The liquid crystal blue phase induced by bent-shaped molecules with different terminal chain lengths

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New Journal of Physics 13 (2011) 063037 (8pp)
Received 30 November 2010
Published 20 June 2011
Online at http://www.njp.org/
doi:10.1088/1367-2630/13/6/063037

Abstract. Several kinds of bent-shaped molecules with different lengths of the terminal chain are doped in chiral nematic liquid crystals (LCs), respectively, to induce the blue phase. The effects of the terminal chain length on the blue phase range are studied. The mechanisms of the phenomena are investigated through molecular dynamics, and the results indicate that molecules with a long terminal chain decrease the interfacial energy between the LCs and defects, whereas they also disturb the alignment of LCs near the interface and make an evident impact on the bent angle of molecules, which is not helpful in forming a stable blue phase. This work provides some useful insights into the molecular design of suitable bent-shaped dopants in order to obtain a wide range of LC blue phases.

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1. Introduction

Since the notion of the ‘blue phase’ was first proposed by Coates and Gray [1], research interest in this intriguing phase has never diminished. The mystical phenomenon, which is normally observed on cooling from the isotropic to chiral nematic state, shows a colorful platelet texture under polarized optical microscopy with a crossed polarizer. The structure of these platelets, put forward based on a great many theoretical and experimental results reported in the 1980s, is a self-assembled cubic constructed by using some double-twisted liquid crystal (LC) cylinders [2–4]. Because it is impossible for the double-twisted arrangement to occupy a three-dimensional space, defects inevitably coexist with the LC phase in such a system. Normally, the generation of defects is associated with some energy consumption; thus the blue phase is unstable unless some energy is supplemented. The energy is usually supplied by a strong twist force, so the blue phase is generally found in a high-chirality system [5].

The exotic structure of the blue phase makes it possess many special physical properties, such as optical isotropy, tunable reflection of circular polarized light with a certain wavelength, microsecond response, etc, which bring up many potential improvements in flat panel display, especially broad viewing angle, high optical efficiency displays and the possibility of color-sequential display [6, 7]. Unfortunately, the blue-phase LC cannot be used at present because of some applied bottlenecks. One of the biggest problems is the narrow temperature range, normally a few kelvins [8]. Many researchers have made great efforts to overcome this shortcoming, and there has also been tremendous progress in recent decades, mainly in two ways. One is employing polymer-stabilized blue phase in which the defects are held by an amorphous polymer chain; a wide blue phase range over 60 °C was achieved by Kikuchi et al [9]; a similar idea of nanoparticle-stabilized blue phase was also proposed by Yoshida et al [10]. The other is widening the blue phase range by changing the molecular geometry or physical characteristics of LCs, such as the dimer–mesogen structure with a high flexoelectric ratio, proposed by Coles and Pivnenko [11], and the ‘T’-shaped molecular geometry synthesized by Yoshizawa et al [12]; the blue phase ranges of 44 and 29 °C have been reported, respectively.

Several years ago, another exotic phenomenon was reported by Nakata et al [13]; they doped a small number of bent-shaped molecules in the chiral nematic LCs (N*LCs) and then the blue phase with a temperature range of 2–5 °C was induced. These results are very exciting; however, the effects of bent-shaped dopants on the blue phase and their mechanisms are not clear, and investigations on this subject have rarely been reported. Recently, our studies indicate that a wide blue phase range can be induced by doping with bent-shaped molecules into N*LCs host, because of the bent geometry structure and the interactions between LCs and defects [14].

To make a deep investigation and to assist the structural design of bent-shaped dopants, in this paper bent-shaped molecules with different lengths of the terminal chain are doped into N*LCs, respectively, with the same concentration, and their effects on the blue phase range are detected and analyzed with experiments and molecular simulations; the theoretical results show good agreement with the experiments.

2. Experiments and results

Five kinds of bent-shaped molecules with the same backbone and different lengths of the terminal chain (shown in figure 1) are synthesized and doped, respectively, into N*LCs host as the testing samples. There is no LC phase for these dopants and the doping ratio is 7.0 wt%.
B1: n=1,  B2: n=4,  B3: n=8,  B4: n=12,  B5: n=16

Figure 1. Molecular structures of bent-shaped molecules.

Figure 2. Microscopic texture of samples doped with B1–B5: on heating at the temperature of $T_{N^* - BP} + 1$ (a–e) and on cooling at the temperature of $T_{BP - N^*} + 1$ (f–j).

The N*LCs host, which contains 67.2 wt% commercial nematic LCs (supported by Slichem, Shijiachuang, China) and 32.8 wt% chiral material R811 (from Merck, Darmstadt, Germany), is observed by polarized optical microscopy, and no blue phase is found upon either heating or cooling. The phase transition from the isotropic to chiral nematic state is 79.3 °C, tested by the hot stage. The samples are settled on the hot stage and heated from the chiral nematic to isotropic state; then they are cooled from the isotropic to chiral nematic state with the same rate of 0.5 °C min$^{-1}$. The texture and blue phase range of the samples are observed and tested. After the cooling process, every sample shows the typical blue phase texture and their microscopic pictures are presented in figure 2. As shown, the colorful platelets are evident in B2- and B3-doped systems, but it is hard to recognize in the case of the other samples. However, there is a slight difference in the case of the heating process. For the samples doped with B2, B3, B4 and B5, the blue phase appears between chiral nematic and isotropic states, but no evident blue phase
texture is observed in the B1-doped sample as shown in figure 2, which indicates that a stable blue phase could be induced by doping a small number of bent-shaped molecules with a certain length of the terminal chain (the length n is at least 4 in this experiment). The temperature ranges of the samples for the heating and cooling processes are determined. As shown in figure 3, blue phase ranges change with increasing length of the terminal chain, presenting a trend of widening up first and narrowing down afterwards, upon either heating or cooling. In addition, we also note that blue phase ranges after the heating process are 30–40% narrower than those after cooling. A similar experimental result has also been reported by Yoshida et al [10], and we attribute that to the super-cooling of blue phase in the case of cooling. According to figure 3, it is also found that the widest blue phase range can be obtained by doping with molecule B2.

3. Molecular simulations and analysis

To understand the effects of the length of the terminal chain, we consider the elastic energy of the blue phase, which can be described as [9]

\[
F = a(T_{\text{iso-BP}} - T)\pi R^2 + 2\pi R\sigma + \frac{1}{4}\pi K \ln\left(\frac{R_{\text{max}}}{R}\right) - \pi(K_{22} + K_{24}).
\]

(1)

As mentioned in [9], a is a constant associated with the Boltzmann constant, \(T_{\text{iso-BP}}\) is the transition temperature from the isotropic to blue phase state, and \(T\) is an arbitrary temperature on cooling; \(K\) is the elastic constant with single constant approximation, and \(K_{22}, K_{24}\) are twist and saddle splay elastic constants, which can be approximated as \(K_{22} + K_{24} = 2K_{24} = K\) [15]; \(R\) is the radius of the defect core, \(R_{\text{max}}\) is the cutoff radius and \(\sigma\) is interfacial tension between LCs and the defect, which is proportional to interfacial energy. Equation (1) shows that the elastic energy is proportional to \(\sigma\), \(R\) and \(K\).

First, molecular dynamics is adopted to calculate the interfacial energy. To start with, the bilayer model should be constructed to simulate the interface. In short, a layer formed by amorphously mixed LCs and a bent-shaped dopant is simulated as the defect; the double-twisted LC layer is approximately simulated as a well-aligned nematic LC layer, because it is reported
that the director field of LCs locally approaches a single twist at the interface of the double-twisted cylinder, whereas the single twist can be further approximated to the well-aligned nematic at the interface [16]. The interfacial energy satisfies the following expression [17]:

\[ E_{\text{int}} = E_0 - (E_{\text{LC}} + E_{\text{def}}), \]

where \( E_0 \), \( E_{\text{LC}} \) and \( E_{\text{def}} \) are the energies of the bilayer, LC layer and defect layer, respectively, and can be calculated through polymer-consistent force field [18].

Thus, five bilayer models are constructed; LC + Bi/LC(N)(\( i = 1, 2, 3, 4, 5 \)) represents the interface of the bent-shaped molecule-doped system, and their interfacial energies are given in table 1. The minus in the table means energy consumption to form the interface. As shown, there is a remarkable decrease in the interfacial energy as the length of the terminal chain increases. The highest value corresponds to the system doped with B1, the shortest terminal chain (\( n = 1 \)), so the blue phase range of such a system is the narrowest as in figure 2, and the lowest energy is reached when the longest molecules B5 (\( n = 16 \)) are doped. However, some other points should be noted; the blue phase range of the B5-doped system is very narrow although the calculated interfacial energy is the lowest; in addition, table 1 shows that there is no evident difference in interfacial energy between B2-, B3- and B4-doped systems, but their experimental results indicate a remarkable variation (shown in figure 3). We consider that there may be some other effects of the terminal chain length on the blue phase range.

It is possible that the terminal chain makes an impact on the interfacial alignment of LCs; this can be investigated by calculating the order parameter, \( S \), which is defined by the expression for the second-order Legendre polynomials [19],

\[ S(d) = 0.5[3\langle \cos^2 \theta_{ij}(d) \rangle - 1], \]

where \( \theta_{ij} \) is the angle between two random directors, \( i \) and \( j \), and \( d \) is their distance. Thus, the order parameter distributions on the doped interface are given in figure 4 (the calculated error bars are labeled). As shown, some fluctuations exist near the interface and their ranges are inversely proportional to the length of the terminal chain of the dopant. There are few fluctuations on the B1-doped interface (the shortest terminal chain, LC+B1/LC(N)) as the distance \( d \) is larger than 8 Å and on the B3-doped interface as the distance is larger than 11 Å, whereas the fluctuation range is more evident in the case of B5 doping even though the distance is over 14 Å. Such results indicate that the longer terminal chain has a great impact on the alignment of LCs near the interface. The reason for that is related to the weaker interfacial energy of such a system, e.g. the B4- and B5-doped interface, and similar effects have also been noted in Pogue’s experiments to study the interaction between LCs and polymer [20]. In addition, according to our previous study [14], a better alignment of LCs on the interface leads
to the shrinkage of the defect core ($R$ in equation (1) is decreased) and thus the elastic energy is decreased; in contrast, the defect core is enlarged and the elastic energy is increased. Therefore, the longer terminal chain is obviously not useful for the stabilization of the blue phase.

From the molecular structure point of view, a bent shape can be seen as biaxial, with two molecular axes, and the angle between axes is defined as the bent angle. Previous research shows that molecular biaxiality plays an important role in the formation of the blue phase [16], and our recent study shows that the bent angle is proportional to the blue phase range [14]. The bent angle is easily influenced by the length of the terminal chain; to prevent this, the semi-empirical quantum chemistry algorithm, AM1 [21], is used to calculate the optimized geometry of the molecules and bent angles $\theta$ and the corresponding atomistic models are presented in figure 5. As shown, the bent angle of the molecule with a short terminal chain,
labeled B1, is only 23°, which is much smaller than those of the longer ones, such as B2 of 38° and B3 of 42°. However, it does not mean that the longer the terminal chain the larger the bent angle; some other factors should be considered. When the terminal chain is too long, such as molecules B4 (n = 12) and B5 (n = 16), two conformations (labeled ‘a’ and ‘b’ in figure 5) can be found in every material: one with a small bent angle of about 15° and 10° as in B4-a and B5-a, respectively, and the other with a relatively larger angle of about 65° and 48° as in B4-b and B5-b, respectively. The conformation with a large bent angle is beneficial to stabilize the blue phase, whereas that with a small bent angle is not. The combined effect of such molecules lies in the probability of two conformations in the system. In the B4 system, the calculated probability of the larger bent-angle conformation is about 35%, whereas in the B5 system, it is less than 20%, so that the blue phase ranges of B4- and B5-doped systems are not as wide as desired.

4. Conclusions

In conclusion, the effects of the length of the terminal chain on the bent-shaped molecule-induced blue phase are investigated through experiments and molecular simulations. The results indicate that a long terminal chain decreases the interfacial energy; this is considered to be useful in stabilizing the blue phase; however, a longer chain can also disturb the alignment of LCs near the interface, which may lead to an unstable blue phase. In addition, a long terminal chain increases the bent angle of molecules, but too long a one leads to multi-conformation with large and small bent angles; in that case, the effect of such molecules on blue phase is determined by the probability of the conformation with large bent angles; the higher it is, the more stable the blue phase.

Acknowledgments

This work was supported by the National Science Foundation of China (grant no. 60878047), the Fundamental Research Funds for the Central Universities (grant no. WM1014015) and Research Foundations of ECUST (grant no. yk0157125).

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