

Fast Switching in the Vicinity of Smectic-to-Nematic Phase Transition in High Birefringence Isothiocyanate Mixtures

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Two series of high birefringence liquid crystal compounds, isothiocyanato phenyl-tolane and terphenyl, and mixtures were prepared and their physical properties evaluated. Depending on the terminal alkyl chain length, different mesomorphic sequences were observed. In the vicinity of nematic-to-smectic transition, the visco-elastic coefficient decreases, instead of increase, as the temperature decreases. We investigated the possibility of extending the observed phenomenon from single compounds to mixtures for practical applications. This behavior is useful for improving the response time of a liquid crystal device, if the operating temperature can be accurately controlled.

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1. Introduction

Liquid crystal (LC) single compounds and mixtures are typically designed to exhibit a wide range of single mesomorphic phase, say nematic or smectic, intended for an application. This desired mesomorphic phase is carried on by single compounds, eutectic mixture, or induced within certain formulations of the mixtures. Numerous reports are available in the literature regarding binary or multicomponent systems exhibiting induced smectic A (specifically Ad) phase, reentrant nematic phase and also ferroelectric and antiferroelectric phases.¹⁻³⁾ Induced phases are often of interest for phase transition boundary study. Typically close proximity of the phase transition introduces unexpected deviations of the major physical parameters, e.g., dielectric permittivity, elastic constants, flow viscosity or rotational viscosity, as the order parameter of the LC changes drastically.⁴⁻¹⁰⁾ The phase transition between nematic phase (which has orientational order) and smectic phase (which has both orientational and positional order) has long been studied for subtle effects that arise from the intrinsic coupling of their order parameters.¹¹⁾ To combine the typical nematic behavior observed by different experimental techniques (optical polarizing microscopy, miscibility studies, and dielectric spectroscopy) and the smectic-like fluctuations (short-range positional order) in the systems with smectic and nematic phase, the term cybotactic nematic has been used. It is known from studies of X-ray diffraction patterns that small domains with a local smectic organization appear in the nematic phase just above the transition point, and the domains are cybotactic clusters.¹²⁾

Recently we have developed some new high birefringence (Δn) single compounds¹³⁻¹⁵⁾ and formulated high Δn mixtures for laser beam steering and optical shutter designed for infrared applications.¹⁶⁻¹⁸⁾ These applications require a fast response time. In order to achieve ~ 5 ms response time, thin cell gap filled with a high Δn mixture and operated at elevated temperature are the common approaches.¹⁹⁻²¹⁾ LC system is typically enclosed in a temperature-stabilized oven because the operating temperature under different laser power levels has to be maintained. Our research focuses on elongated rigid core molecular systems like terphenyl and

phenyl-tolane with isothiocyanato (NCS) terminal polar group. The advantage of using NCS group over the CN group is mainly on the lower rotational viscosity. However, the NCS compounds tend to exhibit smectic phases.¹⁴⁾ It is difficult to suppress the smectic phase without sacrificing the mixture's electro-optical performance, therefore, we investigated this intrinsic smectic-to-nematic (S-N) phase transition phenomenon of some single LC compounds.²²⁾

In this paper, we present some high Δn LC mixtures exhibiting unusual boost of figure-of-merit (FoM) while operated at a temperature near the S-N transition. Measured visco-elastic coefficient was significantly reduced near the S-N transition temperature. As a result, the FoM is improved. Here, FoM is linked directly to the response time of a LC device.

2. Experimental Procedure

Several measurement techniques were used to measure the physical properties of the single compounds and mixtures. Differential scanning calorimetry (DSC; TA Instrument Q-100) was used to determine the phase transition temperatures. Results were obtained from 3–6 mg samples in the heating and cooling cycles with rate 2 °C/min. The electro-optic properties of the LC compounds and mixtures were measured using 5- μ m homogenous cells with indium tin oxide (ITO) electrodes coated in the inner sides of the glass substrates. A thin polyimide layer was overcoated on ITO and buffed in antiparallel directions to produce a small pretilt angle ($\sim 2^\circ$). A linearly polarized He-Ne laser with $\lambda = 633$ nm was used as the light source for the electro-optic measurements. Experimental setup and measurement technique were the similar to those reported in ref. 23.

The physical properties of the single compounds were measured at several temperatures within their nematic phase and results were used to fit with theoretical models. In this study, we focused on the birefringence (Δn), visco-elastic coefficient (γ_1/K_{11}) and figure-of-merit (FoM) which is defined as²⁴⁾

$$\text{FoM} = K_{11} \Delta n^2 / \gamma_1, \quad (1)$$

where K_{11} is the splay elastic constant and γ_1 the rotational viscosity. The temperature dependent birefringence of a LC can be described as

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$$\Delta n = \Delta n_0(1 - T/T_C)^\beta, \quad (2)$$

where Δn_0 represents the birefringence at $T = 0$ K, β is a material constant, and T_C is the clearing temperature of the LC. By fitting the experimental data using eq. (2), we can obtain Δn_0 and β . Once these two parameters are determined, the birefringence of the LC at room temperature can be extrapolated. Similarly, we fit FoM with following equation:²⁴⁾

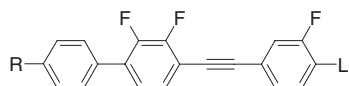
$$\text{FoM} = a(\Delta n_0)^2 \left(1 - \frac{T}{T_C}\right)^{3\beta} \exp\left(\frac{-E}{\kappa T}\right), \quad (3)$$

where a is a fitting parameter. The extrapolated visco-elastic coefficient at room temperature can be calculated from eq. (1).

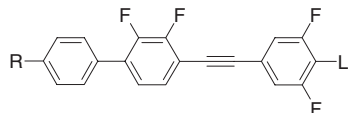
3. Results and Discussion

Compounds with phenyl-tolane (4''-alkyl-2',3'-difluoro-4-(3-fluoro-4-isothiocyanato-phenylethynyl)biphenyl; Structure I and 4''-alkyl-2',3'-difluoro-4-(3,5-difluoro-4-isothiocyanato-phenylethynyl)biphenyl; Structure II) and terphenyl (4-alkyl-3'',5''-difluoro-4''-isothiocyanato-[1,1';4'1'']terphenyl; Structure III) rigid cores were chosen for mixtures under investigation. All three are known as high optical anisotropy LCs and used for high birefringence mixtures formulation.¹⁵⁾

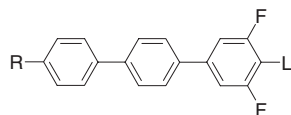
Structure (I)



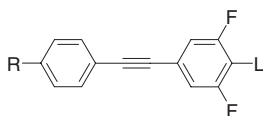
Structure (II)



Structure (III)



Structure (IV)



Typically for isothiocyanates, homologues with longer alkyl chains possess smectic and nematic mesophases while shorter chain members show only a nematic phase.

Included for comparison is a set of fluorinated phenyl-tolanes (compounds **1a–c** and **2a–b**) and a pair of fluorinated terphenyls (compounds **3a–b**). Triple and quatro fluorination of presented phenyl-tolane cores was introduced in order to lower melting point temperature. Phenyl ring with polar terminal group was single or di-fluorinated at the position(s) adjacent to the NCS terminal group. Different alkyl chain length homologues were intentionally chosen to experience different mesomorphic sequence within compared sets. All homologues are listed in Table I with detailed structures and phase transition temperatures included.^{22,25,26)} Isothiocyanato tolane compounds (Structure IV) are included as a dilutant component in our experiment.

In general, the trifluoro substituted 4''-alkyl-2',3'-difluoro-4-(3-fluoro-4-isothiocyanato-phenylethynyl)-biphenyl compounds **1a**, **1b**, and **1c** show a wide nematic range with clearing temperature exceeding 200 °C. Only ethyl homologue (C2) does not show a smectic phase. Both propyl (C3) and butyl (C5) homologues exhibit S–N transition respectively at 89.2 and 135.0 °C. For the pentyl homologue, its ΔH value is 3.4 kcal/mole, which is exceptionally low. The smectic phase which is present for propyl and pentyl homologues is particularly attractive for investigating the S–N transition phenomenon. Similarly, 4''-alkyl-2',3'-difluoro-4-(3,5-difluoro-4-isothiocyanato-phenylethynyl)biphenyl (compounds **2a–b**) does not show smectic phase for short alkyl chain homologue (C2; ethyl homologue). Extending an alkyl chain to five carbons (C5; pentyl homologue) introduces a wide range of smectic phase with S–N phase transition at 116 °C.

Compound **3a**, a short chain homologue of 4-alkyl-3'',5''-difluoro-4''-isothiocyanato[1,1';4'1'']terphenyl series, exhibited only nematic phase while pentyl homologue (compound **3b**) showed also smectic phase with transition to nematic at 112.4 °C. A lower melting point temperature of longer alkyl chain compounds, while smectic phase appeared within the mesomorphic sequence, was revealed in all three sets of the compounds. Compounds without smectic phase had significantly higher melting temperatures. Therefore, their application potential is limited to mixture formulations also because their melting point heat enthalpy is typically significantly higher than their longer alkyl chain counterparts, Table I.

Tolane isothiocyanates (Structure IV) show no mesomorphic phase while double lateral fluorination is exercised on the ring with terminal polar group and propyl or pentyl flexible chains as a second terminal moiety.

As for terphenyl isothiocyanates investigated in our current experiment, their birefringence was lower than that of phenyl-tolane compounds. This effect is mainly because of a shorter, conjugated rigid core as there is no carbon-carbon triple bond involved in terphenyl structure. Molecular modeling supported length difference of the rigid core of 2.56 Å based on 17.92 and 15.36 Å was calculated for structures I(II) and III, respectively. HyperChem molecular modeling software was applied with modified neglect of diatomic differential overlap (MNDO) calculation method.

The measured temperature dependent birefringence followed the theoretical prediction by eq. (2) regardless of compound's rigid core structure and either smectic and nematic or nematic only mesomorphic sequence. Results are detailed in our earlier work.²²⁾ Figures 1(a) and 1(b) show the measured visco-elastic coefficient data that exhibit the opposite trend. Here, it is obvious for the compounds with smectic phase (**1b** and **1c**) that visco-elastic coefficient values resulting from relaxation time measurement do not follow theoretical prediction at the temperatures near the S–N transition. In fact, the γ_1/K_{11} decreases instead of increasing as the temperature decreases, leading to 45 and 35% lower than the expected value from theoretical fitting at the same temperature, respectively, for the phenyl-tolane and terphenyl compound **1c** and **2b**. Meanwhile, compounds without smectic phase behaved within our expectation with their visco-elastic coefficient following closely the theoret-

Table I. Single compounds structures and phase transition temperatures.

No.	R	L	Compound	Phase transition temperature (°C)	$[\Delta H]$ Cr-N (cal/mol)
1a	C ₂ H ₅ -	-NCS	C2PP(23F)TP(3F)NCS	Cr 73.7 N 223.3 Iso	5452
1b	C ₃ H ₇ -	-NCS	C3PP(23F)TP(3F)NCS	Cr 82.2 S 89.2 N 240.5 Iso	5814
1c	C ₅ H ₁₁ -	-NCS	C5PP(23F)TP(3F)NCS	Cr 53.5 S 135.0 N 218.0 Iso	3359
2a	C ₂ H ₅ -	-NCS	C2PP(23F)TP(35F)NCS	Cr 97.2 N 204.3 Iso	5807
2b	C ₅ H ₁₁ -	-NCS	C5PP(23F)TP(35F)NCS	Cr 46.0 S 116.1 N 202.2 Iso	6380
3a	C ₃ H ₇ -	-NCS	C3PPP(35F)NCS	Cr 106.9 N 202.6 Iso	3359
3b	C ₅ H ₁₁ -	-NCS	C5PPP(35F)NCS	Cr 96.9 S 112.4 N 188.6 Iso	2174
4a	C ₃ H ₇ -	-NCS	C3PTP(35F)NCS	Cr 51.6 Iso	6300
4b	C ₅ H ₁₁ -	-NCS	C5PTP(35F)NCS	Cr 46.5 Iso	7100

ical prediction. Consequently, the FoM calculated for the compounds with S-N transition was also affected. As shown in Figs. 2(a) and 2(b), the FoM of phenyl-tolane and terphenyl compounds is 38 and 71% higher than the predicted ones when measured at a temperature close to a S-N boundary.

Most of single compound liquid crystals possess a relatively high melting point and their nematic phase temperature range is not wide enough for practical applications. Therefore formulating eutectic mixtures is a necessary step. Based on previous results for single phenyl tolane and terphenyl compounds we formulated several mixtures with various concentration of the components listed in Table I. Primary interest in this case was to closely monitor S-N pretransitional effect on FoM, similar to single compounds study while changing the temperature of S-N transition. To shift the temperature of smectic-nematic transition we balanced formulation of our "M" mixtures by changing the ratio between phenyl-tolane and terphenyl compounds. Additionally, mixtures were treated with 10–25 wt % of isothiocyanatotolane compounds (Structure IV) to differentiate more the structures involved into composition and, therefore, enforce smectic to nematic transition shift toward lower temperatures. As a result, we obtained several mixtures based on the same set of components but with different S-N phase transition temperature. Three representative mixtures (designated as M1, M2, and M3) with S-N phase transition were chosen for this report. Difference in

the mixture compositions resulted in a gradually decreasing S-N phase transition temperature as shown in Fig. 3. Table II shows the concentration of the components in mixture M1, M2, and M3. The clearing and S-N transition temperatures (°C) of M1, M2, and M3 are [184, 115], [149, 69], and [120, 31], respectively. Similar to the single compounds, the temperature dependent birefringence of these mixtures also follows the theoretical prediction [eq. (2)] well. Birefringence of the mixtures varies upon different concentration of Structures I–IV. Moreover significant drop in clearing point temperature results in a lower Δn at the extrapolated temperature of 25 °C (Fig. 4). Detailed analysis of a visco-elastic coefficient reveals that mixtures M1 and M2 exhibit a similar reversed trend as smectic single compounds.

Figure 5 shows the measured temperature dependent visco-elastic coefficient of the three mixtures investigated. The visco-elastic coefficient of M1 and M2 was significantly lower than the theoretical prediction. Measured γ_1/K_{11} of M1 and M2 is only 56 and 54% of the theoretical value at 2 °C above the respective S-N transition, which is 117 °C for M1 and 71 °C for M2. However, mixture M3 shows no reversed trend in γ_1/K_{11} even in very close proximity to the S-N transition temperature, as depicted in Fig. 5. Consequently, the FoM of M1 and M2 shows significant increase (53 and 48%, respectively) while mixture M3's FoM value decreases with temperature until nematic to smectic transition takes place at 31 °C, as shown in Fig. 6. At this point

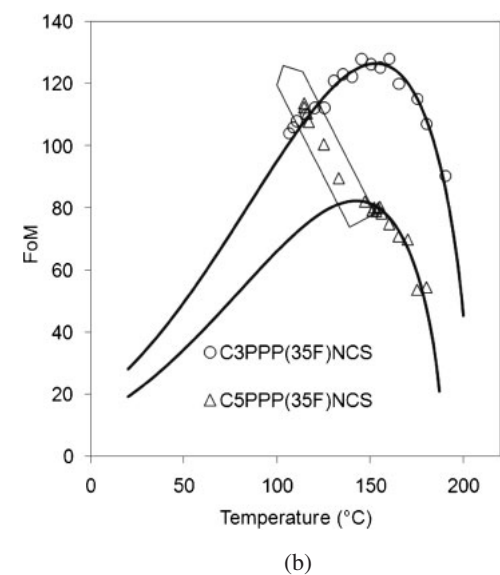
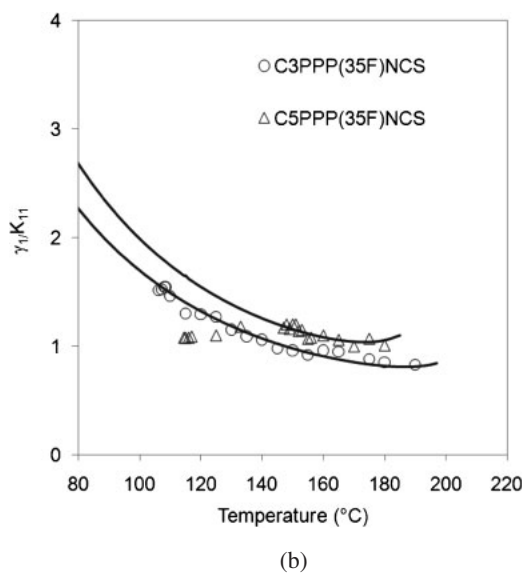
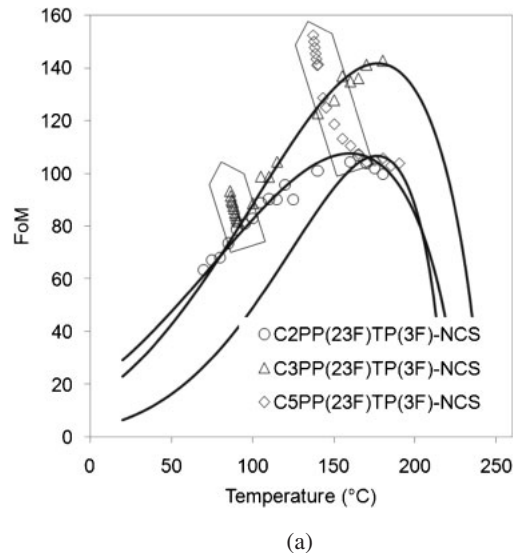
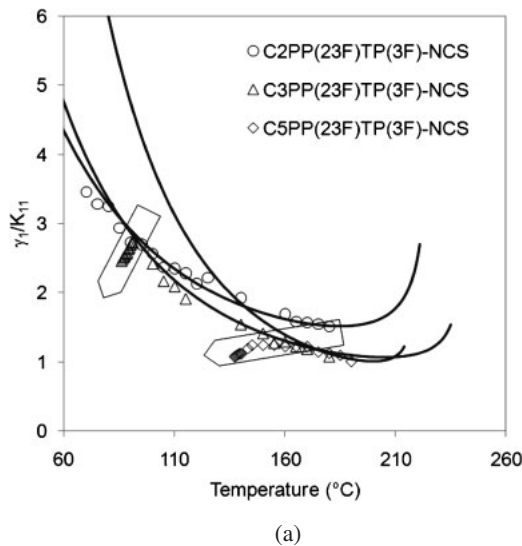


Fig. 1. Temperature dependent visco-elastic coefficient of (a) trifluorinated phenyl-tolane isothiocyanates, and (b) difluorinated tertphenyl isothiocyanates.

Fig. 2. Temperature dependent figure of merit of (a) trifluorinated phenyl-tolane isothiocyanates, and (b) difluorinated tertphenyl isothiocyanates.

we do not fully understand the reason why the reversed trend of visco-elastic coefficient was not observed when the S–N transition took place at below 40 °C. Here we consider that either the amount of tolane compounds (Structure IV) is too high to enable local smectic domain formation or impact of overall higher viscosity at lower temperature of the S–N transition (31 °C in case of M3) may diminish the investigated phenomenon. Increase of the rotational viscosity, as the temperature decreases, reduces molecule’s ability for quick relaxation. At a high operational temperature, rotational viscosity is low. As a result, the effect of reverse change on splay elastic constant can be noticeable.

4. Conclusions

Detailed study of flow viscosities, dielectric anisotropy and elastic constants of the cyanobipheyl systems near smectic to nematic transition are known for cyanobiphenyl type of liquid crystals and are widely described and discussed by

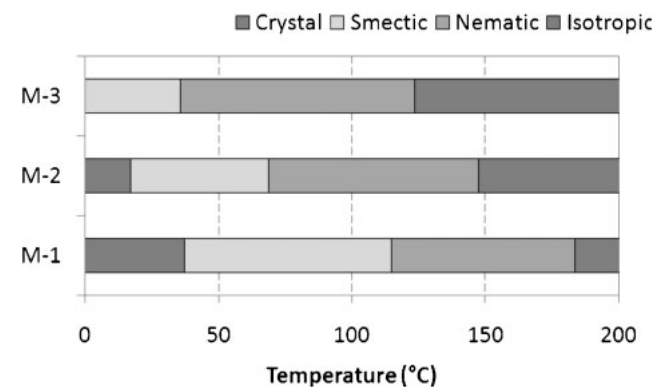


Fig. 3. Mesomorphic properties of isothiocyanates based high birefringence mixtures.

several authors.⁵⁻¹⁰ The conclusion of some of these experiments shows that at the temperatures slightly higher than smectic to nematic transition there is significant,

Table II. Components concentration in M1, M2, and M3 mixtures designed for our experiment.

No	Compound	Eut*	M1	M2	M3
		(wt %)	(wt %)	(wt %)	(wt %)
1a	C2PP(23F)TP(3F)NCS	13			
1c	C5PP(23F)TP(3F)NCS	19			
2a	C3PP(23F)TP(35F)NCS	3	100	80	60
2b	C5PP(23F)TP(35F)NCS	18			
3a	C3PPP(35F)NCS	16			
3b	C5PPP(35F)NCS	31			
			+	+	+
4a	C3PTP(35F)NCS	36	0	20	60
4b	C5PTP(35F)NCS	64			

*Near eutectic composition of smectogenic compounds and diluter (4a–b).

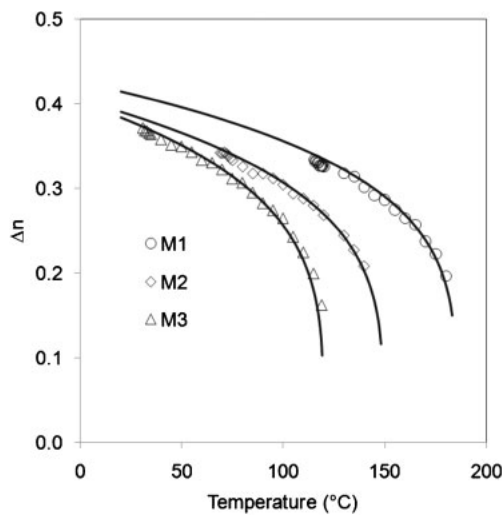


Fig. 4. Temperature dependent birefringence of isothiocyanates based high birefringence mixtures.

opposite to theoretical, change of the splay elastic constant K_{11} . At the same time, rotational viscosity remains rather unaffected.²⁷⁾ Phenomenon of opposite change of visco-elastic coefficient reported here is observed for the high birefringence phenyl-tolane and terphenyl isothiocyanates and first time for their mixtures. Comparison of our results on viscoelastic coefficient from measured optical relaxation time with the results for cyanobiphenyl compounds shows good agreement. Investigation of isothiocyanato phenyl-tolanes and terphenyl compounds shows dramatic decrease of viscoelastic coefficient at the close proximity of a nematic to smectic phase transition. Consequently, FoM achieves the values higher than measured at the optimum operating temperature according to eq. (3). However, to utilize the observed phenomenon, the device temperature should be controlled within 1–4°C. We extended our investigation to high birefringence isothiocyanato phenyl-tolanes and terphenyl based mixtures. Mixtures, based entirely on laterally fluorinated phenyltolane isothiocyanates, terphenyl, and tolane isothiocyanates show similar behavior as reported for single compounds. Exception within several investigated systems was M3 mixture. There was no obvious improve-

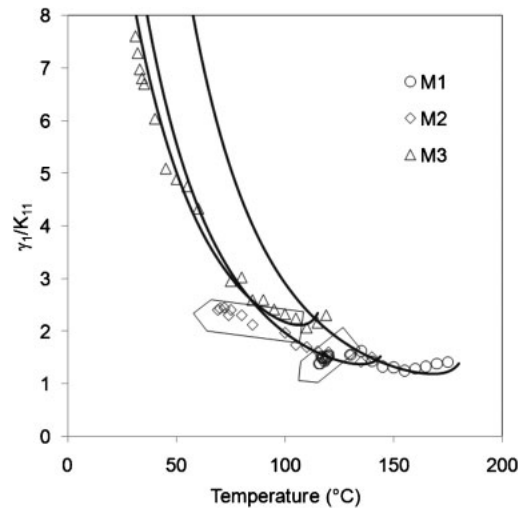


Fig. 5. Temperature dependent visco-elastic coefficient of isothiocyanates based high birefringence mixtures.

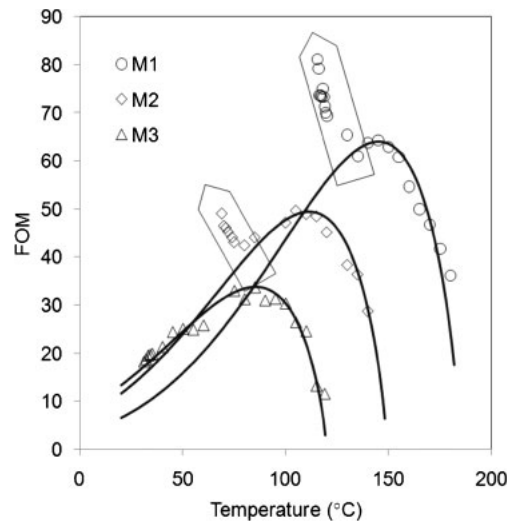


Fig. 6. Temperature dependent FoM of isothiocyanates based high birefringence mixtures.

ment observed in close proximity of smectic to nematic transition. We consider two possible mechanisms of diminishing tailored phenomenon. Firstly amount of tolane compounds (Structure IV) is too high to enable local smectic domains formation. Secondly impact of overall higher viscosity at lower temperature of the smectic to nematic transition could reduce molecules ability to quickly relax back and therefore the expected reverse change of the splay elastic constant cannot be observed. Although, previously reported experiments indicate adequate thermal stability of similar materials,^{16,28)} the temperatures at which we operate single LCs for this experiment could be too high for reliable long term operation. Therefore, we will further continue to search similar systems with reverse trend in γ_1/K_{11} and S–N transition temperature close to room temperature. The low operational temperature will be beneficial from LCs thermal stability standpoint.

- 1) S. Gauza, K. Czupryński, R. Dąbrowski, K. Kenig, W. Kuczyński, and F. Goc: *Mol. Cryst. Liq. Cryst.* **351** (2000) 287.
- 2) S. Gauza, M. Brodzik, R. Dąbrowski, J. Przedmojski, and B. Ważyńska: *Phase Transitions* **60** (1997) 223.
- 3) R. Dąbrowski, K. Czupryński, J. Przedmojski, and B. Ważyńska: *Liq. Cryst.* **14** (1993) 1359.
- 4) P. H. J. Kouwer, S. J. Pickenb, and G. H. Mehl: *J. Mater. Chem.* **17** (2007) 4196.
- 5) A. Yethiraj, Z. Sun, R. Y. Dong, and E. E. Burnell: *Chem. Phys. Lett.* **398** (2004) 517.
- 6) J. Jadżyn and G. Czechowski: *Phys. Rev. E* **64** (2001) 052702.
- 7) W. H. de Jeu, W. J. A. Goossens, and P. Bordewijk: *J. Chem. Phys.* **61** (1974) 1985.
- 8) P. E. Cladis: *Phys. Rev. Lett.* **31** (1973) 1200.
- 9) B. R. Jaishi and P. K. Mandal: *Phase Transitions* **78** (2005) 569.
- 10) S. DasGupta and S. K. Roy: *Phys. Lett. A* **306** (2003) 235.
- 11) *Thermotropic Liquid Crystals: Recent Advances*, ed. A. Ramamoorthy (Springer, Heidelberg, 2007) Chap. 8.
- 12) A. de Vries: *Mol. Cryst. Liq. Cryst.* **10** (1970) 219.
- 13) S. Gauza, H. Wang, C. H. Wen, S. T. Wu, A. Seed, and R. Dąbrowski: *Jpn. J. Appl. Phys.* **42** (2003) 3463.
- 14) A. Spadło, R. Dąbrowski, M. Filipowicz, Z. Stolarz, J. Przedmojski, S. Gauza, Y. H. Fan, and S. T. Wu: *Liq. Cryst.* **30** (2003) 191.
- 15) S. Gauza, C. H. Wen, S. T. Wu, N. Janarthanan, and C. S. Hsu: *Jpn. J. Appl. Phys.* **43** (2004) 7634.
- 16) S. Gauza, C. H. Wen, B. Tan, and S. T. Wu: *Jpn. J. Appl. Phys.* **43** (2004) 7176.
- 17) S. Gauza, C. H. Wen, B. Wu, S. T. Wu, A. Spadło, and R. Dąbrowski: *Liq. Cryst.* **33** (2006) 705.
- 18) S. Gauza, S. T. Wu, A. Spadło, and R. Dąbrowski: *J. Disp. Technol.* **2** (2006) 247.
- 19) S. Gauza, X. Zhu, S. T. Wu, W. Piecek, and R. Dąbrowski: *J. Disp. Technol.* **3** (2007) 250.
- 20) M. Jiao, Z. Ge, Q. Song, and S. T. Wu: *Appl. Phys. Lett.* **92** (2008) 061102.
- 21) J. Harriman, S. Gauza, S. T. Wu, D. Wick, B. Bagwell, T. Martinez, D. Payne, and S. Serati: *Proc. SPIE* **6135** (2006) 61350C.
- 22) S. Gauza, A. Parish, S. T. Wu, A. Spadło, and R. Dąbrowski: *Liq. Cryst.* **35** (2008) 711.
- 23) S. T. Wu, U. Efron, and L. D. Hess: *Appl. Opt.* **23** (1984) 3911.
- 24) S. T. Wu, A. M. Lackner, and U. Efron: *Appl. Opt.* **26** (1987) 3441.
- 25) S. Gauza, A. Parish, S. T. Wu, A. Spadło, and R. Dąbrowski: *Liq. Cryst.* **35** (2008) 483.
- 26) A. Parish, S. Gauza, S. T. Wu, J. Dziaduszek, and R. Dąbrowski: *Liq. Cryst.* **35** (2008) 79.
- 27) Su. DasGupta, P. Chattopadhyay, and S. K. Roy: *Phys. Rev. E* **63** (2001) 041703.
- 28) C. H. Wen, S. Gauza, and S. T. Wu: *Liq. Cryst.* **31** (2004) 1479.