

MOLECULAR FIELD THEORY FOR NEMATIC LIQUID CRYSTAL POLYMER COMPRISING FLEXIBLE SPACER

WANG Xiaogong (王晓工) LIU Deshan (刘德山) and ZHOU Qixiang (周其庠)

(Department of Chemical Engineering, Tsinghua University, Beijing, 100084)

ABSTRACT

Based on the new model and concept of intramolecular orientational order parameter, a molecular field theory was built up for main chain liquid crystalline polymer (MC-LCPs) with flexible spacers. The theory takes account of orientational correlation among all mesogens in a polymer chain and the relationship between the intramolecular orientation and spatial orientation of the mesogens. The free energy, temperature and entropy of the nematic-isotropic transition were determined with the theory and compared with experiments in current work. It was found that many unique transition properties of the MC-LCPs comprising flexible spacer are correctly predicted by the theory and the agreement of the theory with the experiments is impressive.

INTRODUCTION

The thermotropic liquid crystal polymers comprising a rigid core segment and a flexible spacer in each repeating unit have been actively studied during last one or two decades^[1, 2]. Roviello and Sirigu reported their success in preparing the first academic example of LCP with flexible spacer by the reaction of *p, p'*-dihydroxy- α, α' -dimethyl benzalazine and acyl chloride^[3]. Since then, many LCPs with flexible spacers have been successfully developed and their liquid crystalline behaviors have been thoroughly investigated^[4-8]. The liquid crystalline properties of these materials are found to depend critically on the length of the alkyl chain. Two significant effects have been observed and reported: First, an even-odd zig-zag manner occurred for their isotropic transition temperature and entropy. Second, a change in the micromolecular packing structure.

In order to explain the above phenomena, a variety of explanations have been proposed. Any molecular theory of such liquid crystal polymer must allow specifically for the effects of the flexible spacer. The first attempt to develop a theory for non-rigid molecule was made by Marcelja who extended the Maier-Saupe theory for nematic composed of low molecular weight mesogen with flexible tails^[9]. After that, several prominent papers on the research field have been published. Luckhurst put forward a successful molecular field theory for the α, ω -bis (4,4'-cyanobiphenyloxy) alkanes with the length of the flexible spacer^[10]. However, the task to extend the molecular theory for these model compounds to real polymers is formidable owing to the existence of an astronomical amount of possible conformations in polymer chain. In another paper, Abe extended and modified the Flory-Ronca theory, and calculated the degree of order *S* as

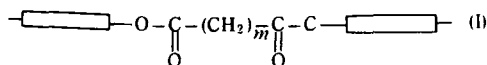
a function of the number of methylene units^[11]. But in his paper, only the angle between two successive rigid cores was considered and the *S* was directly obtained from the angle without considering the difference between intermolecular orientation and intramolecular orientation. Obviously, more detailed theoretical analysis is required in order to understand the orientational correlation among all mesogenic units in LCP chain and to elucidate more reasonably the effects such as the even-odd oscillation of isotropic transition properties on the basis.

In this study, the orientational correlation among rigid cores interconnected by flexible spacers was completely described by the model and concepts called intramolecular orientation and intramolecular orientational order parameter proposed by Wang et al. in current published paper^[12]. On the basis, a molecular field theory was built up by which the free energy and hence the nematic-isotropic transition temperature as well as the entropy of transition can be determined theoretically. With the theory, the relationship of these transitional properties with the length of the flexible spacer can be predicted in quite good agreement for the behavior of LCPs such as 4,4'-dihydroxy-2,2'-methylazoxybenzene-alkanedioic acid polymers. Intramolecular orientation of rigid cores depends strongly on the *trans* and *gauche* conformation, which results in even-odd effect in many transitional properties. The mathematical details of the theory are also given in the following discussion.

THEORY

1. Orientational energy

The liquid crystal polymers including flexible spacers (cf. LCPs II, III, IV following) can be drawn schematically as



where the rectangles on both sides indicate rigid cores (typically, including several aromatic rings). The LCPs are depicted as a sequence of vectors for conformation analysis (Fig. 1). Every mesogenic unit which is a straight rigid core extending between two ester oxygen, is regarded as an orientational unit for its rigidity and represented by a longer vector. For the same reason, every chemical bond in flexible spacer is also regarded as an orientational unit and described by a shorter vector. Intramolecular orientational distribution, which reflects the orientational fluctuations of units with respect to an intramolecular frame, can be expressed by Saupe ordering matrix $S_{\alpha\beta}$ and the

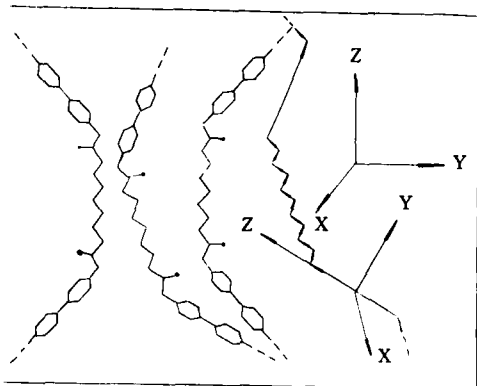


Fig.1 Schematic diagram of chain segment comprising rigid cores interconnected with flexible spacer and a sequence of vectors used for representing orientational units.

intramolecular orientational order parameter $\langle D_{m,n}^L \rangle$ [12]

$$S_{\alpha\beta} = \sum_{k=1} (3 \langle l_{\alpha} l_{\beta} \rangle_k - \delta_{\alpha\beta}) / 2 \quad (1)$$

$$\langle D_{0,0}^2 \rangle = S_{zz} \quad (2)$$

$$\langle D_{0,2}^2 \rangle = (S_{xx} - S_{yy}) / \sqrt{6} \quad (3)$$

where $(l_{\alpha})_k$ ($\alpha = x, y, z$) is the direction cosines of orientational unit j with respect to an intramolecular frame fixed on i th unit and $k = j - i$, $\delta_{\alpha\beta}$ is the Kronecker delta.

By means of the molecular field approximation, the potential of mean torque for j orientational unit $U(\Omega_j)$ can be expanded in a set of second rank modified spherical harmonics $C_{2,-r}(\Omega_j)$ [13]

$$U(\Omega_j) = - \sum_r (-1)^r X_{2,r}^j C_{2,-r}(\Omega_j) \quad (4)$$

($r = -2, \dots, 2$)

The expansion coefficients $X_{2,r}^j$ are components of irreducible spherical tensors whose magnitudes depend on factors such as the orientational order, the molecular distribution and the anisotropic molecular interactions. Ω_j denotes the spherical polar coordinates for the director in the local frame set in the j th orientational unit (cf. Fig. 2). However, the equation is adequate only for the orientational units that are independent of neighbour units in orientation direction. For the LCPs mentioned above, the orientations of the mesogens on the same polymer chain are obviously correlated with each other. Therefore, more sophisticated theoretical analysis is needed.

By fixing the intramolecular frame on any mesogenic unit chosen for discussion and defining its ordinal number as 0, the general expression of the orientational potential of the unit can be deduced as follows.

Obviously, the unit also undergoes a potential of mean torque as Eq. (4)

$$U(\Omega_0) = - \sum_r (-1)^r X_{2,r}^0 C_{2,-r}(\Omega_0) \quad (5)$$

But, when the spherical polar angle of the unit 0 is Ω_0 , the spherical polar coordinates of its neighbouring units must satisfy the relation

$$C_{2,-r}(\Omega_j) = \sum_q D_{-q,-r}^2(\omega_{j,0}) C_{2,-q}(\Omega_0) \quad (6)$$

where $D_{-q,-r}^2$ is a Wigner rotation matrix used for transforming of the frame set in 0th orientational unit to the frame set in j th unit and $\omega_{j,0}$ stands for three Euler angles between two frames. $D_{-q,-r}^2(\omega_{j,0})$ depends on the bond angle and the conformation of each chemical bond in the segment between the 0th and j th units. Therefore, the total orientational potential of unit 0 must include all the anisotropic interaction of neighbouring units in mean field and equal to

$$U_{on}(\Omega, \{\omega\}) = \sum_j U(\Omega_j) \quad (7)$$

Combining Eq. (4)–(7), given

$$\begin{aligned}
 U_{\text{ori}}(\Omega, \{\omega\}) &= - \sum_j \sum_r (-1)^j X_{2,r}^j \sum_q D_{-q,-r}^2(\omega_{j,0}) C_{2,-q}(\Omega_0) \\
 &= - \sum_q (-1)^q X_{2,q} C_{2,-q}(\Omega_0)
 \end{aligned} \quad (8)$$

where

$$\begin{aligned}
 X_{2,q} &= \sum_j \sum_r (-1)^{r-q} D_{-q,-r}^2(\omega_{j,0}) X_{2,r}^j \\
 &= \sum_j \sum_r D_{r,q}^2(\omega_{0,j}) X_{2,r}^j
 \end{aligned} \quad (9)$$

where the summation for r, q is restricted to the second-rank term and j includes all units in intramolecular orientation correlation length^[12]. Eq (9) give the expression of total interaction tensor of unit 0 which is related to the tensors $X_{2,r}^j$ of every units in correlation length.

For further simplification, the orientation units of LCP I are classified into two kinds. One is the mesogen or core unit whose components of irreducible spherical tensor are expressed by $X_{2,r}^c$, and the other is the chemical bond in flexible spacers whose tensor components are expressed as $X_{2,r}^b$. Then

$$X_{2,q} = \sum_r \left\{ \sum_{jc} D_{r,q}^2(\omega_{0,jc}) \right\} X_{2,r}^c + \sum_r \left\{ \sum_{jb} D_{r,q}^2(\omega_{0,jb}) \right\} X_{2,r}^b \quad (10)$$

where, in difference with j, jc and jb count core and bond units respectively. Since $D_{r,q}^2(\omega_{0,jc})$ and $D_{r,q}^2(\omega_{0,jb})$ are conformationally dependent, by averaging all conformations over the segment between every jc, jb and 0, Eq. 10 can be deduced to

$$\langle X_{2,q} \rangle = \sum_r \{1 + 2 \langle D_{r,q}^2 \rangle_c\} X_{2,r}^c + 2 \sum_r \langle D_{r,q}^2 \rangle_b X_{2,r}^b \quad (11)$$

where $\langle D_{r,q}^2 \rangle_c = \sum_{jc \geq 1} \langle D_{r,q}^2(\omega_{0,jc}) \rangle$ and

$\langle D_{r,q}^2 \rangle_b = \sum_{jb \geq 1} \langle D_{r,q}^2(\omega_{0,jb}) \rangle$ are the

intramolecular orientational order parameter for rigid core and bond respectively as defined in our previous paper^[12]. Angular brackets are used here to denote a conformational average.

If orientational unit with cylindrical symmetry, Eq.(11) can be further simplified to

$$\begin{aligned}
 \langle X_{2,q} \rangle &= \{1 + 2 \langle D_{0,q}^2 \rangle_c\} X_{2,0}^c \\
 &\quad + 2 \langle D_{0,q}^2 \rangle_b X_{2,0}^b
 \end{aligned} \quad (12)$$

The interaction tensor can be diagonalized and its principal axis system used as a reference frame to describe the orientation of the director. The potential of mean torques

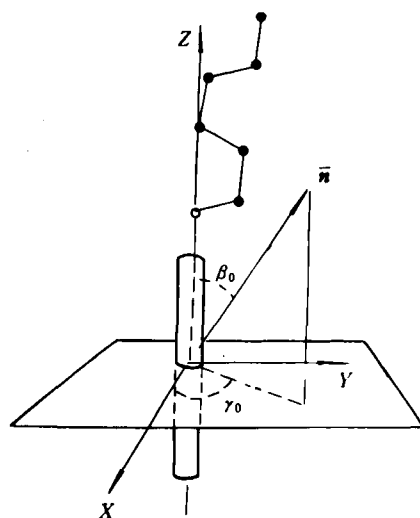


Fig.2 The reference frame set on a mesogen which is used to define the orientation of the director.

can finally be reduced to

$$U_{\text{on}}(\Omega_0) = - \left\{ \langle X_{2,0} \rangle P_2(\cos\beta_0) + \langle X_{2,2} \rangle \left(\frac{3}{2} \right)^{1/2} \sin^2\beta_0 \cos 2\gamma_0 \right\} \quad (13)$$

β_0 , γ_0 are the spherical polar coordinates for the director in the reference frame (cf. Fig. 2) and $P_2(\cos\beta_0)$ is the second Legendre polynomial. Since the mesogenic unit is arbitrarily selected, the above relation is a general one which is suitable for any mesogenic unit in LCP chain and the subscript 0 can be omitted.

2. Spatial orientation distribution function and order parameter

The normalized probability of finding the director in an orientation with the reference frame defined above is

$$f(\Omega) = (1/Z) \cdot \exp \{ -U_{\text{on}}(\Omega)/kT \} \quad (14)$$

$$Z = \int \exp \{ -U_{\text{on}}(\Omega)/kT \} d\Omega \quad (15)$$

Substituting Eq. (13) in equation above, the spatial orientational order parameters that are the ensemble average of second-rank spherical harmonic function are given by

$$\begin{aligned} \overline{C}_{2,0} &= 2\pi Z^{-1} \int P_2(\cos\beta) I_0 \{ (3/8)^{1/2} b \sin^2\beta \} \\ &\quad \exp \{ a P_2(\cos\beta) \} \sin\beta d\beta \end{aligned} \quad (16)$$

$$\begin{aligned} \overline{C}_{2,2} = \overline{C}_{2,-2} &= 2\pi (3/8)^{1/2} Z^{-1} \int \sin^2\beta I_1 \{ (3/8)^{1/2} b \sin^2\beta \} \\ &\quad \exp \{ a P_2(\cos\beta) \} \sin\beta d\beta \end{aligned} \quad (17)$$

where bar indicate an orientational average, $I_n(x)$ is an 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.

3. Method of calculation

If the mesophase contains a mixture of different rod-like particles then the molecular field experienced by one particle will depend both on the order parameters for each species as well as the strength of the anisotropic intermolecular interactions and the composition. It seems reasonable to treat LCPs comprising rigid core segments and flexible spacers as a mixture of core and bond segments. The similar assumption has been adopted as a common practice in previous work^[9,10]. For cylindrical symmetrical particles, we obtain

$$X_{2,0}^c = -\varepsilon_{cc} \overline{C}_{2,0}^c \varphi_c - \varepsilon_{cb} \overline{C}_{2,0}^b \varphi_b \quad (18)$$

$$X_{2,0}^b = -\varepsilon_{bc} \overline{C}_{2,0}^c \varphi_c - \varepsilon_{bb} \overline{C}_{2,0}^b \varphi_b \quad (19)$$

where force parameters ε_{cc} etc. are determined by the average anisotropic interaction between two species. φ_c and φ_b are the volume fraction of the core and the flexible segment. $\overline{C}_{2,0}^c$ and $\overline{C}_{2,0}^b$ are the spatial orientational order parameter of the rigid core and the bond unit in flexible spacer, which is defined by Eq. (16), (17) separately for the core and the bond.

Because the anisotropic interaction between molecules of flexible chain polymers such as polyethylene is too weak to maintain a mesophase above its melting point, it is reliable to believe that the force parameter ε_{cc} should be much larger than ε_{bb} and ε_{bc} , ε_{cb} are between them. Also, $C_{2,0}^c$ is larger than $C_{2,0}^b$. Therefore, as a first order approximation, Eq.(18) and (19) can be further reduced to

$$X_{2,0}^c = -\varepsilon_{cc} \varphi_c \overline{C}_{2,0}^c \quad (20)$$

$$X_{2,0}^b = -\varepsilon_{bc} \varphi_c \overline{C}_{2,0}^c \quad (21)$$

substituting above equations into Eq.(12), then

$$\langle X_{2,q} \rangle = -\varepsilon_{cc} \varphi_c \overline{C}_{2,0}^c \{1 + 2 \langle D_{0,q}^2 \rangle_c + 2\lambda \langle D_{0,q}^2 \rangle_b\} \quad (22)$$

where

$$\lambda = \varepsilon_{bc} / \varepsilon_{cc} \quad (23)$$

Eq.(16), (17) and (20), (22), (23) (or (18) and (19)) were used for self-consistent calculation, some results are given as follows.

RESULTS AND DISCUSSION

1. Spatial orientational order parameter of mesogen

Typical series of LCPs including flexible spacer represented by (I) are chosen for calculation. Intramolecular orientational order parameters of the LCPs are presented in Table 1 which were estimated with the method described in our previous paper^[12]. In order to investigate its variation following the temperature, the intramolecular order parameters under different temperatures were calculated. The results are that the intramolecular orientational order parameter is insensitive to temperature in some range. Considering the relatively high isotropic transition temperatures of these polymers, statistical weight matrices were calculated at the temperature 523.16K.

The spatial orientational order parameters of the LCPs were calculated by the procedure mentioned above. It was found that the only nontrivial component among them is $\overline{C}_{2,0}$ which is written as $\overline{P}_2$ in accordance with convention. Fig.3 and 4 indicate the results for polymers with different number of methylene groups m in the flexible spacer. The curves of $\overline{P}_2$ vs. temperature T include three range. Among them, the range I corresponds to the mesophase, in which mesogen tend to be parallel to a unique direction known as director. As the temperature increasing, the orientational order parameters which reflect the spatial orientation of mesogen with respect to the director decrease. In range II, the curve of $\overline{P}_2$ vs. T undergoes an abrupt decrease, which is related to a first order phase transition called isotropic transition. The range III in which $\overline{P}_2$ approximates zero corresponds to isotropic phase. The tendency and extent of the calculated variation are found in good agreement with experiment data of deuterium NMR spectroscopy^[7]. The differences among various mesogens depend on ε_{cc} .

When the number of methylene groups m in the flexible spacer varies from 4 to 14, the curves of $\overline{P}_2$ vs. T maintain the same tendency as such described above and also include three ranges. But for different length of flexible spacer, the absolute position of three ranges of the curves are changed significantly. In

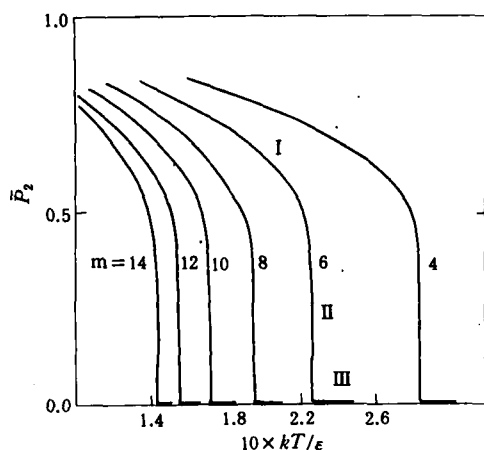


Fig.3 The dependence of the order parameter $\overline{P}_2$ of LCPs with even number of methylene groups in flexible spacer, on the reduced temperature.

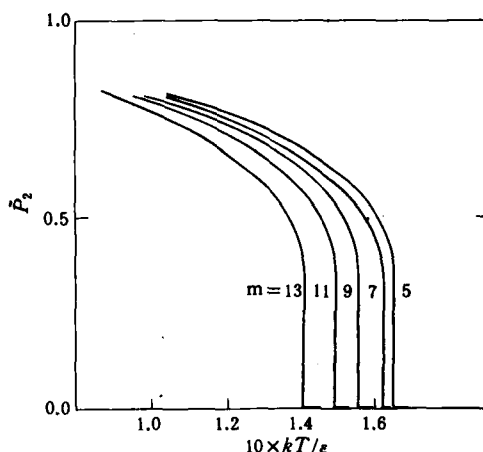


Fig.4 The dependence of the order parameter $\overline{P}_2$ of LCPs with odd number of methylene groups in flexible spacer, on the reduced temperature.

other word, for the same temperature, the spatial orientational order parameter $\overline{P}_2$ changes as m varying. By close examination of Tab.1, Fig.3 and Fig.4, the follows can be proposed reasonably: it is the even-odd oscillation of intramolecular orientational order parameter, which results from conformation variation of the flexible spacer, that results in the change in the mesogen spatial orientation. In consequence of the variation in microscopic packing structure, many transition properties exhibit even-odd zigzag manner when plotted against m .

Table 1 The intramolecular orientational order parameter used in calculation.

m	$\langle D_{0,0}^2 \rangle_c$	$\langle D_{0,0}^2 \rangle_b$
4	0.198	0.756
5	-0.108	0.576
6	0.111	0.675
7	-0.068	0.588
8	0.060	0.672
9	-0.042	0.600
10	0.034	0.650
11	-0.025	0.621
12	0.019	0.644
13	-0.015	0.616
14	0.011	0.644

2. Thermodynamic criterion of isotropic transition

In order to determine the nematic-isotropic transition temperature T_{NI} , the Helmholtz free energies for both nematic and isotropic phase are required because at transition those free energies must be equal.

The Helmholtz free energy for nematic phase can be approximated by

$$A_N = A_{on} + \Delta A_{on} + A_{int} + \Delta A_{int} \quad (24)$$

where A_{int} is identified as the intramolecular free energy resulting from intramolecular interactions such as the potential and the entropy of bond rotation, and A_{on} is the orientational free energy which comes from the averaged anisotropic intermolecular interaction as given above. The spatial orientation of the orientational units cause the statistical weights of conformation differ from their values in the isotropic phase. The proportion of the conformation corresponding a higher intramolecular orientational order will be enhanced. In other words, molecule will become more straight in mesophase and favourable for spatial orientation. Therefore, A_{on} will obtain a negative increment ΔA_{on} . Meanwhile, the restriction put on molecule spatial configuration by anisotropic phase causes a positive increment ΔA_{int} . In equilibrium, both increments should obey

$$\Delta A_{\text{on}} = -\Delta A_{\text{int}} \quad (25)$$

Then Eq. (24) is reduced to

$$A_{\text{N}} = A_{\text{on}} + A_{\text{int}} \quad (26)$$

Therefore the criterion of isotropic transition can be written as

$$A_{\text{N}} - A_{\text{I}} = A_{\text{on}}^{\text{NI}} = 0 \quad (27)$$

The Helmholtz free energy of N independent particles is obtained from the single particle partition function Z via

$$A = -NkT \ln Z \quad (28)$$

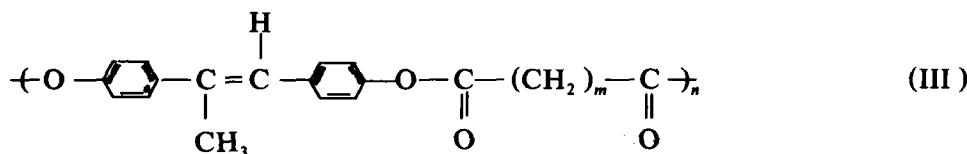
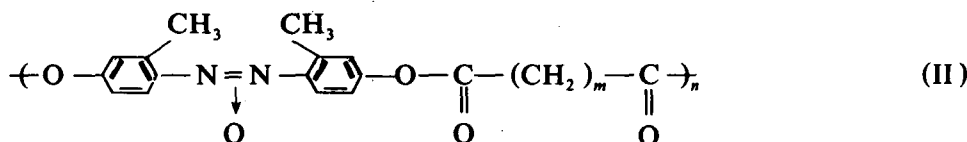
The equation should be modified in mean field calculation because particles both generate and experience the molecular field. Therefore, the thermodynamic internal energy caused by molecular interaction is counted twice in this case^[13]. Then the correct expression of the Helmholtz free energy for phase transition is

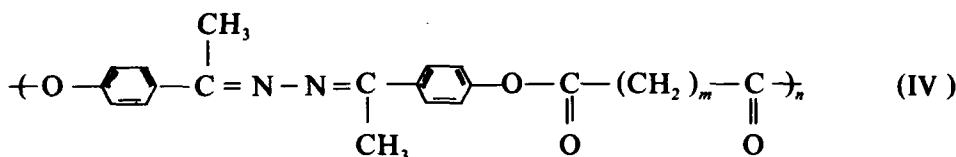
$$A_{\text{on}}^{\text{NI}} = -NkT \ln Z_{\text{on}}^{\text{NI}} + N \langle U_{\text{on}}^{\text{NI}} \rangle / 2 \quad (29)$$

where the factor of 1/2 corrects for the over-counting of the molecular interaction. $\langle U_{\text{on}}^{\text{NI}} \rangle$ is obtain from Eq. (13), (14) and (15).

3. Isotropic transition temperature T_{NI}

The nematic-isotropic transition temperature is one of the most important and most commonly measured properties of nematic liquid crystal. It was found in many laboratories that LCPs with the even number of methylene groups ($m=\text{even}$) in flexible spacer showed higher isotropic transition temperatures T_{NI} than those of the immediate neighbours with $m=\text{odd}$ and the oscillation damped with increasing length of the flexible spacer. It is a well-known phenomenon called even-odd effect. One of our main objectives is to predict how T_{NI} varies with the length of the flexible spacer and to compare with the experiments. The LCPs chosen for calculation are





The interaction tensors given in Eq. (22) were used in calculation, in which φ_c is evaluated from several similar small molecules^[9]. $\lambda = \epsilon_{bc}/\epsilon_{cc}$ is treated as an adjustable parameter. As the core-core interaction parameter is to be expected larger than that for bond-core parameter, λ is less than unit and its magnitude was adjusted for different mesogenic units in the LCPs to optimize the agreement with the variation of T_{NI} observed for a homologous series.

It was found (cf. Fig. 3 and Fig. 4) that T_{NI} have a very similar variation tendency comparing with T_{NI} from experiments for a homologous series of LCPs with different lengths of the alkyl chain. In order to compare with experiment directly, it is need to specify ϵ_{cc} that is the interaction parameter between rigid cores. As a large alternation in the transition temperature and a quick damp of T_{NI} with m increasing were found, which in contrast with the behaviour of low molecular weight LC molecules containing a single rigid core and flexible tails, the variation of ϵ_{cc} with temperature must be concerned. We have made further approximation by assuming that ϵ_{cc} is in proportion to the inverse of T^* ($T^* = kT/\epsilon_{cc}$) as

$$\epsilon_{cc} = \epsilon_{cc}^0 + \epsilon_{cc}^1/T^* \quad (30)$$

The equation resembles to the expression $\epsilon = \epsilon^0 V^{-7}$ which is commonly used in many molecular field calculations^[13]. The two parameters ϵ_{cc}^0 , ϵ_{cc}^1 , which depend on the type of mesogen, have been applied to scale the calculated transition temperature and hence optimizes the agreement with the variation of T_{NI} observed for a homologous series.

Calculated results for three typical series of LCPs (II), (III), (IV) are shown in Fig. (5), (6) and (7) where the experimental data are from the literature^[7,8] and

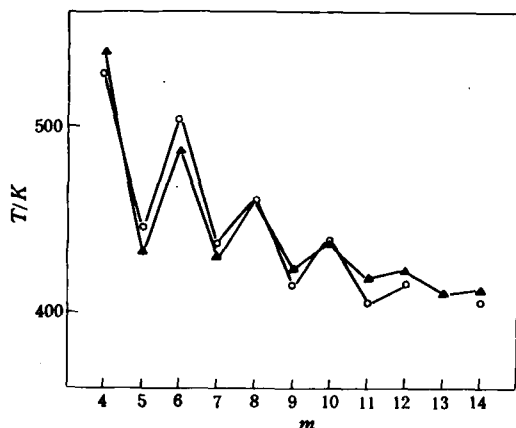


Fig. 5 The variation of the isotropic transition temperature T_{NI} with the number of methylene groups in the flexible spacer for LCPs II.

Circle for exp. Triangle for calcd.

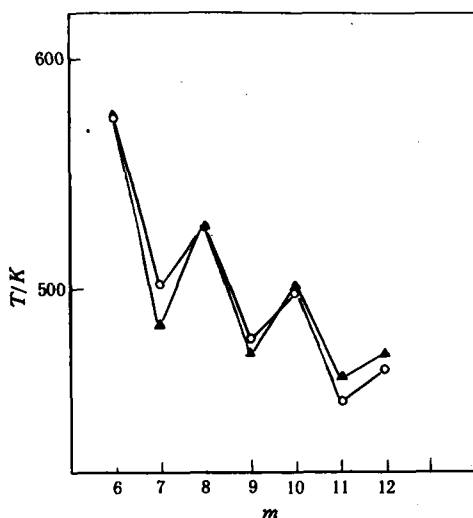


Fig.6 The variation of the isotropic transition temperature with the number of methylene groups in the flexible spacer for LCPs III. Circle for exp. Triangle for calcd.

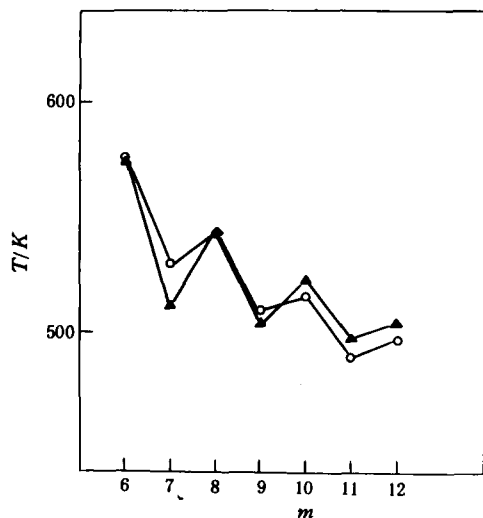


Fig.7 The variation of the isotropic transition temperature with the number of methylene groups in the flexible spacer for LCPs IV. Circle for exp. Triangle for calcd.

$\lambda, \epsilon_{cc}^0, \epsilon_{cc}^1$ are chosen values 0.3, 871.8k, 283.8k; 0.3, 1398.2k, 243.3k; 0.2, 1036.2k, 350.3k for II, III, IV respectively (k is Boltzman constant).

For such complicated systems, the agreement of theory with the experiment is impressive especially when several vital simplifications have been made in the above calculation. The observed strong oscillation in isotropic transition temperature and the damp of this alternation with increasing length of the flexible spacer are correctly predicted by the theory and the numerical data of both is also in good agreement.

To complete this paper, the conclusion can be drawn through above discussion that the theory provides a reasonable account of the relationship between intramolecular orientation and spatial orientation of mesogens in LCPs comprising a rigid core and a flexible spacer in each repeating unit. On the basis, many unique transition properties of the LCPs can be well explained and a favourable agreement of theory with experiment has been found.

Keywords :

New molecular field theory ; Nematic liquid crystal polymer ; Flexible spacer

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