nitrogen at 175 °C (our estimate from the autoaccelerating rate curve of Stapfer and Granick[8a] for a reaction time of ~2.5 h). Other literature values for the nonoxidative dehydrochlorination of PVC in *o*-dichlorobenzene are 0.9×10^{-5} (182 °C, Geon 101),[18] 1.4×10^{-5} (182 °C, polymer prepared at 70 °C and having an "average molecular weight" of about 56 000),[18] and 2.5×10^{-5} mol HCl (g PVC)$^{-1}$ h^{-1} (180 °C, purified commercial polymer, our estimate from Figure 9 of Braun and Bender[19]).

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Conformation Study on Poly(N^ϵ-carbobenzoxy-L-lysine) in Helicogenic Solvents by Small-Angle X-Ray Scattering

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ABSTRACT: Small-angle x-ray scattering of poly(N^ϵ-carbobenzoxy-L-lysine), (CbzLys]$_n$, in four solvents, dimethyl formamide($HCONMe_2$), pyridine, *m*-cresol, and hexamethylphosphoric triamide [$(Me_2N)_3PO$], was measured to determine the mass per unit length, M_q, and the radius of gyration of the cross section, $\langle S_q^2\rangle^{1/2}$. It was confirmed from the values of M_q that $(CbzLys)_n$ exists in an α-helical conformation in these solvents. The value of $\langle S_q^2\rangle^{1/2}$ increases in the order of *m*-cresol < $HCONMe_2$ < pyridine < $(Me_2N)_3PO$. It was indicated that the side-chain conformation was varied in accordance with the kind of solvent. It was elucidated from the calculations on $\langle S_q^2\rangle^{1/2}$ that the side chains are moderately extended in $(Me_2N)_3PO$ and come in loose contact with the main chain in *m*-cresol, and the side chains in $HCONMe_2$ and pyridine exist in an intermediate conformation between those in $(Me_2N)_3PO$ and *m*-cresol.

Studies on poly(amino acids) in dilute solution have been mainly concerned with the determination of the main-chain conformation and the elucidation of the influences of various parameters such as molecular weight, solvent, temperature, salt, pH, amino acid composition, etc., on its conformation.[1,2] However, little has been elucidated on the side-chain conformations.

It is important to clarify the side-chain conformation itself, since poly(amino acids) show various specific structures and properties according to the kind of side chain. The side-chain

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conformations of lowest energy "in vacuo" were calculated with various poly(amino acids) by Scheraga and co-workers.[3-5] It is anticipated that there exist various side-chain conformations in solution without changing the helical structure of the main chain of poly(amino acids).

In solution, the main-chain conformation can be measured by various methods but, with respect to the measurements of side-chain conformations, methods are few. Silverman and Scheraga[6] have indicated from NMR measurements that the side chains of helical poly(γ-benzyl L-glutamate), $(\mathrm{BzlGlu})_n$, in $CDCl_3$–trifluoroacetic acid tend to extend into solution rather than being wrapped around the helical backbone. They postulated that these extended side chains contribute to a secondary side-chain helix in α-helical $(\mathrm{BzlGlu})_n$. It was also reported from NMR and electric dichroism measurements that orientation of the side chains occurs for some poly(amino acids) in helicogenic solvents on account of the side chain–side chain interaction.[7-11]

Small-angle x-ray scattering (SAXS) can afford exact and direct information on the size of the cross section of helical poly(amino acid) which cannot be obtained by other methods. In our previous work,[12] the size and shape parameters of poly(L-tyrosine) in dimethylformamide were determined by SAXS measurements, and it was concluded that poly(L-tyrosine) exists in a form of the right-handed α-helical form in $HCONMe_2$. Luzzati and co-workers[13] also determined the size of the cross section of $(\mathrm{BzlGlu})_n$ in three helicogenic solvents by SAXS.

Poly(N^ϵ-carbobenzoxy-L-lysine), $(\mathrm{CbzLys})_n$, has relatively long side chains. Whence, the side-chain conformation of $(\mathrm{CbzLys})_n$ in helicogenic solvents may depend on the kind of solvent. In this work, SAXS of $(\mathrm{CbzLys})_n$ in four helicogenic solvents, $HCONMe_2$, pyridine, m-cresol, and hexamethylphosphoric triamide, $[(Me_2N)_3PO]$, was measured, and the mass per unit length, M_q, and the radius of gyration of the cross section, $\langle S_q^2\rangle^{1/2}$, were determined. It was confirmed that $(\mathrm{CbzLys})_n$ exists in the α-helical form in these solvents. The solvent dependency of the side-chain conformation will be discussed in the following.

Experimental Section

Materials. $(\mathrm{CbzLys})_n$ of molecular weight 78 000 was prepared by polymerizing N^ϵ-carbobenzoxy-L-lysine in a 1:1 (v/v) mixture of dioxane and methylene dichloride initiated with triethylamine, and the fractionation of the polymer was performed by fractional precipitation from $HCONMe_2$ solution with the addition of a mixture of ethanol–water as the precipitant. Its molecular weight was determined from limiting viscosity number.[14] The ratio of weight-average to number-average molecular weight, M_w/M_n, was obtained as 1.8 by means of gel permeation chromatography (a waters high-speed GPC, Model ALC/GPC 202/R 401) by use of $HCONMe_2$ as a solvent and the monodisperse polystyrene for a calibration.

Solvents. Analytical-grade $HCONMe_2$ and pyridine were used without further purification. $(Me_2N)_3PO$ and m-cresol were purified by distillation under reduced pressure.

Small-Angle X-Ray Scattering. The SAXS measurements were performed with a Kratky U-slit camera. The x-ray source was a broad focus copper anode tube powered by a Rigaku Denki x-ray generator. Room temperature was maintained at 25 ± 0.5 °C.

For the determination of the scattered intensity, a proportional counter was used in connection with a pulse-height analyzer focused on the Cu Kα line and a 10 μ Ni filter to eliminate the Cu Kβ line. The scattered intensity of the sample was measured by the step-scanning method by means of a full automatic step controller. The fluctuation of the primary beam intensity was within 0.3% during a measurement. The widths of the entrance and counter slits were 80 and 250 μm, respectively. The scattered intensity was measured at 65 different scattering angles in a range of 2 to 120 mrad, and as a whole 10^5 pulses were registered for each measuring point. A thin-walled quartz glass capillary, whose inside diameter was about 0.15 cm, was used for the sample cell. The temperature for measurements for $HCONMe_2$, pyridine, and $(Me_2N)_3PO$ was 25°C and for m-cresol the temperature was 40°C. Polymer concentrations were varied from 0.3 to 1.6 g/dL.

The absolute intensity $\tilde{I}/P$ of the scattered beam, i.e., the ratio of the scattered intensity $\tilde{I}$ to the primary beam intensity P, was determined by the use of a Lupolen (polyethylene) platelet. Since we used a primary beam having line-shaped cross section, slit correction was needed for collimation error. This error was eliminated (desmeared) with computer calculations according to the method of Schmidt.[15] In the following, the smeared scattered intensity was designated as $\tilde{I}$ and the desmeared scattered intensity as I.

Partial Specific Volume. For determining the mass per unit length, the partial specific volume $\bar{v}_2$ of $(\mathrm{CbzLys})_n$ in the solvents was measured with a Sibayama Kagaku digital precision densitometer, at 25 °C for $HCONMe_2$, pyridine, and $(Me_2N)_3PO$, and at 40 °C for m-cresol. The values of $\bar{v}_2$ obtained were 0.808 ± 0.003 for $HCONMe_2$, 0.790 ± 0.003 for pyridine, 0.764 ± 0.004 for $(Me_2N)_3PO$, and 0.822 ± 0.003 for m-cresol. The value of $\bar{v}_2$ for $HCONMe_2$ was in good agreement with the value obtained by Deloze and co-workers,[16] 0.806, and with the value by Matsuoka and co-workers,[14] 0.803.

Results and Discussion

In Figure 1, the smeared scattering curves of $(\mathrm{CbzLys})_n$ in $HCONMe_2$ are shown as the plot $\tilde{I}/P\cdot c$ against scattering angle 2θ. The observed scattered intensity curves for other solvent systems were similar to that for $HCONMe_2$.

For a rodlike particle, Kratky and Porod[17] derived the following relation

$$I = I_q/2\theta \qquad (1)$$

where I_q is the cross-section factor determined from the size and shape of the cross section and is equal to $I\cdot 2\theta$. If the cross section is isotropic to some extent, then I_q as a function of 2θ does not differ greatly from the Gaussian form, whence the radius of gyration of the cross section, $\langle S_q^2\rangle^{1/2}$, is obtained from the slope, $(\tan\beta)_0$, of the log I_q vs. $(2\theta)^2$ curve at very low angle

$$\langle S_q^2\rangle^{1/2} = \lambda/\pi[2.303(-\tan\beta)_0/2]^{1/2} \qquad (2)$$

where λ is the wavelength. If the cross section is assumed to be a circle of radius of r_q and homogeneous, then the radius of cross-section r_q is obtained from

$$r_q = 2^{1/2}\langle S_q^2\rangle^{1/2} \qquad (3)$$

The mass per unit length, M_q, is evaluated by inserting the cross-section factor extraporated to zero angle into

$$M_q = K\frac{(I\cdot 2\theta)_0}{P\cdot c}\frac{a^2}{d\cdot z_e^2} \qquad (4)$$

where c (g/dL) is the polymer concentration, a (cm) is the distance from the sample to the plane of registration, d (cm) is the thickness of the sample, z_e is the number of mole excess electrons per 1 g of solute determined by

$$z_e = z_2 - \bar{v}_2\rho_1 \qquad (5)$$

and K is given by

$$K = 2/i_e N_A \lambda \qquad (6)$$

In eq 5 and 6, z_2 is the mole electrons in 1 g of solute, ρ_1 is the electron density of the solvent, i_e is the Thomson-scattering constant of a free electron, and N_A is the Avogadro's number. In the case of the rod of helical structure, the helix pitch h is obtained by dividing the molecular weight of the monomeric unit by M_q.

In Figures 2 and 3, the plots of the logarithm of $I\cdot 2\theta/P\cdot c$ against $(2\theta)^2$ are shown for $(\mathrm{CbzLys})_n$ in $HCONMe_2$ and $(Me_2N)_3PO$, respectively. As is obvious from the figure, the lower the polymer concentration, the experimental points fall on a straight line at lower $(2\theta)^2$ values. The straight line in the figure is drawn through the limiting values of $I\cdot 2\theta/P\cdot c$ at $c \to 0$. The fact that the data points lie on the straight line in a wide

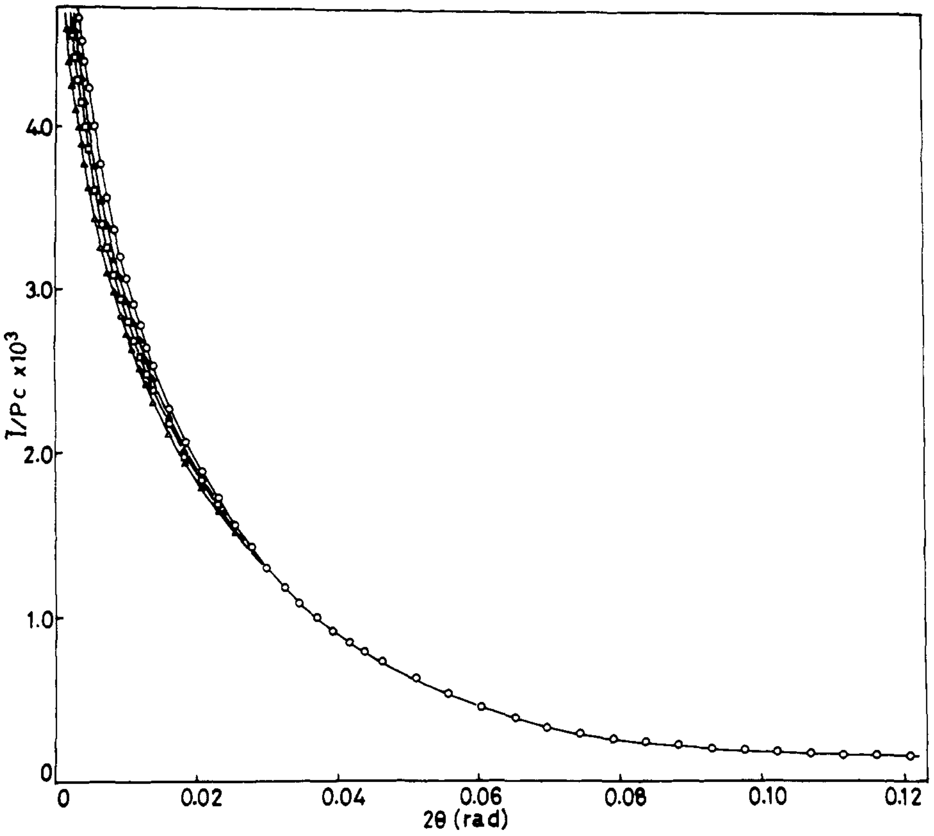

Figure 1. Smeared scattering curve of $(CbzLys)_n$ in $HCONMe_2$: *c* (g/dL) 1.182 (△), 0.765 (■), 0.515 (▲), 0.353 (○).

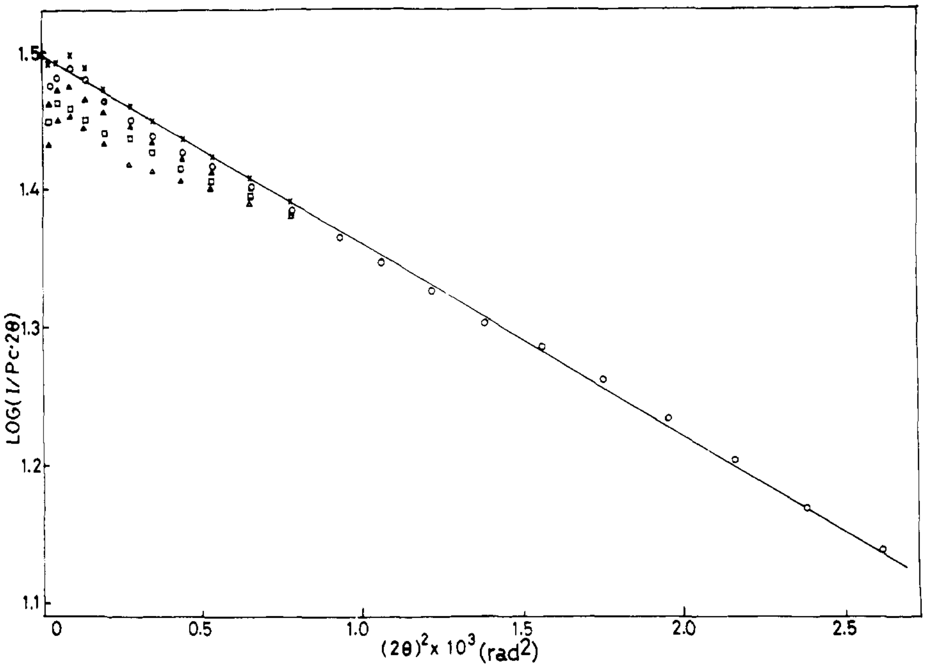

Figure 2. Guinier plot of cross-section factor for $(CbzLys)_n$ in $HCONMe_2$: *c* (g/dL) 1.182 (△), 0.765 (■), 0.515 (▲), 0.353 (○), 0 (×).

range of $(2\theta)^2$ from a low 20 value to a considerably high 2θ value indicate that $(CbzLys)_n$ molecules exist in a helical rod conformation in these solvents. Though the figures for pyridine and *m*-cresol systems are not shown here, the experimental results for four solvent systems are summarized in Table I.

The value obtained from the Guinier plot of the cross-section factor is strictly correct only in the case of an infinitely long rod. Since the poly(amino acid) is polydisperse in chain length, it is necessary to clarify the reliability of the experimental values of M_q and $\langle S_q^2\rangle^{1/2}$. We have calculated the scattering function for rods of constant radius and of Schulz-Zimm-type length distribution and discussed the influences of the length and the length distribution of M_q and $\langle S_q^2\rangle^{1/2}$ obtained from the Guinier plot of the cross-section factor.[20] According to such calculations, errors in M_q and $\langle S_q^2\rangle^{1/2}$ for the present sample are estimated as 2.6 and 0.3%, respectively.

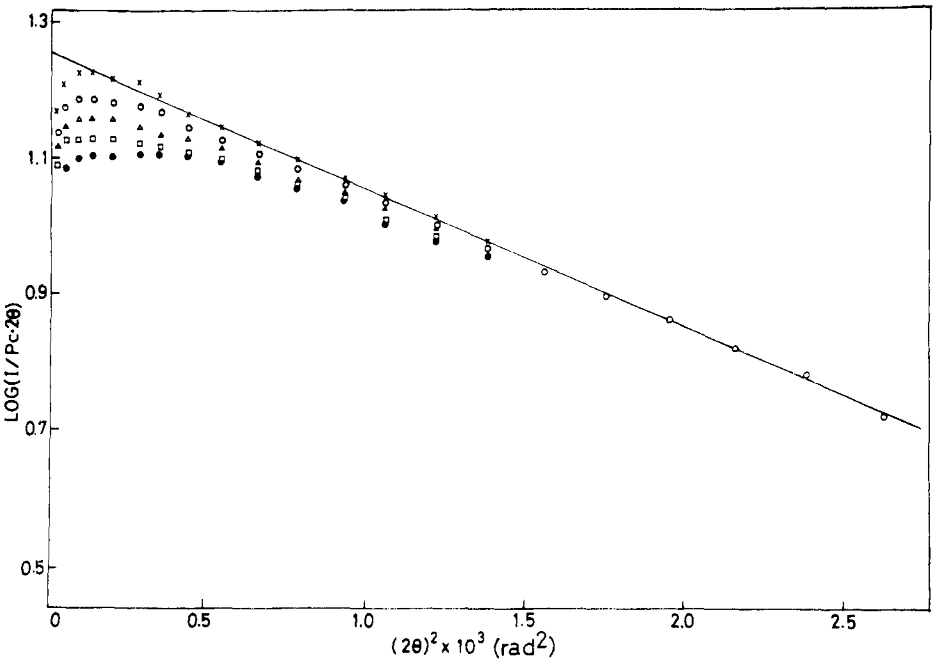

Figure 3. Guinier plot of cross-section factor for $(\mathrm{CbzLys})_n$ in $(\mathrm{Me_2N})_3\mathrm{PO}$: c (g/dL) 1.634 (●), 1.224 (□), 1.013 (△), 0.509 (○), 0 (×).

Table I
Size and Shape Parameters of Poly(N^{ϵ}-carbobenzoxy-L-lysine)

Parameter	HCONMe$_2$	$(\mathrm{Me_2N})_3\mathrm{PO}$	Pyridine	m-Cresol
M_q(/Å)	173 ± 7	175 ± 7	173 ± 8	178 ± 8
h (Å)	1.51 ± 0.06	1.50 ± 0.06	1.53 ± 0.07	1.48 ± 0.07
$\langle S_q^2\rangle^{1/2}$ (Å)	6.2 ± 0.2	7.5 ± 0.3	6.5 ± 0.2	5.3 ± 0.2
r_q (Å)	8.8 ± 0.3	10.6 ± 0.4	9.2 ± 0.3	7.5 ± 0.3

The values of hilix pitch h shown in Table I indicate that $(\mathrm{CbzLys})_n$ molecules exist in the α-helical conformation in four solvents at the temperatures at which SAXS was measured. We have found[21] from optical rotatory dispersion and calorimetric measurements that $(\mathrm{CbzLys})_n$ in m-cresol underwent an extremely sharp thermal helix–coil transition of an inverse type at around 25 °C and concluded that $(\mathrm{CbzLys})_n$ did not include structures other than α-helix and random coil in the course of helix–coil transition in m-cresol and the maxium helical content was somewhat smaller than unity, i.e., about 0.9. Fujita and co-workers[14,22,23] have obtained similar results and indicated from the measurements of dielectric dispersion that the transition of $(\mathrm{CbzLys})_n$ in m-cresol should proceed almost in all-or-none fashion at least at helical contents greater than 0.2. From the value of M_q for m-cresol, it seems that the existence of about 10% of random coil in the α-helix conformation has hardly influenced the Guinier plot of cross-section factor. According to the opical rotatory dispersion measurements,[14] HCONMe$_2$ and $(\mathrm{Me_2N})_3\mathrm{PO}$ are regarded as best helix-forming solvents for $(\mathrm{CbzLys})_n$, and wherein $(\mathrm{CbzLys})_n$ exists in α-helix form. Daniel and Katchalski[24] and Appliquist and Doty[25] from hydrodynamic and optical rotatory dispersion measurements found that the conformation of $(\mathrm{CbzLys})_n$ in HCONMe$_2$ was an α-helix form. The conformation of $(\mathrm{CbzLys})_n$ in pyridine has not been reported so far.

Our value of $\langle S_q^2\rangle^{1/2}$ for $(\mathrm{CbzLys})_n$ in HCONMe$_2$ is approximately in agreement with the value of 6.7 Å obtained from SAXS by Saludjian and Luzzati.[26] As is obvious from Table I, $\langle S_q^2\rangle^{1/2}$ increases in the order of m-cresol < HCONMe$_2$ < pyridine < $(\mathrm{Me_2N})_3\mathrm{PO}$. This fact indicates that the side-chain conformation is varied with the kind of solvent. It is interesting to elucidate what kind of side-chain conformations would correspond to the values of $\langle S_q^2\rangle^{1/2}$ obtained from the experiments.

Since the energy calculation for $(\mathrm{CbzLys})_n$ to find the most stable regular conformation has not been reported yet, calculations of $\langle S_q^2\rangle^{1/2}$ were carried out on a computer by means of eq 7 on a variety of models for side-chain conformations.

$$\langle S_q^2\rangle^{1/2} = \sum_{i=1}^{N} m_i r_i^2 / \sum_{i=1}^{N} m_i \qquad (7)$$

where m_i is the number of electron in the ith atom, r_i is the distance of the ith atom from the center of the helical axis, and N is the number of atoms. The bond lengths and bond angles were cited from ref 4 and 27. For dihedral angles ϕ and ψ about the N–C$^{\alpha}$ and C$^{\alpha}$–C′ bond, respectively, of the backbone chain, the values[4] assigned to the right-handed α-helical conformation of poly(L-alanine) were used. To simplify the calculations, atoms were assumed to exist in the mass points, and only main chain–side chain collisions were taken into consideration. Furthermore, the side-chain conformation was fixed, though the side chains may change their conformation in solution. Such calculation may afford qualitative information on the side-chain conformation.

Ten typical examples of the values of $\langle S_q^2\rangle^{1/2}$, r, and r_q, among the calculations with regard to about 100 kinds of side-chain conformations, were shown in Table II. Figure 4 indicates the models of corresponding side-chain conformations. χ_i is ith rotation angle about the single bond of side chain and the positive direction of χ_i adopted the IUPAC-IUB definitions.[28] The value of χ_0, i.e., the rotation angle about amide bond, was fixed at 0°. r is the distance from the helix axis to the remotest atom. The value of $\langle S_q^2\rangle^{1/2}$ for side chain of all "trans" rotation was not largest, since the direction of the side chain in such conformation was not perpendicular but oblique to the helical axis, as is obvious from the scheme 1 in Figure 4. It was elucidated that the side chain in $(\mathrm{Me_2N})_3\mathrm{PO}$ is moderately extended, the side chain in m-cresol comes in loose contact with the main chain, that is, the side chain is wrapped near the backbone or lies closely parallel to the helix axis, and the side chain in HCONMe$_2$ and in pyridine exists in the intermediate conformations between those in $(\mathrm{Me_2N})_3$-

Table II
Calculated Size Parameters of Poly(N^ϵ-carbobenzoxy-L-lysine)

No.	Rotation angles (deg) about the single bonds of side chain χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7	χ_8	χ_9	$\langle S_q{}^2\rangle^{1/2}$, Å	r, Å	r_q, Å
1	0	0	0	0	0	0	0	0	0	7.46	12.38	10.55
2	−60	180	−60	90	0	0	180	0	90	5.01	7.35	7.08
3	−30	−60	0	0	0	0	30	0	90	5.91	8.91	8.35
4	−60	−60	−60	−60	−60	0	−60	−60	−60	8.29	13.78	11.78
5	−90	180	−60	90	0	0	0	0	0	6.64	11.27	9.39
6	−120	−60	−60	0	0	0	0	0	0	9.35	15.58	13.23
7	−120	−120	−60	60	−60	0	180	0	0	7.51	12.39	10.62
8	−120	0	0	0	0	0	0	0	90	6.89	12.36	9.74
9	90	0	0	0	0	0	0	180	0	4.29	7.37	6.08
10	60	60	60	60	60	0	60	60	60	5.30	8.90	7.49

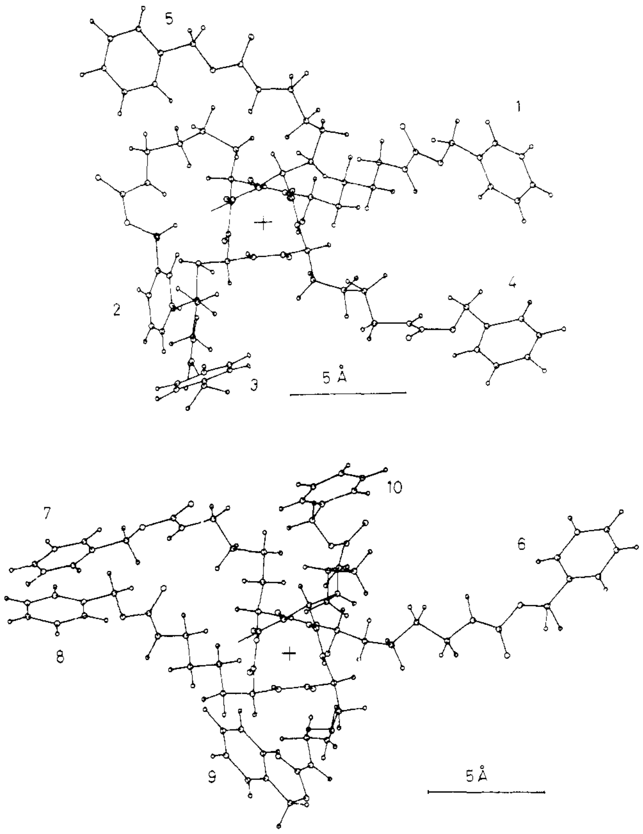

Figure 4. Scheme of the side-chain conformations of (CbzLys)$_n$ shown in Table II.

PO and in m-cresol. However, it should be kept in mind that the values of $\langle S_q{}^2\rangle^{1/2}$ in the solvents measured by SAXS do not always represent such side chain conformation as indicated in Table II.

Stuhrman and Kirste[29-32] showed that if the variation in electron density within the macromolecule is considered, the scattering function is affected in a way which depends not only on the shape of the macromolecule but also on the internal electron density distribution of the macromolecule and the electron density of the solvent. Thus, the radius of gyration depends on the inverse of the mean excess scattering density $\bar{\rho}$ and the internal electron density distribution of the macromolecule. It is necessary, therefore, to clarify that the values of $\langle S_q{}^2\rangle^{1/2}$ in this study are not apparently different due to the solvent. In the case of this study, the values of the inverse of the mean excess scattering density $1/\bar{\rho}$ were 11.40 Å^3/e for $HCONMe_2$, 10.63 Å^3/e for pyridine, 16.10 Å^3/e for m-cresol, and 11.87 Å^3/e for $(Me_2N)_3PO$. Thus the figure increases in the order of pyridine < $HCONMe_2$ < $(Me_2N)_3PO$ < m-cresol. Therefore, the values of $\langle S_q{}^2\rangle^{1/2}$ were not correlated reasonably to the values of $1/\bar{\rho}$. Moreover, the difference in the values of $1/\bar{\rho}$ for four solvents was so small that the big difference of the radius of gyration as depicted by Kirste and Stuhrman[31] could not be found. On the other hand, as is obvious from Table II, since the difference between the values of r and r_q is small, the internal electron density distribution in the helix of (CbzLys)$_n$ is small compared with those of ferritin and low-density lipoprotein.[33] Therefore, the difference in the values of $\langle S_q{}^2\rangle^{1/2}$ due to the kind of solvent is hardly attributable to both the excess mean scattering density and the internal electron density distribution of (CbzLys)$_n$.

With respect to the influence of the solvation on the value of $\langle S_q{}^2\rangle^{1/2}$, the inner solvation, which affects the values of $\langle S_q{}^2\rangle^{1/2}$, is absent since the core of the α-helical conformation of polypeptide is rigid. Even if the outer solvation exists, it is of no importance since the electron density of the solvate envelope hardly differs from that of the solvent.[34] From these considerations, it is reasonable to consider that the difference in the values of $\langle S_q{}^2\rangle^{1/2}$ is not apparent difference but true difference due to the variation of the side-chain conformation.

As mentioned above, Luzzati and co-workers[13] determined M_q and $\langle S_q{}^2\rangle^{1/2}$ of (BzlGlu)$_n$ by SAXS in three helicogenic solvents $HCONMe_2$, pyridine, and m-cresol. The values of $\langle S_q{}^2\rangle^{1/2}$ were 4.6 Å for $HCONMe_2$, 4.4 Å for pyridine, and 3.5 Å for m-cresol, i.e., value increased in the order of m-cresol < pyridine < $HCONMe_2$. Though the differences in the values of $\langle S_q{}^2\rangle^{1/2}$ due to solvents were not discussed in their paper, it is thought that the difference reveals that of the side-chain conformation in (BzlGlu)$_n$ molecules. The order of the magnitudes of $\langle S_q{}^2\rangle^{1/2}$ for (BzlGlu)$_n$ mentioned was similar to that for (CbzLys)$_n$ indicated in this study.

The cause of the variation of the side-chain conformation due to the difference in solvent species may originate from the difference in the side chain–solvent interaction. Since the side chain of (CbzLys)$_n$ has functional groups such as phenyl group and urethane bond, it is supposed that the polarity of the solvents may participate in the dimension of the side chain of (CbzLys)$_n$. The values of dipole moment[35] of the solvents used are 3.86 D for $HCONMe_2$, 2.37 D for pyridine, 4.31 D for $(Me_2N)_3PO$, and 1.543 D for m-cresol. That is, m-cresol < pyridine < $HCONMe_2$ < $(Me_2N)_3PO$. The solvent with a large dipole moment could be, on the whole, regarded to have a large dimension for the side chain. Consequently, it is supposed that the difference in the dipole moment of the solvents may participate in the variation of the side chain conformation due to the solvent.

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Statistical Thermodynamics of Nonintersecting Polymer Coils

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ABSTRACT: The methods of statistical thermodynamics were applied to a model of a polymer coil with the following properties. (i) A polymer coil may adopt a finite number of nonintersecting conformations. (ii) Each conformation has a well-defined number of intersegmental contacts. (iii) The contact energy of a coil is proportioanl to the number of contacts. A knowledge of the average number of contacts $\bar{i}(m,x)$ and of the average end-to-end distance $\overline{R^2}(m,x)$ as a function of reduced molecular weight m and of the interaction parameter x is sufficient for calculation of the reduced number of conformations with i contacts and of their average end-to-end distance. Plausible expressions for $\bar{i}(m,x)$ and $\overline{R^2}(m,x)$ were developed.

The size and shape of polymer coils and their dependence on the thermodynamic properties of the solvent have been studied experimentally and theoretically ever since the linear character of polymers was recognized. Nevertheless, the agreement between the theory and the experiment is still not satisfactory. In the present paper we are trying to outline a way to construct a theory, which is sound from the viewpoint of statistical thermodynamics, yet may be adapted to the observed behavior of polymer coils.

Models of Polymer Coils

Most models of polymer coils are based on the recognition of the similarity between the contour of the coil and the trace left by a randomly moving particle. However, there is a basic difference between these two lines: unlike the latter the coil can never intersect itself. Accordingly, we can classify the theories from two viewpoints: (1) how they simulate the random walk problem, and (2) how they handle the problem of self-intersection.

Most theories model the random walk by a succession of steps of fixed length; the angle between two successive steps is often also fixed. Such a model seems inherently satisfactory for description of chemical bonds. However, quite often the steps represent other quantities than chemical bonds. One group of theories places the steps onto a quasicrystalline lattice.[1] The number of possible conformations of the coil on the lattice, while astronomical for long chains, is still limited. For calculations, a specific crystalline lattice must be selected, which is characterized by some coordination number. There is always a problem what part of the computational results should be attributed to the choice of the lattice and/or of coordination number and what part represents the general properties of polymer coils. The lattice points, which are not occupied by separate polymer segments, are filled by solvent molecules.

Another group of theories[2] does not confine the random walk to lattice points and more options are available for each step. In some theories even the length of an individual step is not restricted to a single value: a Gaussian distribution of the step lengths is introduced. This approach seems to avoid some unnecessary restrictions of the lattice model. On the second look, however, this model implies filling of the unoccupied space by continuous solvent: The spatial requirements of the solvent molecules are not considered and the number of possible conformations is grossly exaggerated.

As far as we know, no proper handling of the problem of self-intersection of the coil has been offered.[14] It is obvious that hypothetical conformations of the coil which intersect themselves do not correspond to any physical entity and should be excluded from consideration. Yet their exclusion presents formidable computational problems: The so-called exact enumeration method,[3,4] which excludes them exactly, has been used only for very short chains and its application to long chains is very unlikely. The Monte Carlo techniques

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