Permanent Electric Dipole–Dipole Interactions in Lyotropic Polypeptide Liquid Crystals

Norio MORI*

The interaction energy between two adjacent α-helical molecules was calculated taking into account for permanent electric dipoles locating on the helical core of a polymer main-chain in order to explain the cholesteric structure of lyotropic polypeptide liquid crystals. It was concluded that the dipole-dipole interactions were responsible for the formation of the cholesteric structure.

INTRODUCTION

It is generally believed that induced dipole-quadrupole interactions as well as induced dipole-dipole ones play an important role in the formation of cholesteric liquid crystals[1]. In a previous paper[2] the author noted that the above theory based on the method of electric multipole expansion was inconsistent with the experimental results in the system of lyotropic cholesteric liquid crystals in concentrated solutions of poly (γ-alkyl L-glutamate)s. The systems of lyotropic polypeptide liquid crystals consist of elongated molecules with dimensions much larger than the mean distance between the center of mass of the nearest neighbors. Van der Meer et. al.[3] have already pointed out that the conditions required for proper convergence of multipole expansion can hardly be satisfied even in the system of thermotropic liquid crystals. This fact casts doubt on the validity of the above method.

On the other hand, a synthetic polypeptide molecule with α-helical conformation has two

permanent electric dipole moments in one residue unit locating on the rigid helical core of the polymer mainchain and sidechain ester linkage respectively. It is necessary to take into account the effect of the dipole-dipole interactions on the formation of cholesteric structure. In this paper, the author shows how a comparable mutual twist angle results from the dipole-dipole interactions between adjacent molecules. In a previous paper[4] the author suggested that a synthetic polypeptide having nonpolar side chains also formed cholesteric liquid crystals. Therefore, as the first step, only the dipoles locating on the mainchain are taken into account in this study.

THEORY

Since a dipole moment is vectorial quantity, the interaction is no longer symmetric with respect to inversion of molecules about their own centers. Accordingly, we calculate the interaction energy on the four types of different combinations of a pair of molecules 1 and 2: $L(+)-L(-)$, $L(+)-L(+)$, $D(+)-D(-)$ and $D(+)-D(+)$, where, for example, the abbreviation $L(+)-L(-)$ represents the

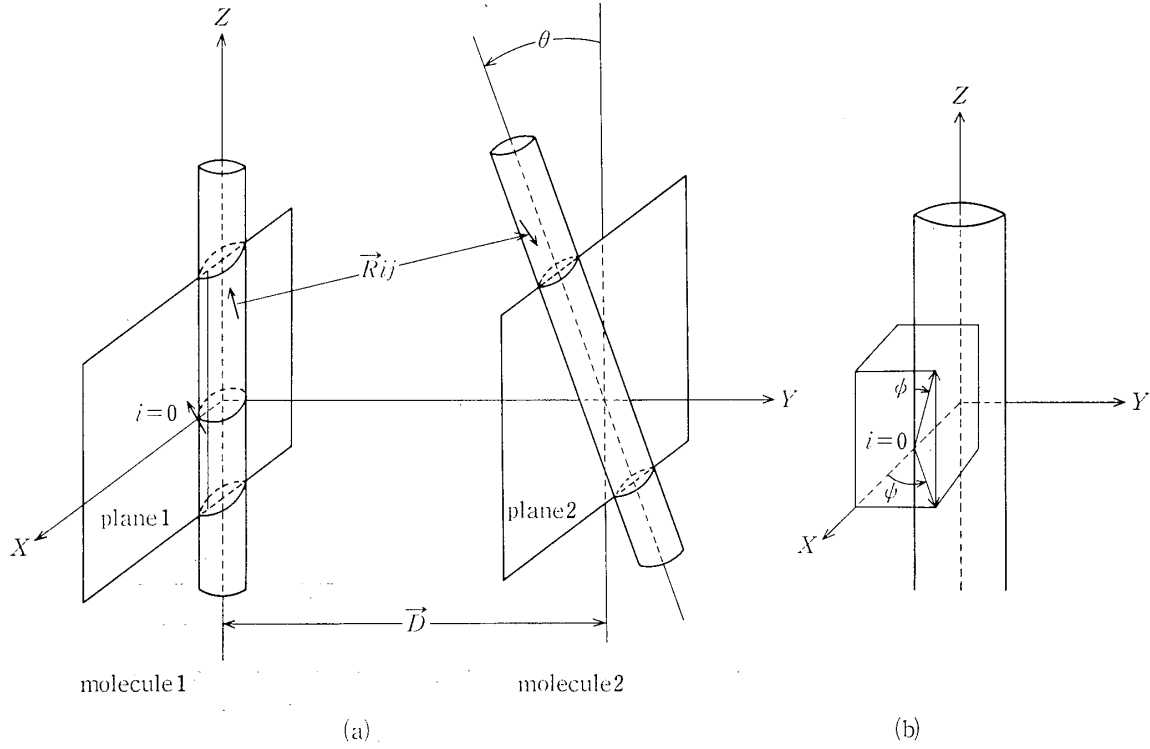* Research Associate, Department of Industrial Chemistry

Fig. 1. (a) Geometry for a pair of molecule 1 (L(+)) and molecule 2 (L(−)).
(b) The direction of a dipole moment at $i=0$.

combination of a pair of right-handed helix (L(+)) and its inverted helix (L(−)) and symbol D denotes left-handed helix.

The geometry under consideration and the direction of a dipole moment on the combination of L(+)−L(−) are shown in Figs. 1(a) and 1(b) respectively, where cholesteric axis is taken along Y-axis and molecule 2 lies in plane 2 parallel to XZ-plane. The three components $R_x{}^i(1)$, $R_y{}^i(1)$, $R_z{}^i(1)$ of the position vector $\vec{R}(1)$ of ith unit of molecule 1 are

$$R_x{}^i(1) = r\cos(\beta i),$$
$$R_y{}^i(1) = r\sin(\beta i),$$
$$R_z{}^i(1) = z.i, \qquad \text{Eq. (1)}$$

where β and z are, respectively, the angle of rotation about the axis of helix and translation along the axis on passing from the ith unit to $(i+1)$th one and r the distance of the unit from the helix axis. The components $P_x{}^i(1)$, $P_y{}^i(1)$, $P_z{}^i(1)$ of corresponding dipole moment $\vec{P}(1)$ are expressed by

$$P_x{}^i(1) = P\sin\phi\cos(\psi+\beta i),$$
$$P_y{}^i(1) = P\sin\phi\sin(\psi+\beta i),$$
$$P_z{}^i(1) = P\cos\phi, \qquad \text{Fq. (2)}$$

where P is the absolute value of a dipole moment and ϕ and ψ are, respectively, demonstrated in Fig. 1(b). The components $R_x{}^i(2)$, $R_y{}^i(2)$, $R_z{}^i(2)$ of the position vector $\vec{R}(2)$ of the jth unit of molecule 2 are given by

$$R_x{}^j(2) = r\cos(\beta(J-L) + W)\cos\theta$$
$$\qquad + z(j-L)\sin\theta,$$
$$R_y{}^j(2) = r\sin(\beta(j-L) + W) + D,$$
$$R_z{}^j(2) = -r\cos(\beta(j-L) + W)\sin\theta$$
$$\qquad + z(j-L)\cos\theta, \qquad \text{Eq. (3)}$$

where molecule 2 translates along the helix axis by $-L$ unit and rotates about the helix axis by the angle of W compared with those of molecule 1 and θ a mutual twist angle. The components $P_x{}^j(2)$, $P_y{}^j(2)$, $P_z{}^j(2)$ of corresponding dipole moment $\vec{P}(2)$ are

$$P_x^j(2) = P \sin \phi \cos(\psi - \beta(j-L) + W) \cos \theta$$
$$- P \cos \phi \sin \theta,$$
$$P_y^j(2) = -P \sin \phi \sin(\psi - \beta(j-L) + W),$$
$$P_z^j(2) = -P \sin \phi \cos(\psi - \beta(j-L) + W) \sin \theta$$
$$- P \cos \phi \cos \theta. \qquad \text{Eq. (4)}$$

The interaction energy U_{ij} between i th unit of molecule 1 and j th unit of molecule 2 is given by

$$U_{ij} = \frac{1}{4 \pi \varepsilon} [\vec{P}(1) \cdot \vec{P}(2) R_{ij}^{-3}$$
$$- 3\{\vec{P}(1) \cdot \vec{R}_{ij}\} \cdot \{\vec{P}(2) \cdot \vec{R}_{ij}\} R_{ij}^{-5}],^{5)}$$
$$\text{Eq. (5)}$$

where ε is the dielectric permittivity of the medium and R_{ij} is the distance between two units given by

$$R_{ij}^2 = \{R_x^j(2) - R_x^i(1)\}^2 + \{R_y^j(2) - R_y^i(1)\}^2$$
$$+ \{R_z^j(2) - R_z^i(1)\}^2. \qquad \text{Eq. (6)}$$

The total interaction energy U between molecules 1 and 2 is

$$U = \frac{1}{2} \sum \sum U_{ij} \quad (i, j = -N \sim N). \quad \text{Eq. (7)}$$

Substituting Eqs. (1)-(6) into Eq. (7) we can obtain the mutual twist angle θ at the minimum interaction energy $(dU/d\theta = 0)$. The interaction energy of the combination of $D(+)$ $-D(-)$ can be obtained by changing the sign of parameters β and ψ ($\beta \rightarrow -\beta$, $\psi \rightarrow -\psi$) in Eqs. (1)-(4).

When the dipoles locating in the ranges of $-r < R_y^i(1) < 0$ and $D < R_y^j(2) < (D+r)$ interact with the other dipoles, the energy will be significantly diminish with its absolute value in order to be shielded its electric field by other atoms. For this reason. we exclude, as a first approximation, these interactions from the summation of Eq. (7).

RESULTS AND DISCUSSION
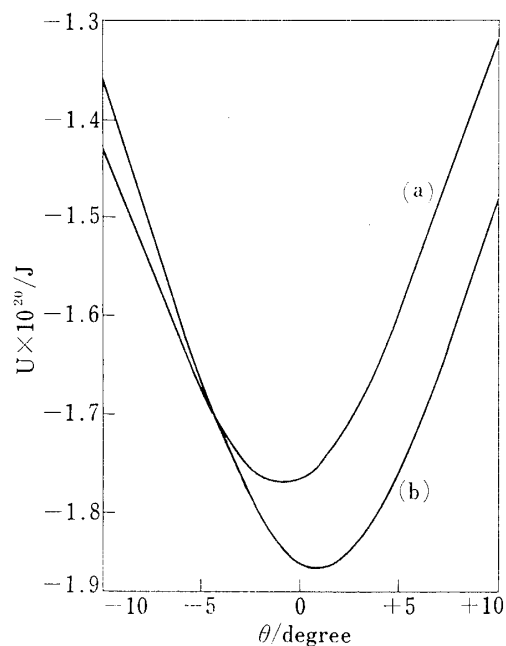
The calculation was performed on an

Fig. 2. Dependeece of θ on the interaction energy U at $W = 0$.
(a): D(+)−D(−)
(b): L(+)−L(−).

OKITAC System 50 computer by use of the following parameters[6]: $z = 1.5$ Å; $r = 3.0$ Å; $\beta = 2\pi/3.6$ rad; $\psi = -0.17453$ rad; $\phi = 0.17453$ rad; $P = 6.0$ Debye; $D = 30$ Å; $L = 20$; $\varepsilon = \varepsilon_0 = 8.85 \times 10^{-12} \text{Fm}^{-1}$; N the degree of polymerization of two molecules, 201. The parameter L is arbitrarily chosen, but the conclusions are confirmed to be independent of this choice.

At first we discuss about two combinations of $L(+) - L(-)$ and $D(+) - D(-)$, where molecules are arranged nearly antiparallel to each other. In Fig. 2 the interaction energy U is shown as a function of θ at a given angle W about helix axis of molecule 2. $U-\theta$ curves are almost symmetric with respect to the θ_0 at the minimum interaction energy U_{min}. The relation between U_{min} and the angle W is plotted every ten degrees of W in Figs. 3 and 4[7]. As can be seen from the figures, a molecule is allowed to rotate freely about its helix
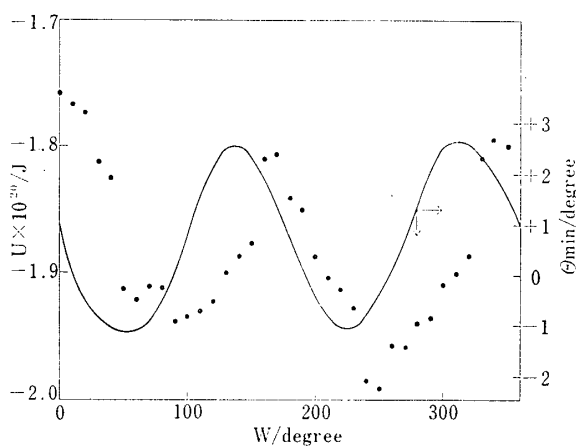
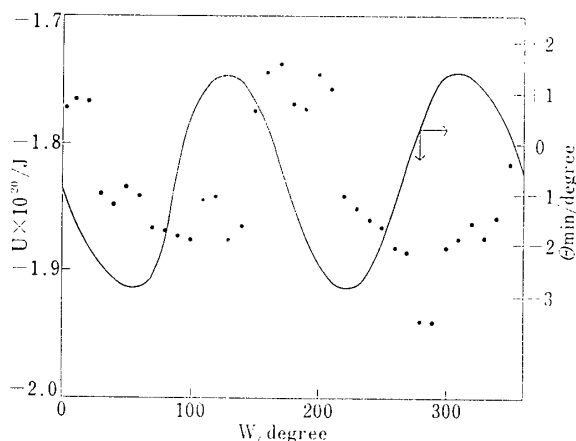**Fig. 3.** Effects of W on U_{min} and θ_0 in the system of the combination of $L(+)$ $-L(-)$.

Fig. 4. Effects of W on U_{min} and θ_0 in the system of the combination of $D(+)$ $-D(-)$.

axis since $\Delta U/KT \ll 1$ at 300°K, where ΔU is the difference in depth of the deep and shallow wells of the rotational potential energy of molecules about their helix axes. Dependence of θ_0 on W is also shown in Figs. 3 and 4. Using these results we can calculate the average cholesteric twist angle $<\theta_0>$ as follows:

$<\theta_0> =$

$$\int_0^{2\pi} \theta_0 \exp(-U/KT)dW / \int_0^{2\pi} \exp(-U/KT)dW.$$
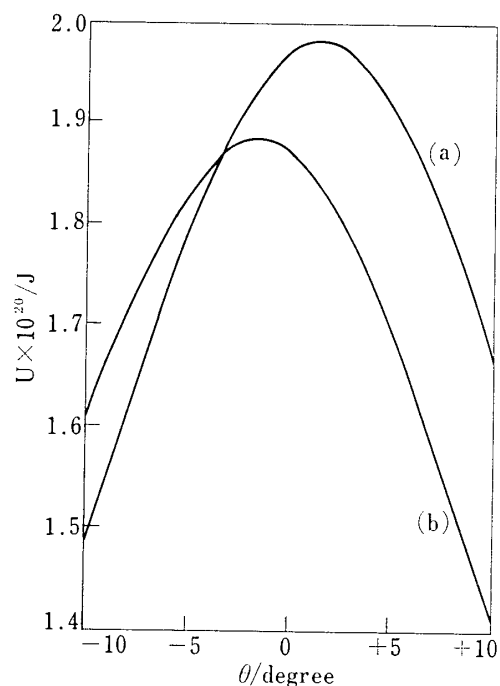
Eq. (8)

The calculation was carried out by replacing

Fig. 5. Dependence of W on the interaction energy U at $W=0$ in the combinations of $L(+)-L(+)$ (a) and $D(+)-D(+)$ (b).

the integration of Eq. (8) by summation. These results indicate that the dipole-dipole interaction causes nonzero cholesteric twist angle of $<\theta_0>$ and that the cholesteric helical sense is right-handed in the right-handed helices and left-handed in the left-handed ones.

The similar calculation was carried out in the case of the combinations of $L(+)-L(+)$ and $D(+)-D(+)$, where molecules are mutually arranged nearly parallel. The relation between U and θ is shown in Fig. 5. Both $U-\theta$ curves are also almost symmertic with respect to the θ_0 at the maximum interaction energy U_{max}. The sign of θ_0 was independent of W. These results imply that the right-handed helices are inclined to be mutually twisted to the left-handed direction. These results are summarized in Table 1. A slight difference of the absolute value of $<\theta_0>$ between the combinations of $L(+)-L(-)$ and $D(+)-D(-)$

Table 1 Summary of the average cholesteric twist angle and its helical sense in four types of combinations of a pair of molecules 1 and 2.

Combination	Twist angle $<\theta_0>$	Cholesteric helical sense
$L(+)-L(-)$	$+0.592$(degree)	right-handed
$L(+)-L(+)$	—	left-handed
$D(+)-D(-)$	-0.675(degree)	left-handed
$D(+)-D(+)$	—	right-handed

may attributed to replacing the integration of Eq. (8) by summation.

It is well known that right-handed helical polypeptides are possible to form cholesteric structures of both right-handed and left-handed helical sense in suitable solvents[8] and that, in some solutions of polyglutamates, the chirality of cholesteric structures changes sign from the right-handed direction to the left-handed one through nematic structure as temperature increases.[9,10]. Therefore we expect that the inversion of cholesteric helical sense is caused by the difference in the proportion of the two combinations of parallel $(L(+)-L(+))$ and antiparallel $(L(+)-L(-))$ arrangements of molecules on the cholesteric axis.

From the above calculation, it is concluded that the permanent electric dipoles locating on the rigid helical core of polymer mainchain are responsible for the formation of cholesteric structure of polypeptide liquid crystals.

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