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Mechanical model study of relationship of molecular configuration and multiphase in liquid crystal materials*

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A mechanical model of liquid crystals (LCs) is applied to study the polymorphism of homologous series of terphenyl compounds. With a semi-experimental molecular orbit method, we calculate the moment of inertia which represents the rotation state to describe the phase transition temperature obtained from experimental data. We propose a novel explanation of the phase sequence or polymorphism of LC materials using the two key parameters, the moment of inertia and critical rotational velocity. The effect of molecular polarity on the appearance of liquid crystalline is also discussed.

Keywords: mechanical model, liquid crystal, multi-phase, moment of inertia
PACC: 3410

1. Introduction

Most of thermotropic LC compounds have a characteristic geometric molecular shape: rod-like or lath-like.[1] An accepted fact is that such a constituent molecule rotates around the molecular long axis.[2,3] Depending on molecular orientational orders in liquid crystalline phases (mesophases), partially restricted rotation or free rotation is expected.[2] Most of researches have discussed the relationship between the phase structure and the static geometric structure, but generally ignoring the molecular rotational mechanics which dominates the mesogenic properties. It seems that people are little interested in the rotational system about intra-molecular structural changes associated with phase changes.

A mechanical model that explains how molecular dynamical parameters can determine the molecular rotation and phase transition of LCs system is being developed. The first study that modelled the LC ensemble as a rotor-bearings mechanical system has given a good explanation for the thermal stability of the smectic phase.[4] In the rotor-bearings machinery system, the rotational balance of the molecular core as a rotor is determined by such parameters as the centre of gravity, eccentricity, moment of inertia and atomic mass distribution. The theory and model have been applied to fluorinated terphenyl LC compounds, and reached a stage in which the model can effectively explain the richness of phase appearance in fluorinated and non-fluorinated terphenyl LCs.[5] Continual studies on the mechanical model have extended the scope of its application. In previous papers,[6,7] one of the authors has investigated some dynamic parameters, namely the moment of inertia and the critical angular velocity (ω_c) around the molecular long axis. Using these parameters, the thermal behaviour for the typical fluorinated terphenyl LCs has been analysed. The author has found a novel molecular structural phenomenon for which have been introduced the concepts of 'slim isomer' and 'fat isomer'. The research results show that the new structural phenomena is related to the smectic as well as the nematic phase properties of the system.

In another study, Toriyama *et al*[8] have proposed the liquid crystalline molecular ensemble as a mechanical string system. The string consists of many

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molecules lying in layers in a smectic phase and is stretched perpendicular to the layers. For polymorphic liquid crystalline compounds, analyses based on the mechanics and dynamics of the strings have clarified a correlation between the molecular structure and the thermal stability of the phase.

In this paper, the authors have carefully chosen some terphenyl compounds to investigate the relationship between the multi-phase, thermal stability, molecule polarity and alkyl terminal radicals. This study, in which the authors calculated simply the molecular dynamic parameters, can provide useful information on the forecast and synthesis of homologous series of LC materials.

2. Model and calculation

2.1. Molecular model

In a rotational system of rigid body, the moment of inertia plays a key role in determining the rotation motion. In the system, one of the principal axes that has the minimum moment of inertia is the longest among the axes. The rigid body will rotate around the long axis because of its minimum moment of inertia. In our mechanical model of LC system, the molecules rotate rapidly around the longest principal axis on which the centre of gravity is located. Therefore, the centre of gravity, eccentricity and atomic mass distribution will strongly affect the rotation state of the LC molecule, and further determine the phase behaviours.

In different phase phenomena, the LC molecules adopt different rotational motions. For thermotropic LC, in the smectic phase, the molecules rotate in a limited space. With increasing temperature, the system obtains sufficient energy and the molecule reaches a more free rotation condition. The molecular symmetry breaking takes place when the temperature of the compounds gets high or low.[9] When the molecules rotate at a determinate level at a critical temperature, the system will achieve a phase transition. Thus, the results of previous studies have shown that the molecular rotation state determines the phase transition in our mechanical model of LC system.

In another paper,[10] the authors have studied simply the terminal length dependence of the moment of inertia and critical angular velocity for some terphenyl compounds. In this paper, we choose the same terphenyl compounds shown in Fig.1 for a deeper and wider investigation. The LC molecule, which holds a rigid terphenyl core, is modelled as a rotor-bearing system. For different LC phase structures, the molecular rotor possesses different rotation characteristics. As having been discussed in the previous paper by one of the authors, a rotor machine system with moment of inertia (I_{A}) causes an inevitable criticality with a critical angular velocity (ω_{c}) at the transition temperature (T_{c}).

In the LC mechanical model, in order to retain conformity to the corresponding thermodynamic system, the energy equipartition law is applied to create an angular velocity around the longest axis given by[6]

$$\frac{1}{2}kT_{\mathrm{c}} = \frac{1}{2}I_{\mathrm{A}}\omega_{\mathrm{c}}^2. \tag{1}$$

The mechanical theory predicts the existence of a critical point or critical angular velocities in an elastic rotor-bearings system.[4,5,8] The molecular rotation around the long molecular axis has been observed in some experiments, and the time scale is approximately $\tau \sim 10^{-11}$s.[11–14] The calculated results of this study have same quantitative series as the above experimental data.

2.2. Calculation process

Plenty of fluorine-substituted terphenyl LCs have been synthesized and well studied by many research groups[15–19] in past years. These LC molecules are useful and representative choice for the mechanical model studies.

In the mechanical model of LC system, atomic mass distribution is a key factor governing the molecular rotation. And being a relatively heavier atom, the mass effect of the fluorine atom in fluorinated terphenyl LC compounds have been well described in previous studies.[5,6] For heavier halogens, there is few data of chlorinated terphenyl LCs, except a few brominates terphenyl LCs. We have chosen carefully three groups of terphenyl LC molecules to study the mechanical behaviour of the molecule. Meanwhile, in order to compare the molecular polar effect, one group that has —CN radical is also analysed. The LC molecular configurations are shown in Fig.1.

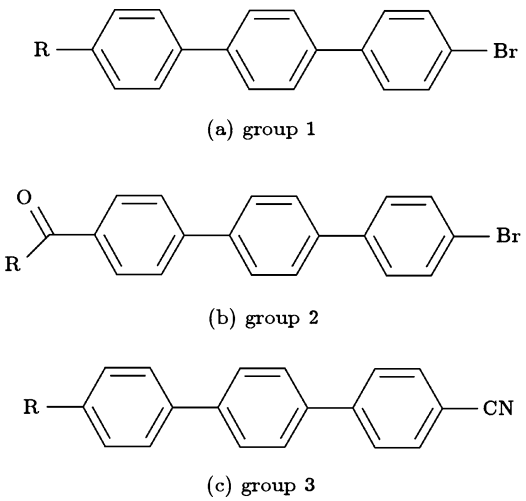


Fig.1. Molecular structures of the studied compound groups (R=C_nH_{2n+1}).

3. Results and discussion

A general molecular orbital package (MOPAC) has been employed in our calculation process.[1)] The molecular energy minimization and structural optimization have been actualized. In optimizing molecular structure, the moment of inertia (I_A) around the long molecular axis and the dipole moment (μ) are obtained by a keyword POLAR. In virtue of the experimental values of the phase transition temperature T_c (see Table 1), the critical angular velocity (ω_c) is obtained from Eq.(1).

3.1. Discussion on the polymorphism and terminal

For each molecular group, different alkyl terminal chains make different compounds as listed in Table 1. The phase transition temperatures were adopted from the works of Gray *et al.*[20−22] The items of the moment of inertia (I_A) and the total dipole moment (μ) are direct results calculated by the MOPAC. Corresponding to different phases and transition temperatures, the critical angular velocities (ω_c) around the principal molecular long axis are obtained from Eq.(1).

Structurally complicated molecules have the potentiality of creating multiple and successive phase changes. Richness of phases appearing in fluorinated terphenyl LCs, which is contrasted to the case of non-fluorinated terphenyl ones, has been analysed and explained by the mechanical model.[5] In this section, the molecular structure and polymorphism in the molecular crystal state of liquid crystalline compounds will be discussed on these molecular groups.

Small changes in molecular structure always make marked changes in phase structure. From Table 1, group 1 shows single phase transition, i.e. the crystal/isotropic phase structure. However, group 2 and 3 possess rich smectic phases and nematic phase due to their different terminal radicals. Comparison of group 1 and 2 indicates that the additions of an oxygen radical on the terminal result in different moment of inertia and total dipole moment. The oxygen radical not only aggravated the molecular mass departure from the principal axis, but also increased the molecular polar. Delicate changes of the mass distribution make the mechanical balance change its rotational motion in the rapid rotating molecule. In view of the mechanical model, it will influence strongly the phase structure of the LC compounds.

Another comment on the rich polymorphism of smectic and nematic phases is that polar or polarizable terminals function as local anchors on π-electron moieties of neighbouring molecules for the organization of a string. They are flexible to achieve local order, which is fundamentally important for long-range organization of the string.[8] According to this comment, it is easy to understand that the group 3 can form multi-phase more easily because of the existence of polar —CN terminal radical.

However, the above explanation is a seconded reason in the multi-phase formation. In the opinion of mechanical model, the hydrocarbon chain terminals, which possess flexible and changeable behaviours on the molecules, are additional marked sources for the appearance of sequential multiphase or rich polymorphism. Poor polymorphism in short alkyl chains are responsible for the simplicity of mechanical functioning of terminals. By increasing n value in group 2 and 3, the phase structure becomes rich and complex. However, the molecular polar is hardly changing when the terminal chain grows longer. The multiphase properties can be explained by the mechanical model. As the terminal chains get longer, the increased mass distribution departs from the principal rotation axis. The molecular moment of inertia has larger influence on its leading rotational state parameters, for instance, the rotation speed, centre of gravity and axis tilt angle, and hence the rich multiphase.

[1)] WinMopac Vec. 3, Fujitsu Limited, copyright: 1997–2000.

Table 1. The phase structure and calculated parameters (n is the carbon numbers of C_nH_{2n+1}).

n	I	μ	Phase	T	ω_c
			Group 1		
3	503	1.932	Cr-I	522.65	11.977
4	587	1.939	Cr-I	510.15	10.954
5	625	1.941	Cr-I	524.15	10.760
7	797	1.945	Cr-I	498.15	9.290
8	939	1.947	Cr-I	508.15	8.644
			Group 2		
2	554	2.179	Cr-N	497.15	11.131
			N-I	555.65	11.768
4	738	2.154	Cr-N	477.15	9.448
			N-I	523.15	9.893
5	907	2.150	Cr-N	478.65	8.536
			N-I	514.15	8.847
6	999	2.146	Cr-SmE	451.15	7.896
			SmE-SmB	476.65	8.116
			SmB-N	485.15	8.188
			N-I	512.15	8.413
7	1199	2.143	Cr-SmE	447.15	7.176
			SmE-SmB	477.15	7.412
			SmB-SmA	484.65	7.470
			SmA-N	491.15	7.520
			N-I	506.65	7.638
			Group 3		
3	501	4.730	Cr-N	455.15	11.200
			N-I	530.65	12.093
4	580	4.739	Cr-N	427.15	10.084
			N-I	515.15	11.074
5	612	4.743	Cr3-Cr2	353.15	8.926
			Cr2-Cr1	388.15	9.358
			Cr1-N	404.15	9.549
			N-I	513.15	10.759
6	720	4.746	Cr-N	397.65	8.732
			N-I	500.15	9.793
7	764	4.748	Cr-S	407.15	8.578
			S-N	397.65	8.477
			N-I	495.15	9.459
8	887	4.751	Cr2-Cr1	352.95	7.412
			Cr1-SmE	359.15	7.477
			SmE-S	390.75	7.799
			S-SmA	393.25	7.824
			SmA-N	470.15	8.555
			N-I	487.05	8.707
9	935	4.752	Cr-SmE	360.55	7.297
			SmE-S	383.45	7.525
			S-SmA	391.45	7.603
			SmA-N	478.95	8.410
			N-I	484.85	8.461
10	1064	4.753	Cr2-Cr1	350.85	6.747
			Cr1-SmE	360.35	6.838
			SmE-S	381.15	7.033
			S-SmA	390.75	7.121
			SmA-I	479.05	7.884

Units: $I/(10^{-47}\mathrm{kg{\cdot}m^2})$; μ/D; T/K; ω_c $/(10^{11}\mathrm{rad{\cdot}s^{-1}})$

3.2. Discussion on the dynamic parameters of the motion system

Figure 2 shows the changing tendency of the moment of inertia and the critical velocities for different compounds with increasing hydrocarbon chain. The data are chosen from Table 1 on phase transition of crystal/smectic and nematic/isotropic phase change. A large molecular moment of inertia corresponds to a small critical velocity. Equation (1) has told us that there is a negative quadric correlation between the moment of inertia and critical velocity. In the mechanical view of LC system, it is easy to understand the molecules carrying larger moment of inertia; the high level rotational velocity is difficult to achieve. The result is in agreement with the previous work of one of the authors for isomers of the fluorinated terphenyl LC.[6]

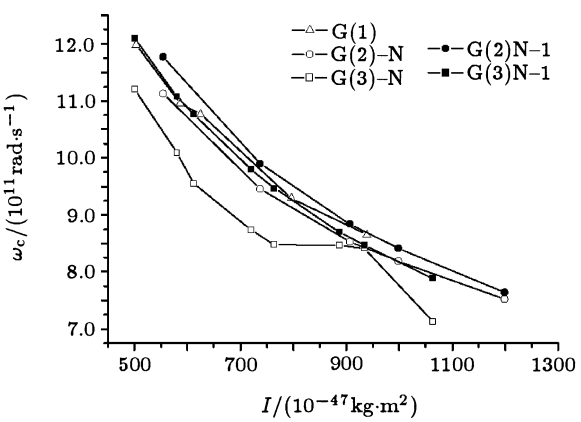


Fig.2. Correlation of the moment of inertia and the critical angular velocities around the long molecular principal axis. The open symbols: crystal/nematic (isotropic) phase transition; the solid symbols: nematic/isotropic phase transition.

The relationship between the phase transition temperature and moment of inertia is shown in Fig.3. The open symbols denote the correlation of transition temperature and moment of inertia at melting point. For melting point, the data correlation of the transition temperature and moment of inertia is in a clutter state. The results hint that the melting point is out of scope of the mechanical model. An important reason is that the external and internal molecular forces exert the first influence on the molecular rotation on crystal/smectic or crystal/isotropic phase transition point, and the mechanical property plays a secondary role meanwhile. The solid symbol expresses the above correlation at the temperature of nematic/isotropic phase transition. The correlation

at nematic/isotropic point presents a quadric, negative and smooth image attributes. It indicates that small moment of inertia makes the molecules rotate in a steady state. Therefore, the stability of molecular rotation corresponds to a high phase transition temperature (nematic/isotropic). The obtained results are in agreement with the findings of previous studies on the mechanical model.

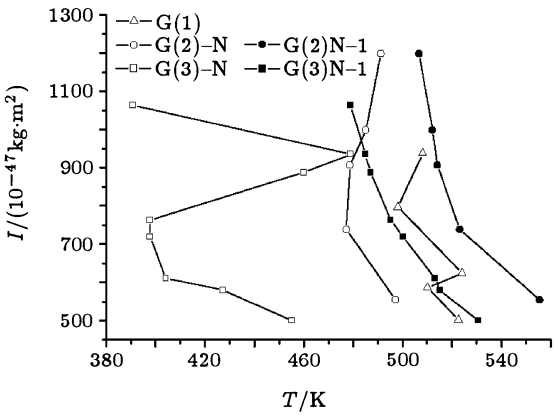


Fig.3. Correlation between the phase transition temperature and the moment of inertia. The open symbols: crystal/nematic (isotropic) phase transition; the solid symbols: nematic/isotropic phase transition.

A similar relationship between phase transition temperature and critical angular velocity on the melting point and nematic/isotropic phase transition point is illustrated in Fig.4. Because the critical angular velocity is deduced from Eq.(1), the obtained results indicate that the transition temperature at nematic/isotropic point is proportional to the square of critical angular velocities (solid symbols). In other words, the higher the speed of the molecular rotation, the higher the phase transition temperature. In connection with the principal moment of inertia about the molecular long axis, one can summarize that a small moment of inertia makes the molecule have a steady rotation condition, i.e. high rotation speed and high nematic/isotropic phase transition temperature. The high phase transition temperature indicates that the LC phase is stable.

Similarly, the open symbols denote the correlative data on the melting point. The data are in a disordered state too. Results obtained from Figs.3 and 4 remind us that the molecules take different shapes at melting point and nematic/isotropic point, respectively. In the crystal phase or crystal/nematic transition phase, molecular interaction plays a key function to influence the conformation itself. In the nematic phase or nematic/isotropic phase transition, the molecular interaction plays a secondary role. The molecules hold an ample rotation freedom, comparably. Therefore, the mechanical rotation behaviour can be explained and described effectively by the mechanical model.

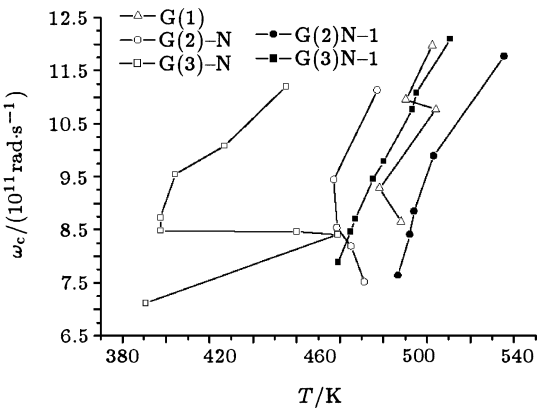


Fig.4. Correlation between the phase transition temperature and the critical velocity. The open symbols: crystal/nematic (isotropic) phase transition; the solid symbols: nematic/isotropic phase transition.

4. Conclusions

The molecular polarity and mechanical behaviour for different terphenyl compounds are analysed in a comparative method. The LC mechanical model is used to explain the multi-phase structure and their dynamic properties. It is found that the polar radical, such as =O and —CN, can easily cause the LC phase to appear. The polymorphism of LC phase is determined by the length of the alkyl terminal radical on the terphenyl core. Stability of the molecular thermo-phase has been explained in view of the moment of inertia and critical angular velocity. Obtained results suggest that the mechanical model is suitable for characterization of LC phase transition, but not for melting or crystal/LC phase transition.

The effectiveness or validity of the simulation method can be applied to various homologous series materials for the forecast of rich LC phase emergence.

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