Conformational Energy and Unperturbed Chain Dimension of Polypeptide Homopolymers

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ABSTRACT: Conformational energy and characteristic ratio $\langle R_0^2 \rangle / nl^2$ were theoretically investigated for polyglycine, poly(L-alanine), poly(N-methylglycine), and poly(N-methyl-L-alanine), assuming *trans* conformation for amide and imide bonds, and employing suitable molecular parameters and plausible potential functions. The theoretically calculated characteristic ratios for polyglycine, poly(L-alanine), poly(N-methylglycine), and poly(N-methyl-L-alanine) were, respectively, $\langle R_0^2 \rangle / nl^2 = 2.17, 8.38, 2.97$, and 0.58 . These results are discussed in connection with the experimental and theoretical results reported to date.

KEY WORDS Polypeptide / Polyglycine / Poly(L-alanine) / Poly(N-methylglycine) / Poly(N-methyl-L-alanine) / Conformation / Unperturbed Dimension / Characteristic Ratio / Statistics / Chain Molecules /

Owing to the partial double bond and planar *trans* characters of the amide bonds, the chain conformation of poly(α -amino acid)s has been described^{1,2} by a single pair of rotation angles ϕ_i and ψ_i about the two single bonds, $N_i-C_i^\alpha$ and $C_i^\alpha-C_i^\beta$ bonds, adjoining C_i^α (see Figure 1). Thus the chain is regarded as a sequence of virtual bonds whose lengths are 3.80 Å. Flory and coworkers³ have calculated the unperturbed chain dimensions of polyglycine and of poly(L-alanine). According to the experimental results,^{1,4-6} the characteristic ratio $\langle R_0^2 \rangle / nl^2$, in which n and l are the number and length of the virtual bonds, respectively, and $\langle R_0^2 \rangle$ is the mean square unperturbed end-to-end distance, of $[-NH-C^\alpha H(C^\beta H_2-R^\beta)-CO]_n$ type poly(α -amino acid)s is estimated as about 8.5 on the average. This figure is somewhat lower than the theoretical value 9.27 given by Brant, Miller, and Flory.¹ Conformation calculation³ has revealed that the characteristic ratios of poly(α -amino acid)s having longer side chains than those of poly(L-alanine), in which $R^\beta=H$, are almost the same as those of poly(L-alanine), but significantly different from those of polyglycine.

Conformational aspects of polymers $[-NR^N-C^\alpha H(C^\beta H_2-R^\beta)-CO]_n$ of *N*-substituted α -amino acids, which include the imide bonds

in place of amide bonds, are also important and should be discussed. Representative polymers in this category are poly(N-methylglycine) and poly(N-methyl-L-alanine). For the former, we have offered some theoretical contributions⁷ on the characteristic ratio. Experimentally available data to obtain the characteristic ratio of this polymer are those reported by Fessler and Ogston,⁸ which led to $\langle R_0^2 \rangle / nl^2 = 1.8 \pm 0.2$. For the latter polymer, Mark, *et al.*,⁹ and Liquori, *et al.*,¹⁰ have offered some contributions on conformational energy estimation, though little has been reported experimentally on high polymers.

In this paper, conformational energies and unperturbed chain dimensions are reexamined for poly(L-alanine), polyglycine, poly(N-methyl-L-alanine), and poly(N-methylglycine), in accordance with more suitable parameters by assuming the planar *trans* conformation for both amide and imide bonds in backbone chains of these polypeptides.

CONFORMATIONAL ENERGY

Molecular Structure and Potential Functions

In Figure 1, two adjacent amino acid residues of a polypeptide chain are shown in their fully extended *trans* conformations, where R_i^N and

Figure 1. Fully extended polypeptide chain.

R_i^{α} denote, respectively, the substituents attached to the nitrogen atom N_i and to α -carbon atom C_i^{α} of the i -th residue. The angles of rotation about the bonds $N_i-C_i^{\alpha}$ and $C_i^{\alpha}-C_{i+1}^{\alpha}$ are, respectively, denoted by ϕ_i and ψ_i . The angle of rotation about the bond $C'-N$ is assumed to be fixed at zero degree assigned for the *trans* conformation. Poly(L-alanine) is represented by $R_i^{\alpha}=\text{CH}_3$ and $R_i^N=\text{H}$; polyglycine by $R_i^{\alpha}=\text{H}$ and $R_i^N=\text{H}$; poly(*N*-methyl-L-alanine) by $R_i^{\alpha}=\text{CH}_3$ and $R_i^N=\text{CH}_3$; and poly(*N*-methylglycine) by $R_i^{\alpha}=\text{H}$ and $R_i^N=\text{CH}_3$. One of the hydrogen atoms in $R_i^N=\text{CH}_3$ for poly(*N*-methyl-L-alanine) and poly(*N*-methylglycine) is fixed at *trans* position against the C_{i-1}^{α} atom, though it was fixed at *trans* against C_i^{α} in our preceding paper⁷ for poly(*N*-methylglycine). The molecular parameters, such as bond angles and bond lengths, and the bond coordinate systems used in the present calculations are the same as those in the preceding paper.⁷

In accordance with the treatment used by Brant and Flory,¹ the conformational energy $V(\phi_i, \psi_i)$ for rotations governing the mutual orientation of virtual bond i and $i+1$ is calculated from the sum of three contributions: the intrinsic torsional potentials $V_{(T)}(\phi_i)$ and $V_{(T)}(\psi_i)$, the sum $\sum V_{(W)jk}(\phi_i, \psi_i)$ of the van der Waals interactions between all pairs of non-bonded atoms j and k , and the dipolar interaction term $\sum V_{(D)jk}(\phi_i, \psi_i)$.

$$V(\phi_i, \psi_i) = V_{(T)}(\phi_i) + V_{(T)}(\psi_i) + \sum_{jk} V_{(W)jk}(\phi_i, \psi_i) + \sum_{jk} V_{(D)jk}(\phi_i, \psi_i) \quad (1)$$

In eq 1 the dipole interaction is given by the sum of electrostatic interaction between atoms j and k by distributing the charges on the atoms composing the dipole by means of vector decomposition. The three-fold intrinsic rotational

potential functions as used earlier⁷ were used for $V_{(T)}(\phi_i)$ and $V_{(T)}(\psi_i)$. The van der Waals interaction $V_{(W)jk}(\phi_i, \psi_i)$ was given by the Lennard-Jones-type 6-12 potential function. The numerical values of bond lengths and bond angles, and of the van der Waals radii of the interacting atoms are the same as those in the previous paper,^{7,12} except that of the effective van der Waals radius for the β -methylene group ($\text{C}^{\beta}\text{H}_2$), for which 2.00 Å is assigned instead of 1.85 Å previously used.¹²

Figure 2 shows the characteristic ratio $\langle R_0^2 \rangle / nl^2$ of poly(α -L-amino acid), calculated in this

Figure 2. The characteristic ratio $\langle R_0^2 \rangle / nl^2$ of poly(L-alanine) [or poly(α -L-peptide)s] as a function of the van der Waals radius of $\text{C}^{\beta}\text{H}_2$ group.

work, as a function of the van der Waals radius r_{CH_2} for β -methylene group. It is pointed out that the value of r_{CH_2} significantly affects the

resulting characteristic ratio. Comparison with the experimental values indicates that $r_{\text{CH}_2} = 2.00 \text{ \AA}$ is to be used for calculations. This value was used also for poly(*N*-methyl-L-alanine). In these calculations, the numerical values for the group polarizability α_{CH_2} and the effective number of valence shell electrons, N_{CH_2} , necessary to obtain the coefficient e_{jk} in the dispersion term of the Lennard—Jones function, are taken from Brant, *et al.*,³ as $1.77 \times 10^{-24} \text{ cm}^3$ and 7, respectively. The numerical value $r_{\text{CH}_2} = 2.00 \text{ \AA}$ assigned for the β -methylene group is the same as the value $r_{\text{CH}_3} = 2.00 \text{ \AA}$ for the methyl group estimated by Pauling.¹¹ Linear side chains longer than methyl should have little influence on the main chain conformation, as mentioned previously.¹² Thus the characteristic ratio calculated for poly(L-alanine) for which $\text{R}^\alpha = \text{CH}_3$ is also applicable to poly(α -L-amino acids) for which $\text{R}^\alpha = \text{C}^\beta \text{H}_2 - \text{R}^\beta$.

The partial charges to calculate the term $\sum V_{(\text{D})jk}(\phi_i, \psi_i)$ for the amide group are taken from Ooi, *et al.*¹³ For the imide group, the data calculated for *N,N*-dimethyl acetoamide by Yan, *et al.*,¹⁴ are used according to semi-empirical molecular orbital calculation. The values of these partial charges are summarized in Table I. The effective dielectric constant ϵ appearing

Table I. Partial charges^a on amide and imide groups

Atom	Partial charge	
	Amide	Imide
H'	0.272	
N	-0.305	-0.282
C'	0.449	1.056
O	-0.416	-1.240
C ^N		0.165
H ₁ ^N		0.020
H ₂ ^N		0.022
H ₃ ^N		0.022

^a The numerical values are in unit (electronic charge/elementary charge).

in the term $V_{(\text{D})jk}(\phi_i, \psi_i)$ was assumed^{1,3,7,12} to be $\epsilon = 3.5$.

The contribution from the term $V_{(\text{D})jk}(\phi_i, \psi_i)$ for imide—imide dipole interaction to the total

Figure 3. Contour diagram of nearest neighbor imide—imide dipole interaction energy, $\sum V_{(\text{D})jk}(\phi, \psi)$ in eq 1, for poly(*N*-methylglycine) and poly(*N*-methyl-L-alanine). Numerals on the contours are the absolute energy values.

conformational energy $V(\phi_i, \psi_i)$ is shown in Figure 3. The numerals on the contour denote the absolute energy values. The contour map for the amide—amide dipole interaction is not reproduced here. It is similar to that reported by Brant, *et al.*³

Conformational Energy Contour Diagrams

The conformational energy $V(\phi_i, \psi_i)$ was calculated from eq 1 at 20° intervals from 0° to 340° for ϕ_i and ψ_i . Figures 4—7 are, respectively, contour diagrams for poly(L-alanine), polyglycine, poly(*N*-methyl-L-alanine), and poly(*N*-methylglycine). The symbol $\times$ in these Figures denotes the lowest energy positions, and the contours are drawn by the energy levels relative to the lowest energy value. Relatively stable regions in each contour diagram are designated as region I, II, III, etc. The conformation represented by (ϕ, ψ) and its absolute energy value for lowest energy position in each region are summarized in Table II. The conformational energies without the dipole interaction term *i.e.*, $\sum V_{(\text{D})jk}(\phi_i, \psi_i) = 0$ or $\epsilon = \infty$, are shown in column 6 of Table II. Thus the effect of the dipole interaction term is understood by comparing columns 5 and 6.

The contour map of the poly(L-alanine) chain does not differ significantly from that reported

Table II. Low-energy conformations on the energy contour diagrams

Residue	Regions designated on the contour diagrams, Figure 4 to 7	Rotational angles (in degree)		Absolute conformational energy, $V(\phi, \psi)$, kcal/mol	
		ϕ	ψ	including $V_{(D)}(\phi, \psi)$ in eq 1	excluding $V_{(D)}(\phi, \psi)$ in eq 1
Ala	I	20	340	-1.5	-0.2
	II	120	140	0.1	-0.5
	III	240	240	0.9	0.2
Gly	I(I')	100(260)	260(100)	-3.4	-2.0
	II(II')	120(240)	120(240)	-2.4	-1.7
NMG	I(I')	100(260)	0(0)	-3.5	-3.4
	II(II')	60(300)	260(100)	-2.1	-3.0
	III(III')	120(240)	100(260)	-2.7	-3.0
NMA	I	60	260	0.8	-0.1
	II	60	340	2.4	1.5
	III	240	260	0.2	-0.2
	IV	240	340	0.9	0.9

Figure 4. Contour diagrams of total conformational energy for the poly(L-alanine) or poly(α -L-peptide) chain as calculated from eq 1. The absolute minimum indicated by $\times$ corresponds to -1.47 kcal/mol. The numerals on the contours are in the units kcal/mol relative to this minimum.

previously.^{1,3,12,15,16} The most stable region is I, in which, however, the energy minimum appears at $\phi=20^\circ$, $\psi=340^\circ$ instead of the location $\phi=120^\circ$, $\psi=330^\circ$ as shown in a previous paper.¹² Such shift of energy minimum position is attributed to the change in the van der Waals radius of the β -methylene group from 1.85 Å to 2.00 Å. The contour map given in Figure 4

Figure 5. Contour diagrams of total conformational energy for the polyglycine chain as calculated by eq 1. The absolute minima indicated by $\times$ correspond to -3.40 kcal/mol.

results in $\langle R_0^2 \rangle / nl^2 = 8.4$.

The contour map for the polyglycine shown in Figure 5 is centrosymmetric and almost the same as that reported by Brant, *et al.*³ The energy minima locate at $\phi=100^\circ$, $\psi=260^\circ$ and at $\phi=260^\circ$, $\psi=100^\circ$.

With respect to poly(*N*-methyl-L-alanine), the contour map of the conformational energy shown in Figure 6 is similar to those reported by Mark, *et al.*,⁹ and Liquori, *et al.*,¹⁰ though both have

Figure 6. Contour diagram of total conformational energy for the poly(*N*-methyl-L-alanine) chain as calculated from eq 1. The absolute minimum indicated by $\times$ corresponds to 0.18 kcal/mol.

Figure 7. Contour diagram of total conformational energy for the poly(*N*-methylglycine) chain as calculated from eq 1. The absolute minimum indicated by $\times$ correspond to -3.46 kcal/mol.

used potential functions different from ours; *i. e.*, Mark, *et al.*, omitted the dipole interaction and moreover used different parameters for the Lennard-Jones equation. Liquori, *et al.*, took into account only non-bonded interactions. According to Mark, *et al.*, the absolute minimum occurs at $\phi=30^\circ$, $\psi=250^\circ$ (which is included in region I by our notation in Figure 6), the second stable position at $\phi=210^\circ$, $\psi=250^\circ$

(region III), and less stable positions are included in regions IV and II. On the other hand, the conclusion drawn from the present work (see also Figure 6 and Table II) is that region III is the most stable, followed by regions I and IV. This means that the conformation assigned near the left-handed α -helix is the most stable for this polymer. Further characteristic features of this diagram are that the regions corresponding to less than 8 kcal/mol are so narrow that the rotations about ϕ and ψ are extremely hindered. The sum of the statistical weights of regions I to IV amount to 98%, and in particular, region III occupies 64% of the whole partition function. Therefore, we can discuss the conformational aspects by taking into account only regions I to IV.

For poly(*N*-methylglycine), the conformational energy was recalculated by assuming that one of the hydrogen atoms in $R_i^N=\text{CH}_3$ is fixed at *trans* position against the C_{i-1}^α atom, though it was fixed at *trans* position against the C_i^α atom in a previous paper.⁷ Moreover, both the parameters d_{jk} and e_{jk} in the Lennard-Jones potential function, and the values of the partial charges (see Table I) used in this work are somewhat different from those used previously.⁷ As seen in Figure 7 and Table II, the absolute energy minima occur at $\phi=100^\circ$, $\psi=0^\circ$ and at $\phi=260^\circ$, $\psi=0^\circ$, and correspond to -3.46 kcal/mol of peptide units.

UNPERTURBED CHAIN DIMENSION

The characteristic ratio $\langle R_0^2 \rangle / nl^2$ is evaluated by the method proposed by Brant, *et al.*³ When the degree of polymerization is $n+1$, the number of virtual bonds is n . The coordinate systems used are the same as those used previously.⁷ On the coordinate system (X_i, Y_i, Z_i) , the virtual bond vector I is represented by $I=(l00)$. The matrix transforming the coordinate system $(X_{i+1}, Y_{i+1}, Z_{i+1})$ to the coordinate system (X_i, Y_i, Z_i) is denoted by T . The unperturbed root mean square end-to-end distance $\langle R_0^2 \rangle$ of a chain composed of n virtual bonds is given by

$$\langle R_0^2 \rangle = nl^2 + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^n I_i^T \langle T_i T_{i+1} \cdots T_{j-1} \rangle I_j \quad (2)$$

in which I_i^T denotes the transpose of I_i . The

planar *trans* conformation assumed for amide and imide groups simplifies eq 2 as

$$\frac{\langle R_0^2 \rangle}{nl^2} = 1 + \frac{1}{nl^2} \sum_{i=1}^{n-1} \sum_{j=i+1}^n \mathbf{l}_i^T \prod_{k=i}^{j-1} \langle \mathbf{T}_k \rangle \mathbf{l}_j \quad (3)$$

The statistical average $\langle \mathbf{T} \rangle$ of the transformation matrix $\mathbf{T}$ is given by⁷

$$\langle \mathbf{T} \rangle = \frac{\int_0^{2\pi} \int_0^{2\pi} \mathbf{T}(\phi, \psi, \theta''', \xi, \eta) \exp[-V(\phi, \psi)/RT] d\phi d\psi}{\int_0^{2\pi} \int_0^{2\pi} \exp[-V(\phi, \psi)/RT] d\phi d\psi} \quad (4)$$

Thus, eq 3 is reduced to the following form

$$\begin{aligned} \langle R_0^2 \rangle / nl^2 = & \{ (\mathbf{E} + \langle \mathbf{T} \rangle) (\mathbf{E} - \langle \mathbf{T} \rangle)^{-1} \\ & - (2/n) \langle \mathbf{T} \rangle (\mathbf{E} - \langle \mathbf{T} \rangle)^n (\mathbf{E} - \langle \mathbf{T} \rangle^2)^{-1} \}_{11} \end{aligned} \quad (5)$$

where $\mathbf{E}$ is the unit matrix of the order 3 and subscript 11 denotes the (1, 1) element of the matrix.

RESULTS OF NUMERICAL CALCULATION AND DISCUSSION

The averaged transformation matrix $\langle \mathbf{T} \rangle$ at 25°C was evaluated from eq 4, on the basis of the conformational energy contour maps shown in the previous section, replacing the integral by the summation over ϕ and ψ from 0° to 330° in 30° intervals. The averaged transformation matrices obtained for poly(L-alanine), polyglycine, poly(*N*-methylglycine), and poly(*N*-methyl-L-alanine) are, respectively, eq 6, 7, 8, and 9.

$$\langle \mathbf{T} \rangle_{\text{Ala}} = \begin{bmatrix} 0.565 & 0.370 & 0.499 \\ -0.055 & -0.573 & 0.417 \\ 0.566 & -0.417 & 0.330 \end{bmatrix} \quad (6)$$

$$\langle \mathbf{T} \rangle_{\text{Gly}} = \begin{bmatrix} 0.368 & -0.004 & 0 \\ -0.163 & -0.392 & 0 \\ 0 & 0 & -0.140 \end{bmatrix} \quad (7)$$

$$\langle \mathbf{T} \rangle_{\text{NMG}} = \begin{bmatrix} 0.578 & 0.653 & 0 \\ -0.267 & -0.032 & 0 \\ 0 & 0 & 0.146 \end{bmatrix} \quad (8)$$

$$\langle \mathbf{T} \rangle_{\text{NMA}} = \begin{bmatrix} 0.332 & 0.132 & 0.835 \\ -0.166 & 0.552 & -0.222 \\ -0.557 & -0.027 & 0.223 \end{bmatrix} \quad (9)$$

The characteristic ratios for chains with infinite chain length $n \rightarrow \infty$ as calculated using eq 5 are presented in column 2 of Table III, together with the experimental results appearing in column 3.

The characteristic ratio 8.4 of poly(L-alanine) is considerably lower than 9.27 reported by Brant, *et al.*² Experimental difficulties are preventing the compilation of data on poly(L-alanine). However, the experimental results on poly(α -L-amino acid)s may be used for the comparison with the theoretical result. Brant, *et al.*,¹ derived characteristic ratios based on the experimental data on several poly(α -L-amino acid)s. Since then, more data have become available. Data analyses using Stockmayer—Fixman plots¹⁷ on the results of Fujita, *et al.*⁵, for poly(γ -benzyl-L-glutamate), and of Terbojevich, *et al.*,⁶ for poly(γ -ethyl-L-glutamate) result in the characteristic ratios 7.5 ± 1.2 and 8.2 ± 0.3 , respectively.

Table III. Characteristic ratios of polypeptides

Polymer	$[\langle R_0^2 \rangle / nl^2]_{n=\infty, \text{calc}}$	$[\langle R_0^2 \rangle / nl^2]_{\text{obs}}$
Poly(L-alanine)	8.38	
Poly(γ -benzyl-L-glutamate)		8.8 ¹
Poly(γ -benzyl-L-glutamate)		7.5 ± 1.2^5
Poly(β -benzyl-L-aspartate)		9.6 ¹
Poly(γ -ethyl-L-glutamate)		8.2 ± 0.3^6
Na-Poly(L-glutamic acid)		8.8 ¹
HBr-Poly(L-lysine)		8.6 ¹
Polyglycine	2.17	
Poly(<i>N</i> -methylglycine)	2.97	1.8 ± 0.2^8
Poly(<i>N</i> -methyl-L-alanine)	0.58	

The gross average of the whole numerical values may amount around 8.5. To discuss the difference between the theoretical values 9.27 (Brant, *et al.*) and 8.4 (present work) may not be appropriate at this stage, however.

For polyglycine, experimental data on the characteristic ratio are not available. Significantly, the, $\langle R_0^2 \rangle / nl^2 = 2.17$ obtained here is in accord with 2.16 reported by Brant, *et al.*³

With respect to poly(*N*-methylglycine), we should like to correct a numerical value reported in a previous paper.⁷ Because of a mistake in numerical calculation, the characteristic ratio 1.5 reported in the previous paper [eq 29 in ref 7] should be corrected[#] to $\langle R_0^2 \rangle / nl^2 = 3.01$. As mentioned above, one of the hydrogen atoms in $R_i^N (=CH_3)$ was fixed at *trans* against C_i^α in the previous paper. Additional calculation, with this model but neglecting the dipole—dipole interaction, led to $\langle R_0^2 \rangle / nl^2 = 2.76$. On the other hand, the characteristic ratio calculated in this paper, with one of the hydrogen atoms in R_i^N fixed at *trans* against C_{i-1}' , is 2.97, and this figure shifts to 3.26 by neglecting the dipole—dipole interaction effect. Accordingly, we conclude that the characteristic ratio of this polymer is not largely affected by the mode of fixing the *N*-methyl group, so far as the dipole—dipole interaction effect is taken into account. The averaged value around 3 may be compared with the experimental value 1.8 ± 0.2 . Bovey, *et al.*,¹⁸ as already cited,⁷ have pointed out the possible presence of *cis* imide bonds from NMR studies on this polymer. The effect of *cis* imide bonds has been partly discussed in the previous paper and is under further investigation.

Finally we refer to the characteristic ratio of poly(*N*-methyl-L-alanine). The value 0.58 obtained is smaller than not only that of 1.93 expected for free rotation chain but also that of unity for the random flight chain. Such unusually small values have not been found for other homopolymers, but can be cited as an example with the D, L-alanine copolymer reported by Miller, *et al.*¹⁹ The potential minimum occurs at $\phi = -120^\circ$, $\psi = -100^\circ$ in region III (Figure 6). We may say that the contribution from conformations corresponding approximately to the left-handed α -helix is large, but we should not

simply decide that the chains are in helix conformation. If the whole chain is in helix conformation, then $\langle R_0^2 \rangle / nl^2$ should diverge for $n \rightarrow \infty$. For the helix conformation, at least three successive units should have particular values for ϕ , ψ ($\phi = -122^\circ$, and $\psi = -133^\circ$ for the left-handed α -helix). In the present treatment, such conditions have not been secured because $V(\phi, \psi)$ and $\langle T \rangle$ concerns a single unit. The present treatment is essentially that for a random chain. As pointed out by Schimmel, *et al.*,²⁰ for proline chains, if there exists, even slightly, a conformationally available region around the ϕ , ψ -value for the α -helix, then $\langle R_0^2 \rangle / nl^2$ rapidly converge to a definite value at $n \rightarrow \infty$. Such a conformational basis may result in a shift from the rigid rod (α -helix) to the "worm-like chain." The chain of poly(*N*-methyl-L-alanine) may be regarded on the whole compact coil. It is not experimentally known to date whether this polymer takes a coil or a helix conformation in solution. If it, even slightly, takes a helix conformation, then other methods should be tried to evaluate the chain dimension.

The computations were carried out on the FACOM 236-60 computer at the Kyoto University Computation Center.

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Eq 27 and 29 in ref 7 should be corrected as follows:

$$\langle T \rangle = \begin{bmatrix} 0.612 & 0.756 & 0 \\ -0.305 & -0.035 & 0 \\ 0 & 0 & 0.210 \end{bmatrix} \quad (27)$$

$$\langle R_0^2 \rangle / nl^2 = 3.01 \quad \text{for case B} \quad (29)$$

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