

비키랄성 강전성 고분자 액정의 Monte Carlo 시뮬레이션

류 주 환

충남대학교 공과대학 고분자공학과
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Monte Carlo Simulation of Nonchiral Ferroelectric Polymer Liquid Crystals

Juwhan Liu

Dept. of Polymer Science and Engineering, Chungnam National University,
220 Gung-dong, Youseong-ku, Taejon 305-764, Korea
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요약 : 비키랄성이면서도 강전성을 나타낼 수 있는 분자 시스템들이 제안되어 있는 바, 그 중 한 시스템에 대하여 Monte Carlo 모사를 통하여 전이 현상을 규명하였다. 여기서 각각의 분자는 막대 모양 부분들과 유연 사슬 부분들의 조합으로 이루어져 있다. 모사에는 분자들이 한쪽 방향으로만 움직일 수 있는 준격자 모델이 사용되었다. 분자들의 자발적인 극성 정렬화는 화학적 성질이 다른 부분들이 각각 분리하려는 성질에 기인한다고 가정하였다. 두 개의 전이가 확인되었으며 그것들의 성격이 온도에 따른 에너지, 열용량, 스멕틱 오더 파라미터, 극성 오더 파라미터, 그리고 오더 파라미터들의 요동 등의 거동으로부터 규명되었다. 그 결과 저온 측에서 일어나는 전이는 극성-비극성 전이이며, 반면 고온 측에서 일어나는 전이는 스멕틱-네마틱 전이임이 밝혀졌다.

Abstract : Monte Carlo simulation was performed for the characterization of transition phenomena involved in a nonchiral molecular system exhibiting the ferroelectricity. In this system, each molecule is consisted of a combination of rigid and flexible moieties. In the simulation, a quasi-lattice model was used in which molecules move in one direction only. The driving force for the spontaneous polar ordering of molecules was assumed to arise from the tendency of chemically distinct moieties to segregate. Two transitions have been identified and their nature was characterized through the use of temperature behavior of energy, heat capacity, smectic order parameters, polarity order parameter, and fluctuations of the order parameters, and so on. As a result, the transition that occurred at a lower temperature was due to the polar to nonpolar transition, while the transition at a higher temperature was found to be the smectic to nematic transition.

Keywords : ferroelectric, nonchiral, Monte Carlo simulation, transition phenomena.

INTRODUCTION

Ferroelectrics are the substances that in a certain temperature interval have a permanent spontaneous electric polarization which is reversible or reorientable by an external electric field or external stress.¹ They can ex-

hibit piezoelectric effect, large electro-optical effect (i.e., birefringence induced by an electric field), refractive index change by light, strong pyroelectric effect (i.e., strong temperature dependence of the spontaneous polarization), and so on. Hence ferroelectric materials can be used as electromechanical transducers,

light modulators, optical information storage, real time optical processors, thermal and infrared sensors, etc. Among non-liquid crystal polymeric materials, polyvinylidene fluoride and some of its copolymers exhibit ferroelectric behavior.^{2, 3} On the other hand, owing to the existence of various types of low molecular weight liquid crystalline substances which exhibit ferroelectricity, several polymeric liquid crystalline ferroelectrics have been synthesized where mesogenes are attached to flexible chains via flexible spacers.⁴

Though it was first shown that dipolar ordering should arise in smectic C or H phases of liquid crystals which consist of optically active(chiral) molecules, i.e. in S_C^* or S_H^* phases,⁵ it is also possible that spontaneous polarization arise in any other system having a layered structure, tilt, and chirality of the constituent molecules. Furthermore, it was proposed that certain "nonchiral" molecular architectures such as disk-shaped molecules, bowl-shaped molecules, and "fraternal-twin"

liquid crystal molecules may be capable of forming ferroelectric liquid crystalline phases.^{6,7} The basic idea in ref. 6 is to form a fraternal-twin type ferroelectric smectic A phase as shown in Fig. 1. In detail, it is suggested that if a layered phase with three or more sublayers, e.g., A, B, and C, is formed in such a way that the layers occur in an ordered fashion throughout the system, and if the middle layer (B) contains a dipole pointing toward the A layer, then the system would be ferroelectric.

In this study, a simple quasi-lattice model was applied to test the feasibility of the ferroelectric smectic A phase. Specifically we investigated the possibility of nematic to smectic phase transition and characterized the nature of the transition. Initially, low molecular weight substances of a combination of rigid and flexible moieties were subjected to the simulation, with the notion that, in the first approximation, the side chain liquid crystalline polymers can be expected to behave in a similar fashion. All the simulation and analysis programs were written in FORTRAN77 for a VAX 6610 computer.

METHOD

Various types of structures for the molecules can be considered; one of the simplest cases is a molecule with a rigid moiety and two flexible moieties attached to it. However, this type of molecule will show little differences in interaction characteristics whether it is inverted or not. For the ferroelectricity, the molecule should attain the sense of direction as depicted in Fig. 1. Hence, we considered a structure with two rigid moieties with different interaction characteristics and three flexible chains as shown in Fig. 2. Here, the rigid moieties R_1 and R_2 are represented by blocks with lengths l_{R1} and l_{R2} , respectively. On the other hand, the flexible moieties A_1 ,

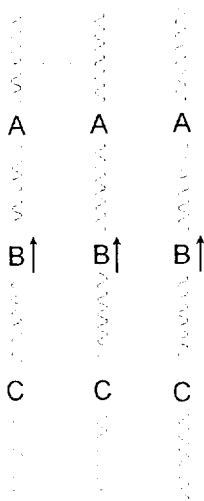


Fig. 1. Layered structure for a "fraternal-twin" type nonchiral molecular architecture. When moiety B contains a dipole moment represented by an arrow, ferroelectricity can be achieved.

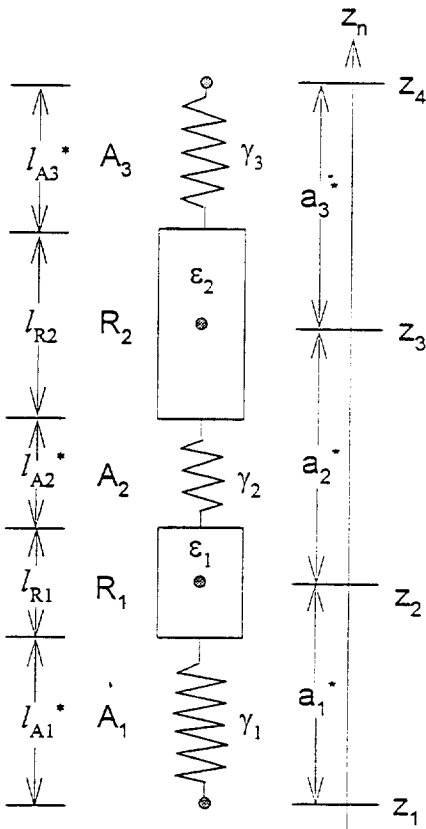


Fig. 2. A molecular structure with two rigid (R_1 , R_2) and three flexible (A_1, A_2, A_3) moieties. * means that the lengths are those at equilibrium, respectively. z : positions of sites; l : lengths of the moieties; a : separations between sites; γ : spring constants of the flexible moieties; ϵ : overlap interaction parameters.

A_2 , and A_3 are represented by springs with equilibrium lengths l_{A1} , l_{A2} , and l_{A3} , respectively.

As for the lattice model, all the other aspects irrelevant to the study of nematic to smectic transition were neglected. As a result, hexagonal lattices with a number of layers were implemented to accommodate the packing typical to smectics with in-plane order (see Fig. 3). Each n_z molecules are placed at each of the $n_x \times n_y$ hexagonal lattice points.

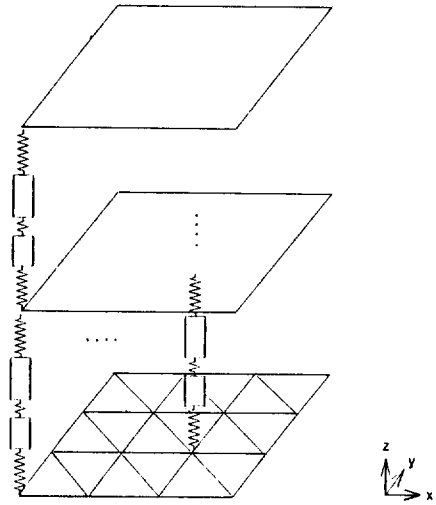


Fig. 3. A quasi-lattice model for nonchiral ferroelectrics.

So the total number of molecules in the lattice, N , is given by $n_x \times n_y \times n_z$. The molecules are allowed to move only in the direction normal to the layer planes (z); hence the term quasi-lattice is used throughout the paper. As a consequence, the system is already in nematic state.

The driving force to form smectic states from nematic states is the tendency of chemically distinct moieties to segregate. Thus, for the molecular architecture under consideration, it is appropriate to impose some type of energetic penalty when an overlap occurs between the rigid moieties and the flexible moieties. The total internal energy of the system, E , is considered to be made up of two parts, intramolecular energy, E_{intra} , and intermolecular energy, E_{inter} :

$$E = E_{intra} + E_{inter} \quad (1)$$

E_{intra} is assumed to result from the spring energies of the flexible moieties that are characterized by spring constants ($\gamma_1, \gamma_2, \gamma_3$):

$$E_{\text{intra}} = \frac{1}{2} \sum_i \sum_{v=1}^3 \gamma_v (z_{i,v+1} - z_{i,v} - a_v)^2 \quad (2)$$

where $z_{i,v}$ is the position of the v -th site of the i -th molecule and a_v is the equilibrium separation between the sites, i.e.,

$$\begin{aligned} a_1 &= l_{A1} + l_{R1}/2 \\ a_2 &= l_{R1}/2 + l_{A2} + l_{R2}/2 \\ a_3 &= l_{R2}/2 + l_{A3} \end{aligned} \quad (3)$$

On the other hand, E_{inter} is assumed to result from the overlap energy between rigid and flexible moieties. Since the three flexible moieties will exhibit more or less the same extent of overlap energy with a given rigid moiety, and since there are two kinds of rigid moieties, the overlap energy can be characterized by two interaction parameters ϵ_1 and ϵ_2 . An example is shown in Fig. 4. For a given molecule, there are six neighbors corresponding to the hexagonal lattice and all the overlaps are accounted in E_{inter} . As usual, periodic boundary conditions were applied to overcome the limitation due to the finite lattice size.

The molecules were randomly chosen in sequence and one of the three kinds of trial moves of translation, distortion, and inversion was made. Translation involves the movement of the chosen molecule as a whole along the z direction. Distortion means the movement of a site of the chosen molecule, while in inversion, the whole molecule is inverted about the geometric center of the molecule. In view of Fig. 2, the latter is equivalent to exchanging the sites corresponding to z_1 and z_4 . In the case of translation and distortion, movements by random fractions (f_{trans} and f_{site} ; between 0.0 and 1.0) of the maximum allowable movements defined initially (Δ_{trans} and Δ_{site}) were made respectively. A trial move that violates the hard-core interaction is rejected at once. When the hard-core interaction is not

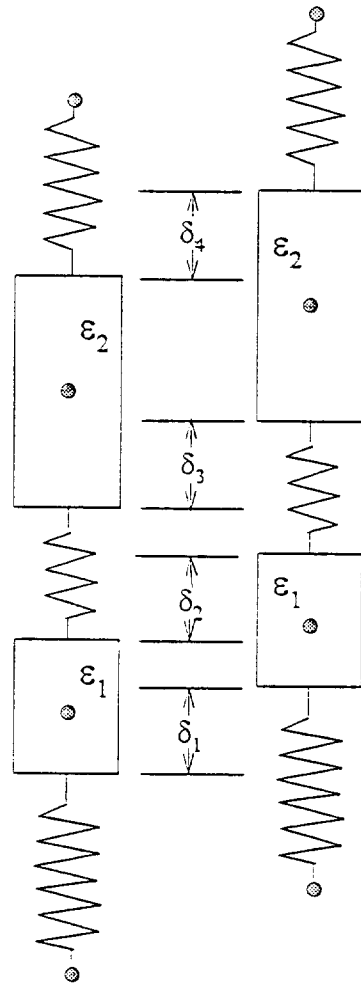


Fig. 4. The intermolecular energy contribution is assumed to be proportional to the extent of overlap between the rigid and flexible moieties. Here, it is given by $E_{\text{inter}} = \epsilon_1 \cdot \delta_1 + \epsilon_1 \cdot \delta_2 + \epsilon_2 \cdot \delta_3 + \epsilon_2 \cdot \delta_4$.

violated, the accompanying change in internal energy, ΔE , is calculated to decide, according to the Metropolis scheme,⁹ whether or not to accept the trial move based on the quantity of $\exp(-\Delta E/kT)$ in which T is the absolute temperature. A Monte Carlo (MC) cycle is completed when all the molecules are covered in this way. The sum of the energy changes accompanying the accepted trial moves com-

prises the energy of the system for the current MC cycle. Finally, after E reaches an equilibrium after sufficient iterations of MC cycles, various quantities are calculated based on the energy as well as the molecular geometry of the system. They include the average internal energy, specific heat, various scattering factors for rigid centers and molecular centers, and smecticity, and they will be described below.

In order to facilitate the simulation, a scheme regarding Δ_{trans} and Δ_{site} was devised in current study. The scheme involves updating Δ_{trans} and Δ_{site} at some intervals of MC cycles. First the success rate, f_{suc} , was calculated as the ratio of the number of trial moves that were successfully carried out to the total number of trials. Then Δ_{trans} and Δ_{site} values were replaced by $2\Delta_{\text{trans}} \cdot f_{\text{suc}}$ and $2\Delta_{\text{site}} \cdot f_{\text{suc}}$, respectively. Consequently, more crude movements can be attempted when the movement of the molecules is less restricted, for example, at higher temperatures. In this way, the extent of translation and distortion is regulated according to the circumstance at hand.

RESULTS AND DISCUSSION

In order for the layered structure shown in Fig. 1 to be achieved, the moieties of liquid crystal molecules should be sufficiently incompatible to each other chemically and/or sterically. This will lead to the layering when the temperature is lowered sufficiently to overcome the unfavorable interactions between the parallel dipole moments. The fact that the incompatibility between the moieties is the major factor for the layering was demonstrated when a four-block mesogen composed of a biaryl group, an alkyl chain, and two perfluoroalkyl chains was synthesized.¹⁰ This molecule was shown to exhibit a smectic C structure at a certain range of temperature due

Table 1. Parameters Used in the Simulation of Nonchiral Ferroelectrics

Parameter	Value
n_x	6
n_y	6
n_z	6
N	216
L	113.7
l_{A1}, l_{A2}, l_{A3}	3.0
l_{R1}	3.0
l_{R2}	6.0
ϵ_1, ϵ_2	0.3
$\gamma_1, \gamma_2, \gamma_3$	2.0
V_f	0.95
f_{trans}	0.4
f_{site}	0.4
Δ_{trans}	0.2
Δ_{site}	0.3

to its triphasic character.

A set of typical parameters that were used in the simulation are shown in Table 1. Although the simulation program developed in this study can handle up to three different spring constants and two different overlap in interaction parameters (see Fig. 4), actually one spring constant was used for the flexibles and also one overlap parameter was used for the rigids to simplify the problem. In order to make the contributions from inter- and intramolecular interactions comparable, γ value of approximately an order larger than ϵ was taken, considering the fact that there are six neighbors for each lattice site. Volume fraction v_f is simply defined as the ratio of the length in z direction actually occupied by the molecules when they are at relaxed state (i.e., flexibles at equilibrium lengths) to the total length of the lattice in z direction (L). Since the length of a molecule at relaxed state is given by $l = l_{A1} + l_{A2} + l_{A3} + l_{R1} + l_{R2} = 18$, one obtains $v_f = n_z \cdot l / L = 0.95$. Typically 2000~3000 MC cycles were allowed for the system to reach an equilibrium with respect

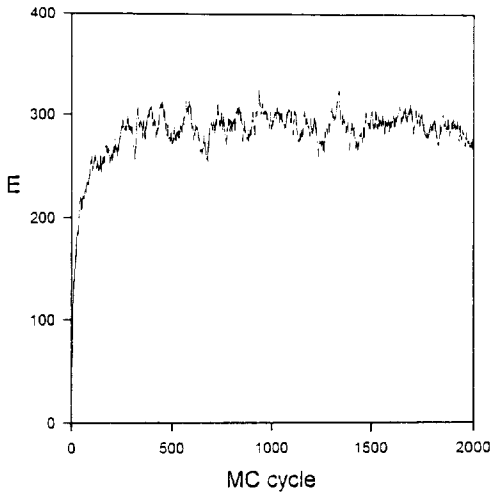


Fig. 5. Development of energy as a function of MC cycle at $T_k=0.5$ for a perfectly ordered and relaxed initial configuration.

to the energy. Fig. 5 shows a typical behavior of energy as a function of the MC cycle. When the temperature was raised slowly, the system reached equilibrium within about 200 to 500 MC cycles in most cases. In the simulation, it is convenient to use the product $k \cdot T (=T_k)$ as a variable. Thus temperature is to be understood in unit of k hereafter. In Fig. 5, T_k of 0.5 was used, and the initial configuration of the molecules was perfectly ordered with the flexibles at equilibrium lengths, so the energy is zero at the start and increases as the iteration develops.

Average energy, $\langle E \rangle$, as a function of T_k is shown in Fig. 6. The energy increases with T_k as expected. Under close inspection, curvature changes are revealed at two regions of T_k , 1.4~1.7 and 2.3~2.7. Heat capacity, C_v , is given by

$$C_v = \frac{\langle E^2 \rangle - \langle E \rangle^2}{kT^2} \quad (4)$$

The plot of C_v as a function of T_k is shown in Fig. 7. In this figure, the two curvature changes in the plot of $\langle E \rangle$ vs. T_k appear as

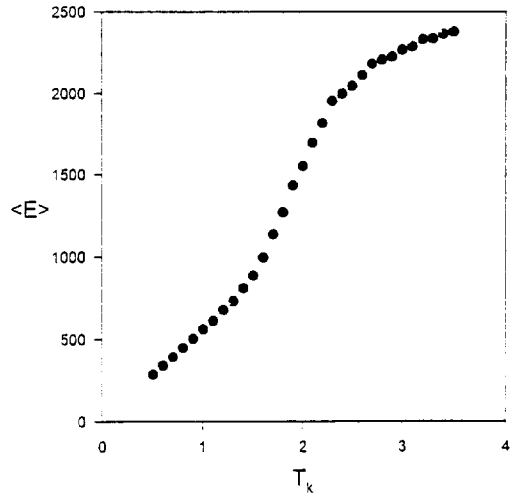


Fig. 6. Average energy vs. T_k .

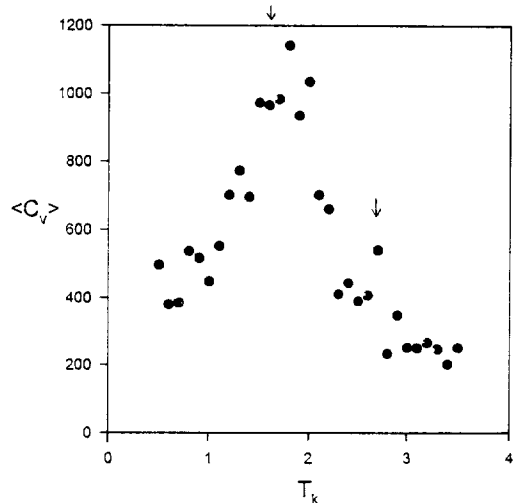


Fig. 7. Average heat capacity as a function of T_k .

discrete maxima around the same regions of T_k , respectively.

The molecules of our interest are noncentrosymmetric in structure, and as a result, can assume one of the two directional senses of 'up' (R_2 above R_1) and 'down' (R_1 above R_2). At lower temperatures, it is expected that the molecules are more or less aligned in terms of the directional sense. On the other hand, at sufficiently higher temperatures, the

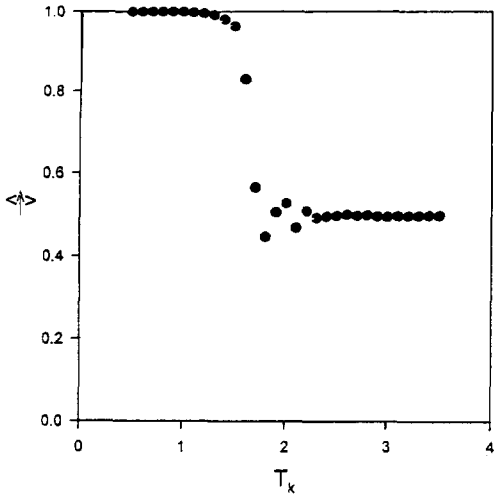


Fig. 8. Average of the fraction of the molecules in up positions as a function of T_k .

molecules are expected to point up or down in a random fashion. Fig. 8 shows the fraction of molecules in up positions as a function of T_k . At lower temperatures, almost all the molecules are pointing in the same direction, and they become random in terms of the directional sense at higher temperatures. In between the two extremes, there will be some temperature region in which this type of alignment undergoes transition. In Fig. 8, the transition seems to occur rapidly around $T_k=1.6\sim 1.7$. In order to characterize the behavior of the two transitions further, several quantities were considered and used as follows.

In analogy to the usual smectic A order parameter,¹¹ two smectic order parameters can be defined. The first one is smectic order parameter for the rigid moieties :

$$\Psi_r = \exp[-j \Delta z_{cm} \frac{4\pi}{d}] \left\{ \frac{1}{2N} \sum_{i=1}^N \exp [j z_{i2} \frac{4\pi}{d}] + \exp [j z_{i1} \frac{4\pi}{d}] \right\} \quad (5)$$

where $j=\sqrt{-1}$, N is the number of molecules, and d is the lattice cell thickness ($d=L/n_z$). It is possible for the whole molecules to

translate by a finite distance. But this possibility should not affect the smectic order parameter especially when the latter is averaged over the MC cycles. Hence the first term in the product of the right hand side of Eqn. (5) is required. Here Δz_{cm} is given by

$$\Delta z_{cm} = z_{cm} - z_{cm}^0$$

where z_{cm} is the z coordinate for the center of mass of the whole molecules, and z_{cm}^0 is z_{cm} at the start of the simulation. Here the center of mass of a molecule is defined by the average of positions of the two rigid moieties. This kind of smectic order parameter can also be defined for the molecular centers :

$$\Psi_c = \exp[-j \Delta z_{cm} \frac{2\pi}{d}] \left\{ \frac{1}{N} \sum_{i=1}^N \exp [j z_{ic} \frac{2\pi}{d}] \right\} \quad (6)$$

where $z_{i,c}$ is the center of mass of i -th molecule.

Since the alignment of polar groups, in other words, the characterization of the senses of directions of the molecules is one of the major interests in ferroelectrics, some measure for the polarity of the system is required. For this purpose, the following polarity order parameter was used in this study.

$$\Psi_p = \exp[-j \Delta z_{cm} \frac{2\pi}{d}] \left\{ \frac{1}{N} \sum_{i=1}^N \exp [j z_{ic} \frac{2\pi}{d}] \text{sign}_i(\uparrow \downarrow) \right\} \quad (7)$$

where $\text{sign}_i(\uparrow \downarrow)=1$ when the i -th molecule is up and -1 when down. Note that $\Psi_p \cdot \Psi_p^*$ (where $*$ stands for conjugation) is unity for a perfect smectic and polar structure and decreases rapidly as the smectic order and the polarity order are disrupted.

The fluctuations corresponding to these order parameters may also be effectively utilized in the characterization of the transition behavior. For a given order parameter Ψ , the fluctuation is given by

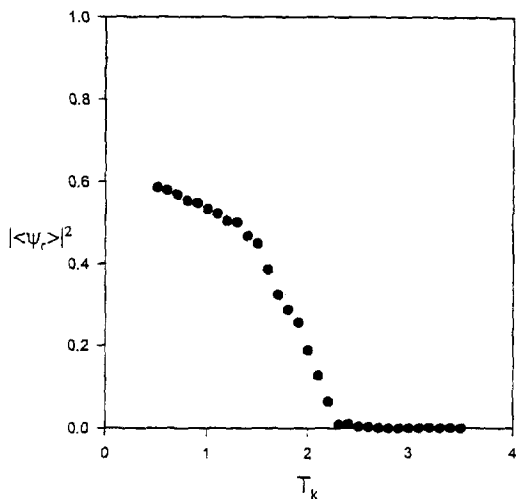


Fig. 9. Average smectic order for the rigid moieties as a function of T_k .

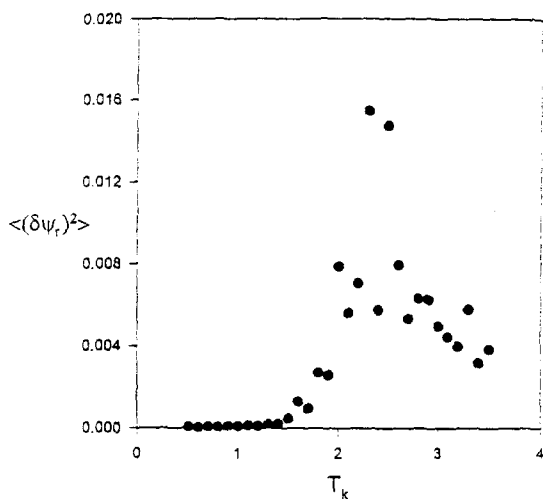


Fig. 11. Average of fluctuation of the smectic order parameter for the rigid moieties as a function of T_k .

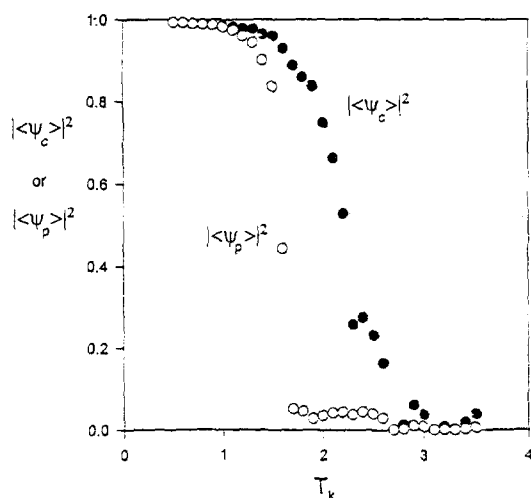


Fig. 10. Average smectic and polarity orders for the molecular centers as a function of T_k .

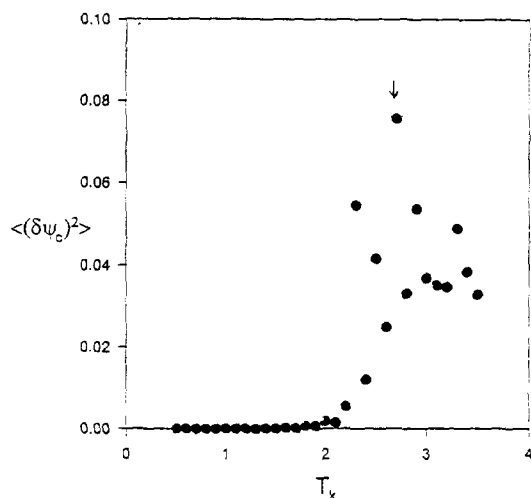


Fig. 12. Average of fluctuation of the smectic order parameter for the molecular centers as a function of T_k .

$$\langle(\delta\psi)^2\rangle = \langle\psi^2\rangle - \langle\psi\rangle^2 \quad (8)$$

$|\langle\psi_r\rangle|^2$ is shown in Fig. 9, while $|\langle\psi_c\rangle|^2$ and $|\langle\psi_p\rangle|^2$ are collected in Fig. 10 for comparison. $\langle(\delta\psi_r)^2\rangle$, $\langle(\delta\psi_c)^2\rangle$, and $\langle(\delta\psi_p)^2\rangle$ are displayed in Figs. 11, 12, and 13, respectively. From Figs. 9 and 10, it is clear that the first transition is related to the polarity order. The smectic order is seen to per-

sist even after the polarity order disappears completely as the temperature is increased. This polar to nonpolar transition is again distinctively appears as a maximum in $\langle(\delta\psi_p)^2\rangle$ shown in Fig. 13. The transition temperature T_k is readily determined to be 1.7 from from this figure. From Figs. 11 and 12 along with Figs. 9 and 10, the second transition is obvi-

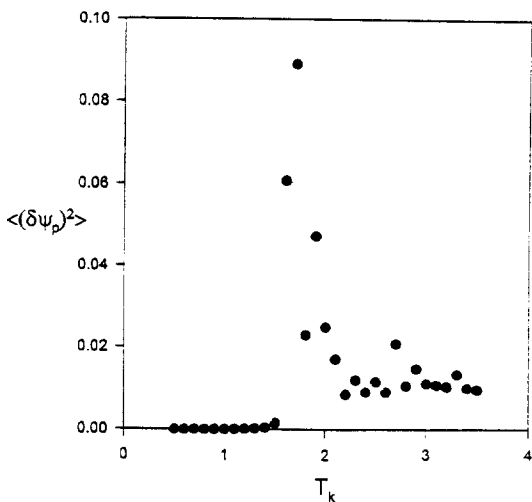


Fig. 13. Average of fluctuation of the polarity order parameter as a function of T_k .

ously related to loss of the smectic order. The fluctuations $\langle(\delta\psi)^2\rangle$ and $\langle(\delta\psi_c)^2\rangle$ appear scattered extensively around this smectic to nematic transition. This behavior is a typical consequence of the long range nature of transition phenomena, and calls for longer simulation time for the averaging to be more specific. However, current results of simulation runs seem to be sufficient for the characterization of the nature of the transition.

In this way, the transitions associated with the system under study were fully characterized. The transition at lower temperature side was seen to be polar to nonpolar transition while the smectic order was persisting. On the other hand, the transition at higher temperature side was characterized as smectic to nematic transition. Note that the interactions between polar groups that are required within the rigid moieties for the ferroelectricity were not considered in this simulation. That interaction is expected to affect the transition behavior to some extent and is open to further investigation. Based on the methodology for the characterization of the transition behavior for a particular molecular structure developed in this study, we are examining the effect of

the molecular architecture and the related parameters on the locations, disappearance, etc., of the transition phenomena. Moreover, the quasi-lattice model used in this study may also be applied to the study of main chain liquid crystalline copolymers after some modifications, and we are also pursuing this possibility.

CONCLUSION

The possibility for the existence of nonchiral ferroelectric substances has been raised, and a Monte Carlo simulation technique was used to test one of the potential molecular architectures. The molecules considered in this study are made of two rigid and three flexible moieties. These two types of moieties have the tendency to segregate from each other due to the chemical differences. A quasi-lattice was devised to accommodate this tendency. The internal energy of the system was calculated as the sum of (i) the spring energy of the flexible moieties within a molecule and (ii) the overlap energy of the rigid and flexible moieties between neighboring molecules. Several quantities were calculated from the simulation and they include energy, heat capacity, smectic order parameters, polarity order parameter, and fluctuations of the order parameters, among others, as a function of the scaled temperature $T_k (=k \cdot T)$. Two transitions were revealed from the simulation results. The transition that occurred at lower temperature side was characterized as the polar to nonpolar transition, while the transition at higher temperature side was seen to be the smectic to nematic transition.

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