

THEORY OF INTRAMOLECULAR ORIENTATIONAL ORDER OF MESOGENIC UNITS IN MC-LCPs AND ITS APPLICATION

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ABSTRACT

New concepts such as intramolecular orientational order parameter and corresponding model as well as theory were proposed to describe the intramolecular orientation of mesogenic units in the liquid crystalline polymer chains. The relationship between the intramolecular orientational order parameter and the molecular geometrical parameters such as the bond angle, the bond rotational angle and the rotational potential energy of chemical bonds was deduced. A significant even-odd oscillation of the intramolecular orientational order parameter of LCPs with different length of flexible spacer was found and rationally related to even-odd zig-zag manner of transition properties. The verification and application of the theory are also discussed. The isotropic transition temperature predicted by the theory is shown to be in favourable agreement with the experiments.

INTRODUCTION

Main chain liquid crystalline polymers (MC-LCPs), which are being used to manufacture self-reinforced plastics, high strength and high modulus fibers and in-situ composites, have obtained a very rapid development during last one or two decade. Most of them recently investigated are thermotropic LCPs for which have some processing advantages over lyotropic LCPs^{1, 2}.

It is well known that straight rigid cores called mesogenic units are necessary for forming MC-LCPs. However, a complete rigid rodlike macromolecule such as poly(benzoate) can hardly be used as a thermotropic liquid crystal, because its melting temperature T_m is so high that it is even higher than decomposition temperature T_d of the polymer. Therefore, various flexible spacers and kink units have been used as constitutional units of MC-LCPs in order to reduce T_m of the polymers³⁻⁹. Comprising flexible spacers and kink units in MC-LCPs can efficiently decrease the T_m of the LCPs, but, meanwhile, a significant change of orientation direction of mesogenic units in the polymer chain also occurs, which has an extraordinarily important effect on spatial orientational order and thermodynamic properties of liquid crystalline phase.

Therefore, for the sake of understanding the exact role of these groups in MC-LCPs, it is necessary to specify the intramolecular orientation of mesogenic units in polymers containing flexible spacers and kink units and to look for an insight about the relationship between the orientation and the fundamental molecular parameters such as bond angle, bond rotation angle and rotational potential. Even though the concepts such as mean square end-to-end distance $\langle r^2 \rangle$, radius of gyration and persistence length, which have been well established for random coil macromolecules⁷, can be used to describe the spatial configuration of LCPs. However, it is orientation of mesogenic units rather than their spatial position that is more important in LCPs. No suitable concepts dealing with the intramolecular orientation of mesogenic units have been proposed.

In order to solve the problem just mentioned, the new concepts such as intramolecular

orientational distribution and intramolecular orientational order parameter and corresponding model as well as theory based on them were proposed in this work to describe the orientation of mesogenic units in LCP chains. The relationship between the orientation and the molecular geometrical parameters such as bond angle, bond rotation angle and rotational potential energy were thoroughly investigated. The intramolecular orientational order parameter for series of typical MC-LCPs were calculated. The results are very useful for illustrating many phenomena in MC-LCP, e. g. even-odd effect of LCPs with flexible spacer. Finally, the predictions of the theory were compared with the data available for some typical series of MC-LCPs.

THEORY

1. Intramolecular orientational distribution function

For low molecular weight nematic liquid crystal, the orientational order is described by orientational singlet distribution^[8].

$$f(\Omega) = N/(\rho Z) \int \{dr_1^N\} \{d\Omega_1^N\} \exp[-\beta U(\{r^N, \Omega^N\})] \quad (1)$$

where $U(\{r^N, \Omega^N\})$ is the potential energy of the N particles and, as usual, the β is the inverse of a product of the Boltzman constant k and the absolute temperature T . r is a vector specifying position of rigid particle and Ω is three Euler angle about the director. Curly brackets to denote collectively N variables. Thus

$$\{r^N, \Omega^N\} \equiv (r_1, r_2, \dots, r_N, \Omega_1, \Omega_2, \dots, \Omega_N) \quad (2)$$

$$\{dr_1^N\} \equiv dr_1 dr_2 \dots dr_N \quad (3)$$

$$\{d\Omega_1^N\} \equiv d\Omega_1 d\Omega_2 \dots d\Omega_N \quad (4)$$

$f(\Omega)$ can be expanded in a Wigner series, that is in a basis of Wigner rotation matrices

$$f(\Omega) = \sum f_{lm} D_{m,n}^L(\Omega) \quad (5)$$

$$f_{lm} = (2L+1) \langle D_{m,n}^{L*} \rangle / (8 \times \pi^2) \quad (6)$$

where

$$\langle D_{m,n}^{L*} \rangle = \int D_{m,n}^{L*}(\Omega) f(\Omega) d(\Omega) \quad (7)$$

The average $\langle D_{m,n}^{L*} \rangle$ which completely define $f(\Omega)$ are just the orientational order parameters^[8].

For non-rodlike liquid crystal polymer (cf. Fig. 1), there should be two different kinds of orientational distributions. One reflecting orientation fluctuation of mesogenic units with respect to the director or a space frame, which mainly results from anisotropic intermolecular interaction, is called spatial orientational distribution in this paper for distinguishing. The other specifies the orientation fluctuation of mesogenic units with respect to an intramolecular frame which mainly depends on the molecular geometrical parameter such as bond angle, bond rotational angle and rotation potential energy for each bond. A new concept called intramolecular orientational distribution is defined in this paper for the latter.

The former, the spatial orientational distribution function, can be expressed by Eq. (5), (6) as mentioned above. In order to specify the latter, we defined a new function $g(\omega)$ for intramolecular orientational distribution, where ω is three Euler angles of each orientational unit about an intramolecular frame. Similarly, $g(\omega)$ can be expanded in a basis of Wigner rotational matrices

$$g(\omega) = \sum g_{lm} D_{m,n}^L(\omega) \quad (8)$$

$$g_{Lm} = (2L+1) \langle D_{m,n}^L(\omega) \rangle / (8 \times \pi^2) \quad (9)$$

$\langle D_{m,n}^L(\omega) \rangle$ is defined as the intramolecular orientational order parameter.

In current paper, we mainly deal with $g(\omega)$ and $\langle D_{m,n}^L(\omega) \rangle$ and leave the problem such as the relationship between the two kinds of orientation distribution for further study.

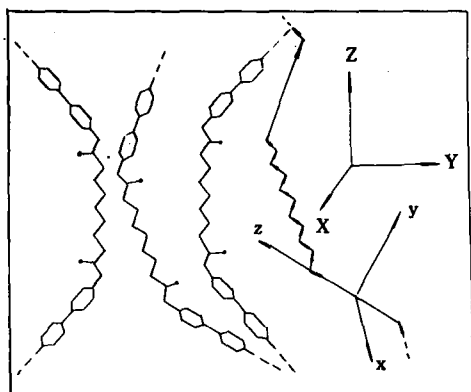


Fig. 1 Schematic diagram of the semiflexible polymer chains comprising rigid core interconnected with flexible segments, corresponding vector chain and coordinate system.

(X, Y, Z): spatial, (x, y, z): intramolecular frame.

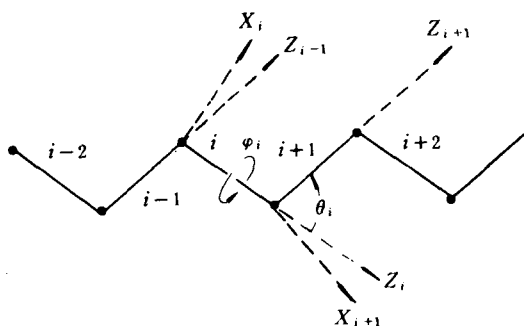


Fig. 2 A part of bond sequence and the reference frames fixed on them

2. Direction cosines and transformation matrices

A typical liquid crystalline polymer with flexible spacer can be depicted as a sequence of vectors in Fig. 1, every mesogenic unit which is a straight rigid core is regarded as an orientational unit for its rigidity and represented by a longer vector. Similarly, each chemical bond in a flexible spacer is also regarded as an orientational unit and represented by a shorter vector (cf. Fig. 1). The intramolecular orientation of orientational units can be expressed by the direction cosines of the units in cartesian coordinate fixed on any mesogenic unit.

A part of bond sequence and the reference frame fixed on them are depicted in Fig. 2 where the angle θ_i is the supplement of the skeletal bond angle at chain atom i and bond rotational angle φ_i measures the dihedral angle between two planes defined respectively by bond $i-1, i$ and $i, i+1$. By transforming the representation of (n_j) successively from the reference frame for any of the intervening bond to that of its predecessor, we can obtain the direction cosines $(l_{\alpha k})$ ($\alpha = x, y, z$) of any orientational unit j with an intramolecular frame fixed on i unit. Then

$$(l_{\alpha k}) = (n_{\alpha i}^T) T_i T_{i+1} \cdots T_{j-1} (n_j) \quad (10)$$

where $k = j - i$, $n_{\alpha} (\alpha = x, y, z)$ are

$$n_x = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad n_y = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad n_z = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (11)$$

Transformation matrix T_i corresponding to the i th orientational unit can be written as

$$T_i = \begin{pmatrix} -\cos\theta_i \cos\varphi_i & \sin\varphi_i & \sin\theta_i \cos\varphi_i \\ -\cos\theta_i \sin\varphi_i & -\cos\varphi_i & \sin\theta_i \sin\varphi_i \\ \sin\theta_i & 0 & \cos\varphi_i \end{pmatrix} \quad (12)$$

3. Intramolecular orientational order parameter

In order to obtain the intramolecular orientational order parameter, it is necessary to know the relationship between the order parameter and the direction cosines defined above. It can be deduced as the following.

The intramolecular orientational distribution function $g(\omega)$ can be expanded in terms of the direction cosines l_α ($\alpha = x, y, z$) of the orientational units with respect to a molecular fixed frame. Thus

$$g(\omega) = \{1 + 5 \sum_{\alpha, \beta} S_{\alpha\beta} l_\alpha l_\beta + 9 \sum_{\alpha, \beta, \gamma, \delta} S_{\alpha\beta\gamma\delta} l_\alpha l_\beta l_\gamma l_\delta + \dots\} / 8\pi^2 \quad (13)$$

where

$$S_{\alpha\beta} = (3 \langle l_\alpha l_\beta \rangle - \delta_{\alpha\beta}) / 2 \quad (14)$$

It is also called the Saupe ordering matrix in accordance with the definition of low molecular weight liquid crystal^[8].

From Eq. 10 and theory of direct product of matrix, it can be written as

$$\begin{aligned} \langle (l_\alpha l_\beta)_k \rangle &= (n_\alpha^T \otimes n_\beta^T)_i \langle (T_i \otimes T_i) (T_{i+1} \otimes T_{i+1}) \dots \\ &\quad (T_{j-1} \otimes T_{j-1}) \rangle (n_z \otimes n_z)_j \end{aligned} \quad (15)$$

where $\langle \dots \rangle$ means average for all conformation and $\otimes$ signifies direct product of two matrices or vectors. The equation is resemble in form with the equation proposed by Flory for fourth moment of chain molecule^[9]. Then, it can be written as

$$\begin{aligned} \langle (l_\alpha l_\beta)_j \rangle &= Z^{-1} J^* U_1^{(j-1)} [(U \otimes n_\alpha^T \otimes n_\beta^T) | T \otimes T |]_i \\ &\quad [(U \otimes E_9) | T \otimes T |]_{i+1}^{(j-i-1)} \\ &\quad (U \otimes n_z \otimes n_z)_j U_{j+1}^{(n-j-1)} J \end{aligned} \quad (16)$$

where U_1 to U_n are the statistical weight matrices of corresponding bond rotation. $|\dots|$ means the pseudodiagonal matrix of order $3v \times 3v$

$$|T \otimes T| = \begin{pmatrix} T(\varphi_1) \otimes T(\varphi_1) & & \\ & \ddots & \\ & & T(\varphi_n) \otimes T(\varphi_n) \end{pmatrix} \quad (17)$$

obtained by placing the $T \otimes T$ matrices for various rotational states of corresponding bond in diagonal array. J^* and J are respectively the row and column vectors

$$J^* = (1 \ 0 \ \dots \ 0) \quad (18)$$

$$J^T = (1 \ 1 \ \dots \ 1) \quad (19)$$

For the liquid crystalline polymer with flexible spacer, the bond rotational potential of the chemical bonds in both side of a mesogenic unit can be regarded as independent. Eq. (15) can be reduced to

$$\begin{aligned} \langle (l_\alpha l_\beta)_k \rangle &= (n_\alpha^T \otimes n_\beta^T)_i \langle (T \otimes T)_i^{(k)} \rangle^x \\ &\quad \langle (T \otimes T)_i^{(k)} \rangle = (n_z \otimes n_z)_j \end{aligned} \quad (20)$$

where

$$(T \otimes T)_i^{(k)} = (T \otimes T)_i (T \otimes T)_{i+1} \dots (T \otimes T)_{i+k} \quad (21)$$

The elements of the second rank S matrix for each orientational unit are given as

$$S_{\alpha\beta,k} = (3 \langle l_\alpha l_\beta \rangle_k - \delta_{\alpha\beta}) / 2 \quad (22)$$

where $\delta_{\alpha\beta}$ is kronecker delta. $S_{\alpha\beta}$ for all orientational unit can be obtained by summing

$$S_{\alpha\beta} = \sum_{k=1} S_{\alpha\beta,k} \quad (23)$$

Since $S_{\alpha\beta,k}$ converge at zero rapidly, the above sum only needs limited terms.

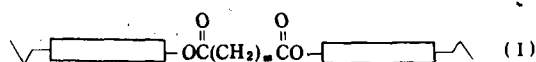
Then, the intramolecular order parameter can be obtained from the relationship between Saupe's ordering matrix elements $S_{\alpha\beta}$ and the order parameter $\langle D_{0,n}^2 \rangle$ ^[8]. Some are written for example as the following

$$\langle D_{0,0}^2 \rangle = S_z \quad (24)$$

$$\langle D_{0,2}^2 \rangle = (S_{xx} - S_{yy})/\sqrt{6} \quad (25)$$

RESULTS AND DISCUSSION

The series of MC-LCPs that have been carefully synthesized and characterized in many laboratories can be expressed in a general form as



the rectangles indicate various types of mesogenic units extending between two ester oxygen. These LCPs were chosen as typical examples to carry out theoretical investigation by the method developed above. The results are given as follows.

1. Intramolecular orientation

For the LCPs (I), $S_{\alpha,k}$ were calculated by Eq. (16) to (22). The parameters of molecule geometry and data of statistical weight matrices used in calculation have been given in literature^[9]. $S_{\alpha,k}$ indicate the components of the Saupe's ordering matrix of j th orientational unit about the intramolecular coordinate fixed on i th unit (a mesogenic unit) where $k=j-i$. Some calculated results are depicted in Fig. 3. As k increases, the absolute value of $S_{\alpha,k}$ decreases and finally approaches zero. When k is large, the correlation between orientational unit i and j is weak. In other word, the orientations of both units become independent with each other.

Another interesting point can be seen from Fig. 3 is that the odd-even zig-zag manner occurs in $S_{\alpha,k}$ vs. k curves. As k is odd or even, $S_{\alpha,k}$ are less than zero or larger than zero alternatively. $S_{\alpha,k} > 0$ means that the orientational unit j is liable to parallel to z axis of the intramolecular coordinate fixed on the i unit, and $S_{\alpha,k} < 0$ means that orientational unit j is tend to lie perpendicular to i unit. Among the orientational units, the mesogenic units are more important for forming liquid crystalline phase. When the number of methylene groups m in flexible spacer is even or odd, the nearest mesogenic unit is in even or odd position counting from the intramolecular frame and its order parameter S_z^I is positive or negative respectively. It is the different orientational correlation between two successive rigid cores interconnected by a flexible spacer with m even or odd, which affect intramolecular orientational order parameter of mesogenic units $\langle D_{m,n}^2 \rangle$, most significantly as follows, that results in even-odd effect in transition properties of many LCPs with flexible segment.

The calculated S_z^I of the mesogenic units are given in Table 1 where superscript I indicate the ordinal number counting from the intramolecular frame. As I increases, absolute value of S_z^I decreases and approaches zero for any m . However, when the number of methylene group m in flexible spacer becomes larger, the orientational correlation of

mesogenic units with the same l becomes weaker.

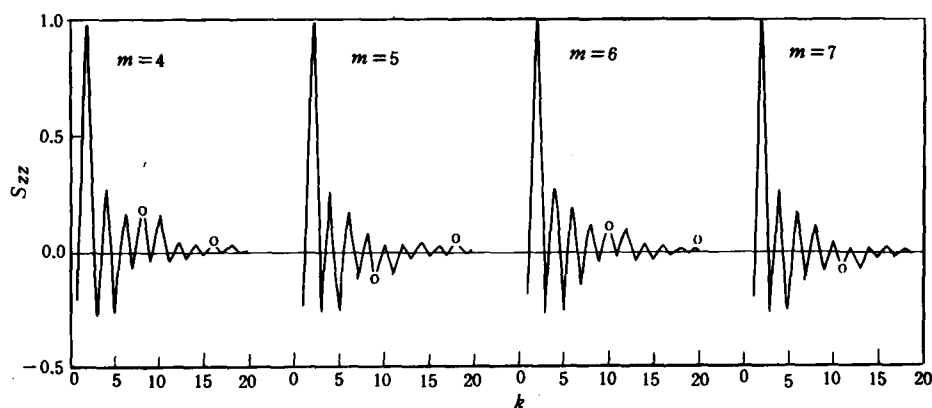


Fig. 3 Variation of S_{zz} with the k ($k=j-i$)

The circles were used for S_{zz} of mesogenic unit.

Table 1 The relationship between Saupe's ordering matrix element of mesogenic units S_z and the number of the methylene groups in flexible spacer.

m	S_z			
	$l=1$	$l=2$	$l=3$	$l=4$
4	0.166	0.028	0.005	0.001
5	-0.120	0.015	-0.002	
6	0.100	0.010	0.001	
7	-0.074	0.005		
8	0.057	0.003		
9	-0.043	0.002		
10	0.033	0.001		
11	-0.025	0.001		
12	0.019			
13	-0.015			
14	0.011			

2. Intramolecular orientational distribution

Table 1 shows that the orientation tendency of the nearest mesogenic unit is most significant among all mesogenic units within correlation length. Therefore, a close examination of intramolecular orientational distribution of the nearest rigid core is helpful to rationalize the disparity of the intramolecular orientational order parameter and the even-odd effect.

The intramolecular orientational distribution function (PDF) and the orientational distribution density (PDD) of the nearest mesogenic unit for LCPs with $m=4$ and $m=5$ are given in Fig. 4. The results lead to the following remarks: The orientations of mesogenic units in species are completely different. For polymers with $m=\text{even}$ ($m=4$), a sizable amount (31%) of units is found in a range $P_2 > 0$ ($P_2 = \{3(l_z l_z) - 1\}/2$) and most of their concentration near $P_2 = 1$. As a result of averaging, $S_{zz} = 0.166$ was given (cf. Tab. 1) and two successive mesogenic units have a tendency to be parallel with each other. In contrast

for polymers with $m=\text{odd}$ ($m=5$), a large fraction of orientation is distributed in a range $P_2 < 0$. Only small amount of orientation occur near $P_2=1$. For averaging, $S_z^1 = -0.120$ and two successive mesogenic units tend to orientate perpendicular to each other. In consequence of the disparity in the intramolecular orientational distribution, many transition properties of the LCPs exhibit even-odd effect.

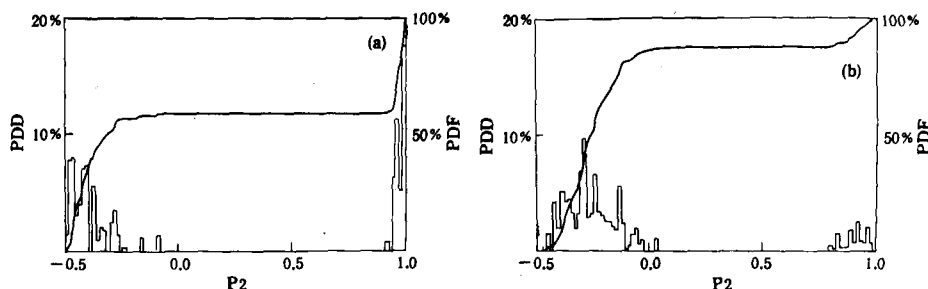


Fig. 4 The intramolecular orientational distribution function (PDF) and the orientational distribution density (PDD) of the nearest mesogenic units for LCP I with (a) $m=4$, (b) $m=5$.

3. Intramolecular orientational order parameter

Calculation of intramolecular orientational order parameter were carried out by using Eq. (23), (24) (25). Among the second rank elements, only $\langle D_{0,0}^2 \rangle$ not equal zero, i. e. the orientational distribution has a $D_{\infty h}$ symmetry.

According to their major character, the orientational units of LCPs such as (I) can be divided into two groups. One is straight rigid core called mesogenic unit and the other is chemical bond in flexible spacer. The intramolecular orientational order parameters of the two groups are expressed as $\langle D_{0,0}^2 \rangle_c$ and $\langle D_{0,0}^2 \rangle_b$, respectively. Fig. 5 indicates both of them varying with the number of methylene groups m in flexible spacer. The curves of $\langle D_{0,0}^2 \rangle_c$ and $\langle D_{0,0}^2 \rangle_b$ vs. m were found to show a significant even-odd variation.

As $S_{z,k}$ converge at zero rather rapidly, Eq. (23) can be truncated after several terms (in our calculation, the terms $S_{z,k} < 0.0005$ were truncated). The number of remaining terms after truncating is defined as the correlation length CL. The correlation length of rigid core (CL)_c decreases monotonously as m increases. (CL)_c decreases from 3 to 1 as m increases from 4 to 14. For the polymer such as (I), (CL)_c is much smaller than the number of mesogenic units in a polymer chain. In consequence, we can divide chain of LCPs into many orientational segments in which orientations of units are correlated, but the orientations of the units in different segments are rather independent with one another. It is clearly much easier to develop a molecular theory based on this understanding and enable us to solve the frustrating calculational problem

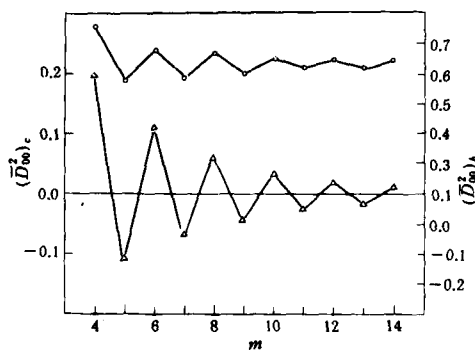


Fig. 5 The relationship between the intramolecular order parameter and the number of methylene groups m in flexible spacer. triangle and circle for core $\langle D_{0,0}^2 \rangle_c$ and bond $\langle D_{0,0}^2 \rangle_b$, respectively.

existing in many molecular theory successfully.

4. Verification and application

Although, there is no experiment that can directly measure the intramolecular orientational order parameter so far, the theory can be verified by some experimental methods. First, the geometrical parameters and data of the statistical weight matrices used in the above calculation have been used to calculate mean square end-to-end distance $\langle r^2 \rangle$, dipole moment and other physically measurable parameters. The favourable agreement between experiment and calculation have shown the reliability of the parameters^[10]. Second, the intramolecular orientational order parameter obtained above can be applied to calculate many useful parameters of LC phase such as the nematic-isotropic transition temperature, the entropy and free energy of transition, and spatial orientational order parameter etc. These parameters can be measured by experiments. Some results of experimental verification by the latter is given below.

For series of LCPs with flexible spacers, one of the most interesting and commonly found phenomena is that the nematic-isotropic transition temperature T_{NI} decreases oscillationally in even-odd sequence when m increases^[11]. The curve of $\langle D_{0,0}^2 \rangle$ vs m (cf. Fig. 5) exhibits even-odd variation of the intramolecular orientation. In consequence of this nature, the calculated T_{NI} exhibits an oscillation when plotted against m . The T_{NI} was calculated by a molecular field theory based on intramolecular orientational order parameter obtained in current paper.

Based on the model and concepts proposed above and mean field assumption, the spatial orientational order parameter of mesogenic units can be obtained as

$$\begin{aligned} \overline{C}_{2,0} = 2\pi Z^{-1} \int P_2(\cos\beta) I_0 \{ (3/8)^{1/2} b \sin^2\beta \} \\ \exp \{ a P_2(\cos\beta) \} \sin\beta d\beta \end{aligned} \quad (26)$$

$$\begin{aligned} \overline{C}_{2,2} = \overline{C}_{2,-2} = 2\pi(3/8)^{1/2} Z^{-1} \int \sin^2\beta I_1 \{ (3/8)^{1/2} b \sin^2\beta \} \\ \exp \{ a P_2(\cos\beta) \} \sin\beta d\beta \end{aligned} \quad (27)$$

where bar indicates an orientational average, $I_n(x)$ is a n th order modified Bessel function and parameters a , b are equal to $\langle X_{2,0} \rangle / kT$ and $2 \langle X_{2,2} \rangle / kT$ respectively.

$$\langle X_{2,q} \rangle = -\epsilon_\alpha \varphi_c \overline{C}_{2,0} \{ 1 + 2 \langle D_{0,q}^2 \rangle_c + 2\lambda \langle D_{0,q}^2 \rangle_b \} \quad (29)$$

where

$$\lambda = \epsilon_{bd} / \epsilon_\alpha \quad (30)$$

Eq. (26), (27) and (29), (30) were used for self-consistent calculation and the obtained orientational order parameter were used to calculate the free energy and hence nematic-isotropic transition temperature. Here we will only discuss the comparison of the results with experiments and leave the details of the theory in another paper.

The experimental data given in the literature^[9] for series of typical LCPs called 4,4'-dihydroxy-2, 2'-dimethylazoxybenzene alkanedioic acid polymers and theoretical T_{NI} vs. m curve is shown in Fig. 6. The figure leads to the following conclusion that the curve of T_{NI} vs. m successfully predicts the even-odd oscillation tendency of the phase transition. The favourable agreement between theory and experiment can be used not only to explain the inherent mechanism of even-odd effect but also to prove the reliability of the theory. The success of the theory is also demonstrated by comparison its other prediction with the

experimental results.

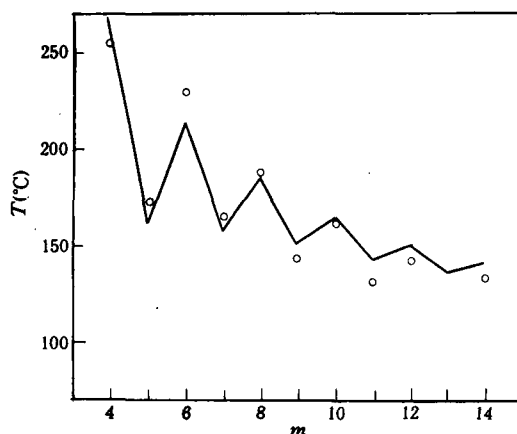


Fig. 6 The variation of the nematic-isotropic transition temperature with the number of methylene groups in flexible spacer m . Experiment: circle, Theoretical prediction: solid line.

Keywords:

Liquid crystal polymer; Intramolecular orientation; order parameter; Theory.

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