Enhanced Flexoelastic Ratio of Mesogenic Dopant-doped Nematic Liquid Crystals

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ABSTRACT

The enhanced flexoelastic ratio of mesogenic dopants (MDs)-doped nematic liquid crystals (NLCs) is studied. The flexoelastic ratio increased up to 139 % than pure nematic liquid crystals (NLCs) after doping MD. The mechanism of the enhanced flexoelastic ratio is presumably related to the large dipole moment of MDs.

1 INTRODUCTION

Dielectrics have a flexoelectricity where the electric polarization generates with non-uniform strain. Liquid crystals (LCs) and oxide semiconductors are known to have strong flexoelectricity. The flexoelectricity of LCs can be applied in a variety of fields such as displays, phase modulator, and energy harvesting [1-3]. The strong flexoelectricity is desirable for practical applications. The flexoelectric polarization of nematic LCs is given by

$$\boldsymbol{P}_f = e_{11}\mathbf{n}(\nabla\cdot\mathbf{n}) + \mathrm{e}_{33}(\nabla\times\mathbf{n})\times\mathbf{n},$$

where e_{11} and e_{33} are the splay and bend flexoelectric coefficients, respectively [4]. Therefore, the flexoelectricity can be enhanced by increasing the magnitude of flexoelectric coefficients. Variety of studies have reported that bent-core liquid crystals (BLCs) and liquid crystal (LC) dimer has large flexoelectric coefficients.

In this study, the enhanced flexoelectricity of mesogenic dopant (MD) doped-nematic liquid crystals (NLCs) is studied. We used two types of mesogenic molecules ferroelectric liquid crystals (FLCs) and newly synthesized hydrogen bondable mesogen as MD. The hydrogen bondable mesogen was synthesized, and the molecules form an LC dimer by hydrogen bonding. We experimentally measured the flexoelastic ratio e^* of MD-doped-NLCs, where $e^*=(e_{11}-e_{33})/K$, and K is the average of splay (K_{11}) and bend elastic constant (K_{33}). In experimental result, e^* of MD-doped NLCs significantly enhance than pure NLCs.

2 EXPERIMENT

The commercial FLC mixtures CS1031 (JNC) and R0323 (Clariant) was doped into commercial NLC mixture T68 (JNC). A hydrogen bondable mesogen 4-[7-(4′-Cyanobiphenyl-4-yl)hexyloxy]bezoic acid (CBO7OBA) was newly synthesized [Fig. 1]. A cyclic dimer state of CBO7OBA molecules was checked by FT-IR spectroscopy [8]. The CBO7OBA was doped into two commercial NLC mixtures T04 (JNC) and ZSM50089 (JNC), respectively. All three MDs was doped into pure NLC mixtures by 5 wt%.

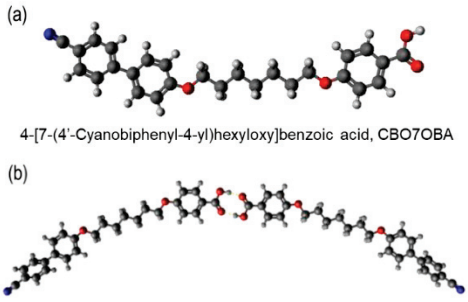

Fig. 1 Chemical structure of CBO7OBA molecule. (a) Simulated chemical structure of a CBO7OBA molecule and (b) its cyclic dimer form in trans state.

To measure e^* using the chiral flexoelectro-optic method, 2 wt% right-handed chiral dopant R6N (HCCH) was mixed with LC mixtures. From the free-energy minimization, the relationship between tilt angle ϕ and electric field E is given by

$$\tan\phi = (e_{11}-e_{33})\boldsymbol{E}/(K_{11}+K_{33})\boldsymbol{q}_0,$$

where q_0 is initial wavevector of the helix, where $q_0=2/p_0$ and p_0 is the pitch of the helix at E=0, K_{11} and K_{33} are splay and bend elastic constants [5]. The uniform-lying helix cell was fabricated to measure the ϕ. The experimental details are described in previous literature [6, 7]. All experimental measurements were done at room temperature (25 °C).

3 RESULTS

Figure 2 shows experimentally measured $q_0\cdot\tan\phi$ of each mixture as a function of the applied electric field. The solid line at each measurement data is a linear fitting result. The slope of CS1031- (solid square) and R0323-doped (half square) T68 are larger than pure T68 (empty square). In addition, the slope of pure T04 (empty circle)

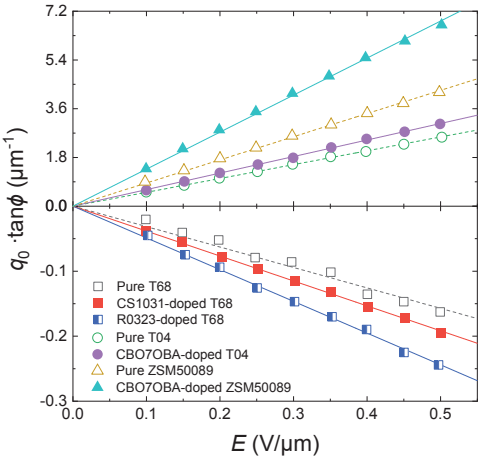

Fig. 2 Experimentally measured $q_0 \cdot \tan\phi$ as function of applied electric field.

The data obtain with 300Hz bipolar square wave at room temperature (25 °C). Note that the y-scale of FLC-doped NLCs and CBO7OBA-doped NLCs data is different.

and ZSM50089 (empty triangle) increased dramatically after doping CBO7OBA into T04 (solid circle) and ZSM50089 (solid triangle). The slope in Fig. 2 is corresponding to the e^*. Thus, the increased slopes represent the enhanced e* after doping MDs.

In the experimental result, relative dielectric constants along perpendicular ($\varepsilon_\perp$) and parallel ($\varepsilon_{/\!/}$) direction to the LC director of the pure T68 is 3.97 and 3.93, respectively, while that of CS1031-doped T68 is 3.93 and 15.8, respectively, and that of R0323-doped T68 is 3.97 and 15.9. The $\varepsilon_\perp$ and $\varepsilon_{/\!/}$ of pure T04 are 4.21 and 17.3, respectively, while that of CBO7OBA-doped T04 is 4.7 and 18.1, respectively. In addition, The $\varepsilon_\perp$ and $\varepsilon_{/\!/}$ of pure ZSM50089 are 6.10 and 32.7, respectively, while that of CBO7OBA-doped ZSM50089 is 6.02 and 32.6, respectively.

Table 1 Experimentally measured relative dielectric constants, elastic constants, wavenumber and flexoelastic ratio of the LC mixtures.

Sample	$\varepsilon_\perp$	$\varepsilon_\parallel$	K_{11} (pN)	K_{33} (pN)	q_0 (μm^{-1})	e^* (C/Nm)
Pure T68	3.97	16.4	10.6	17.9	13.0	-0.63
CS1031-doped T68	3.93	15.8	11.3	18.1	10.2	-0.77
R0323-doped T68	3.97	15.9	11.5	17.5	14.2	-0.94
Pure T04	4.21	17.3	6.2	9.3	18.9	1.96
CBO7OBA-doped T04	4.37	18.1	6.4	9.9	21.9	2.72
Pure ZSM50089	6.10	32.7	6.0	11.0	11.4	1.97
CBO7OBA-doped ZSM50089	6.02	32.6	4.8	14.9	16.5	4.57

The K_{11} and K_{33} of the pure T68 are 6.2 and 9.3, respectively, while that of CS1031-doped T68 is 6.4 and 9.9, respectively, and that of R0323-doped T68 is 11.5 and 17.5. The K_{11} and K_{33} of pure T04 are 6.2 and 9.3, respectively, while that of CBO7OBA-doped T04 is 6.4 and 9.9, respectively. In addition, The K_{11} and K_{33} of pure ZSM50089 are 6.0 and 11.0, respectively, while that of CBO7OBA-doped ZSM50089 is 4.8 and 14.9, respectively.

The e^* of the pure T68 is -0.63 C/Nm, while that of CS1031- and R0323-doped T68 is -0.77 and -0.94 C/Nm, respectively. In addition, e^* of pure T04 and ZSM50089 is 1.96 and 1.97 C/Nm, respectively, while that of CBO7OBA-doped T04 and ZSM50089 is 2.72 and 4.57 C/Nm. The experimental results are summarized in Table 1.

4 DISCUSSION

The absolute value of e^* after doping FLCs increased up to 49 % than pure T68. On the other hand, The relative dielectric constants and elastic constants have no significant change after doping FLCs [Table 1]. Following the Helfrich's theoretical model, the flexoelectric coefficients are proportional to the geometrical anisotropy, dipole moment and elastic constant of molecules [6]. It is known to FLCs have a large transverse dipole moment ($\mu_\perp$). Therefore, the enhanced e^* of FLC-doped NLCs seems to be related to the large $\mu_\perp$ of FLCs [7]. Note that we used the commercial FLC mixtures consisting of several kinds of FLC molecules and the chemical structure of them cannot be known. Thus, the exact physical mechanism of the increased magnitude of e* after doping FLCs is not clear at the current state.

After doping CBO7OBA, e^* is 139 % increased. The difference of relative dielectric constants between pure NLCs and CBO7OBA-doped NLCs are very small. Meanwhile, the elastic constants of CBO7OBA-doped ZSM50089 are significantly different compared to pure ZSM50089. The K_{33} of ZSM50089 35 % increased after doping CBO7OBA. The e^* is inversely proportional to the elastic constants. Therefore, the increased e^* after doping CBO7OBA cannot be explained by changed elastic constants. Thus, the large e^* of CBO7OBA-doped NLCs might be related to the large $\mu_\perp$ of CBO7OBA cyclic dimers in trans-state [8].

5 CONCLUSIONS

We studied the flexoelastic ratio e^* of FLC- and CBO7OBA-doped NLCs. After doping MDs, the e^* of FLC- and CBO7OBA-doped NLCs increased up to 49 and 132 % than pure NLCs, respectively. In experimental results, changes in e^* due to changes in $\varepsilon_\perp$, $\varepsilon_{/\!/}$, K_{11}, and K_{33} could be ignored. Therefore, the enhanced e^* of MD-doped NLCs seems to be related to the large dipole moment of MDs and intermolecular interaction between molecules in mixtures.

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