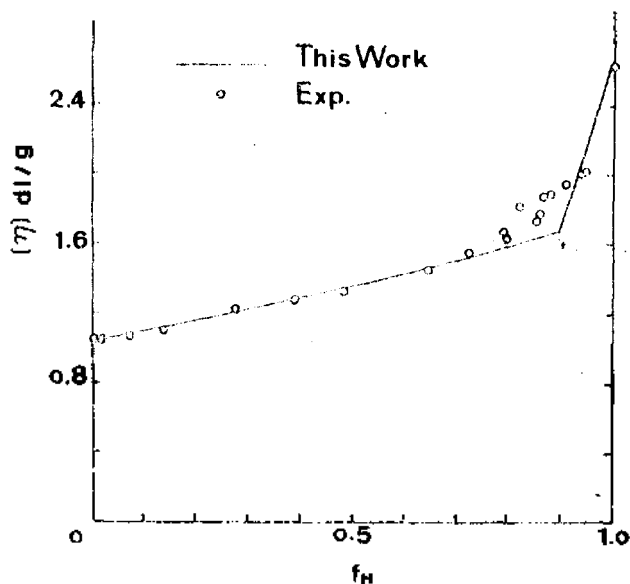


Figure 6. Variation of $[\eta]$ with the helical content. The experimental points²⁴ are for PBLG ($\bar{N}_n=600$) in DCA-EDC mixtures; at $f_H=1$ the DMF solvent was used.

ing from Figures 5 and 6, our theory well explains the unperturbed dimensions of polypeptides in the transition region.

A theoretical research for the region where α_{η} increases abruptly, is an urgent problem and may be very important. We plan to study this problem in the near future.

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MO Theoretical Studies on Stereoelectronic Control in the Addition Reaction of 1, 4-Benzoquinone-4-(*O*-methyloxime)*

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The chlorine addition and Diels-Alder cycloaddition of cyclopentadiene to 1, 4-benzoquinone-4-(*O*-methyloxime) have been studied MO theoretically. It has been shown that the reactions occur predominantly to the quinone ring double bond which is oriented anti to the nitrogen lone pair due to an $n-\sigma^*$ interaction between the nitrogen lone pair, n , and the adjacent vicinal bond, causing the π bond to be weakened and destabilized due to the less conjugation from reduced delocalization.

Structure-reactivity relation has been a subject of great interest in organic chemistry. In the kinetic controlled chlorine addition and Diels-Alder cycloaddition of cyclopentadiene (CPD) to 1, 4-benzoquinone-4-(*O*-methyloxime) (1), the overwhelming predominance of products which have the configuration (2) where the oxime group is anti to the remaining double bond was found over the alternative arrangement (3). The NMR studies of Baldwin and Norris have shown 70 % and 90 % of anti products in the two addition reactions respectively.¹

*Taken as part 24 of the series "Determination of Reactivity by MO Theory".

TABLE I: Energy Components (a.u.) (Relative Values are in kcal/mole)

Energy	1a	1b
E_{TOT}	-103.2438	-103.3720
ΔE_{TOT}	80.5	0.0
$\Delta 2 \sum \epsilon_i$	0.0	281.9
$\Delta(V_{nn} - V_{nn})$	362.4	0.0

In this work we report results of an MO theoretical investigation on a difference in chemical reactivity of the two quinonoid double bonds focussing our attention on the effect of orientation of nitrogen lone pairs. Since we are prima-