

Electro-optic bistability in organosiloxane bimesogenic liquid crystals

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In this paper we report the electro-optic characterization of two homologous series of low molar mass bimesogenic siloxane-containing liquid crystals. The materials used have two alkoxyphenyl mesogenic units with variable alkyl chain joined by a two- or five-siloxane moiety and all exhibit stable smectic *A* mesophases over wide temperature ranges (up to 100 °C wide). Due to their inherent ruggedness these materials have potential for use in polarizer-free, bistable, scattering display and storage devices. The bistable modes are at low and high frequencies. The low frequency mode (write) is a highly scattering focal conic texture resulting from electrohydrodynamic instabilities while the high frequency mode (erase) is a clear state due to dielectric reorientation of the material. Both modes are preserved upon removal of the applied electric field. We present threshold voltages as a function of temperature, frequency, and cell thickness and response times as a function of voltage for each of the bistable modes. We find reduced threshold voltages ($5 \leq V_{th} \leq 12 \text{ V}/\mu\text{m}$) and response times that are strongly dependent on applied voltage ($50 \text{ ms} \leq \tau \leq 10 \text{ s}$). These operating conditions would suggest that these materials are particularly suitable for slow update, large area, low power information panels and displays.

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I. INTRODUCTION

In contrast to nematic and ferroelectric based displays, devices based upon the smectic *A* (S_A) mesophase have received relatively little attention. Devices have been proposed that can be switched thermally and electrically.¹ In addition, recent developments have shown that S_A devices can be formed on flexible substrates.² Advantages include polarizer-free operation and bistability of the write and erase states. Disadvantages, hitherto, have been slow response times (10–100 ms) at high applied voltages and sensitivity to mechanical shock. Attempts have been made to improve ruggedness by the use of high molecular weight side chain liquid crystalline polymers,³ but with relatively slow response times. Previous work has shown the benefit of low molar mass siloxane-containing monomesogens,^{4,5} for inherent ruggedness and faster electro-optic response in comparison with such polymers. The aim of this paper is to examine in detail the electro-optic behavior of two series of bimesogenic organosiloxane liquid crystals and compare their electro-optic properties both with the polymer and the organosiloxane monomesogens.

A schematic of a bistable S_A device is shown in Fig. 1. The write mode is a highly scattering texture induced by electrohydrodynamic instabilities (EHDIs) resulting from the motion of doped charged impurities at dc/low ac frequencies. The erase mode, to the optically clear state, is by dielectric reorientation at higher ac frequencies. The scattering and clear textures show long term stability, with no degradation

observed even in samples older than 10 years. Although we are mainly concerned with electro-optic bistability in this work, it is also possible to generate gray scale by applying an erase voltage less than the threshold for full erasure.

Theoretical descriptions of such a device have been proposed,^{6,7} predicting the threshold of both the onset of EHD and the dielectric reorientation. The general forms of these are given by Eqs. (1) and (2).

$$V_{\text{write}}^2 \propto \frac{d}{\epsilon_{\parallel} [1 - (\sigma_{\parallel}/\sigma_{\perp})]}, \quad (1)$$

$$V_{\text{erase}}^2 \propto \frac{d}{\Delta\epsilon}. \quad (2)$$

In these proportionalities, d is the sample thickness, σ_{\parallel} and σ_{\perp} are the conductivities parallel and perpendicular to the

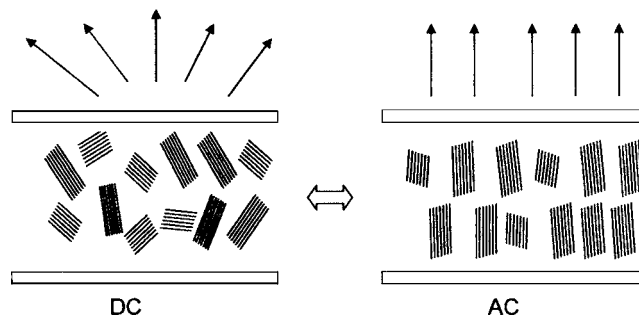


FIG. 1. Schematic operation of the smectic *A* scattering device.

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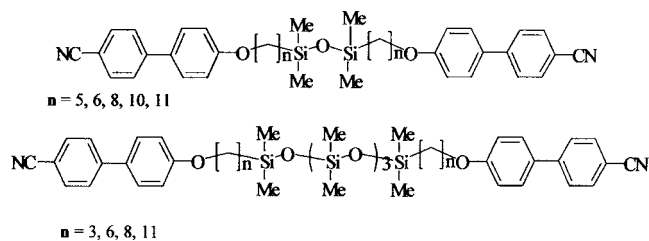


FIG. 2. Structure of the liquid crystalline materials used in the paper.

director, ϵ_{\parallel} and ϵ_{\perp} are the dielectric constants along and perpendicular to the director, respectively, and $\Delta\epsilon(=\epsilon_{\parallel}-\epsilon_{\perp})$ is the dielectric anisotropy of the molecule. V_{write} refers to the induction of the highly scattering texture while V_{erase} refers to the scattering to clear transition.

II. MATERIALS

In this paper two series of bimesogenic organosiloxane materials synthesized by Newton *et al.*⁸ are studied. The materials are referred to as *ABA* compounds, where *A* the length of the alkyl chain attached to a 4-(ω -alkenyloxy)-4'-cyanobiphenyl mesogenic unit and *B* a dimethylsiloxane joining moiety. The series in the present study are referred to as *A/2/A* and *A/5/A*, respectively, with the schematic structures shown in Fig. 2. All the materials exhibit enantiotropic S_A phases and are stable over wide temperature ranges (Table I). The effect of the extra siloxane spacer on the phase behavior is evident; the *A/5/A* materials exhibit stable S_A phase ranges of the order of 50–100 °C. In addition, all of the materials supercool readily to well below their crystallization temperatures. The phase behavior was characterized by differential scanning calorimetry (DSC) and polarizing optical microscopy. X-ray studies⁹ have revealed that organosiloxane mesogens adopt a partially interdigitated bilayer arrangement (Table II). All of the materials exhibited small 2–3 °C wide biphasic regions before the S_A to isotropic transition, which is unrelated to sample purity and is a reproducible property of these organosiloxane materials. To enhance optical scattering in the samples, due to EHDI, a small

TABLE I. Transition temperatures of the materials used in the work determined by DSC and polarizing microscopy (see Ref. 8).

Material	Crystal- S_A (°C)	S_A -I (°C)
5/2/6	72.1	92.1
6/2/6	96.4	91.1
8/2/8	87.7	102.1
10/2/10	78.0	109.0
11/12/11	74.6	111.1
3/5/3	-52.7 ^a	29.1
6/5/6	-56.7 ^a	55.5
8/5/8	16.0	72.5
11/5/11	33.0	81.9

^aIndicates glass transition temperature.TABLE II. Calculated molecular lengths and smectic layer spacing from Ibn-Elhaj *et al.* (see Ref. 9).

Material	Smectic period d (nm)	Calculated molecular length L (nm)	$2d/L$
6/2/6	3.06	4.17	1.47
8/2/8	3.53	4.51	1.56
10/2/10	3.96	4.96	1.60
11/2/11	4.24	5.3	1.60
3/5/3	3.57	4.3	1.58
6/5/6	4.2	5.17	1.62
11/5/11	5.24	6.16	1.70

quantity of cetyltrimethylammonium bromide (CTAB, Sigma-Aldrich Ltd.) ionic dopant is added at a concentration of approximately 0.01 % w/w.

III. EXPERIMENT

The experimental setup used in the work is a microscope based, temperature-controlled electro-optic characterization rig. In this arrangement the test cell is mounted on a heating stage and controller (Linkam Ltd. TMS 600 and TP91) attached to a polarizing microscope (Olympus BH-2). The accuracy of the heating stage is 0.1 °C. Voltages are applied to the electro-optic cells using a function generator (Thurlby Thandar TG1304) amplified by an in-house amplifier capable of applying square wave pulses of up to 300 V rms. The electro-optic response is detected by a photodiode/amplifier circuit mounted on the top of the microscope, with experimental control and data analysis automated by personal computer (PC)/digital storage oscilloscope. The test cells employed in the work were manufactured to specification by EEV Ltd. (Lucid). They are 14 μm thick with 25 mm² ITO electrodes and have rubbed polyimide alignment layers; however, it was noted that all the materials aligned in a focal conic texture irrespective of alignment agent used. Dielectric and conductivity measurements were made with an LCR meter (Wayne Kerr 4250) using the defect planar and homeotropic textures for measurements parallel and perpendicular to the smectic layers, respectively. Electro-optic measurements on the samples were carried out between parallel/parallel polarizers as this gives the greatest transmission ratio and is indicative of real device performance. Phase behavior of the samples was characterized using polarized optical microscopy.

In this work the threshold voltage is defined as the rms voltage producing a 50% light modulation for either the write (scattering) or erase (clear) mode. For the erase switch the voltage was applied at 1 kHz and for the write mode a frequency of 1 Hz was used. The following measurements were made on the samples: threshold voltages as a function of shifted temperature, frequency, and cell thickness and

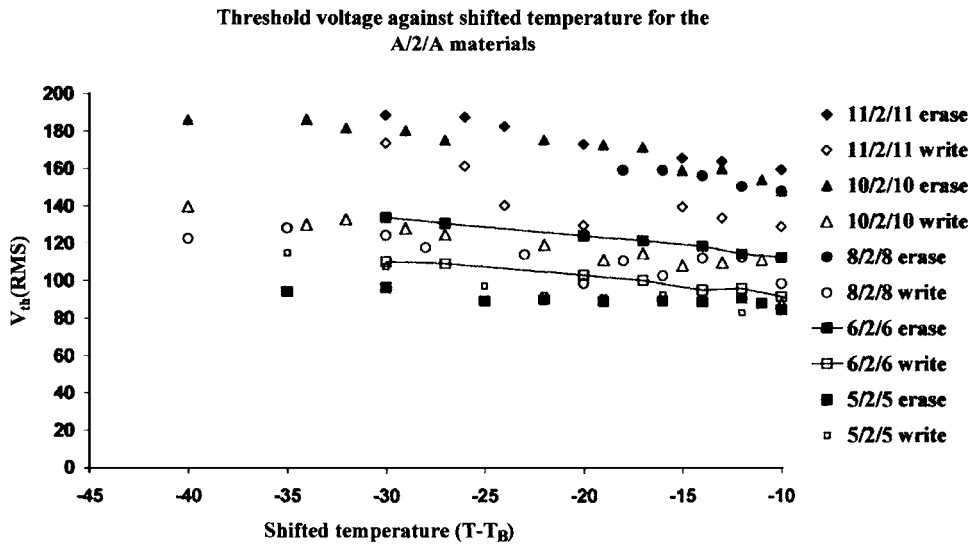


FIG. 3. Threshold voltages for the write and erase modes against shifted temperature for the A/2/A series.

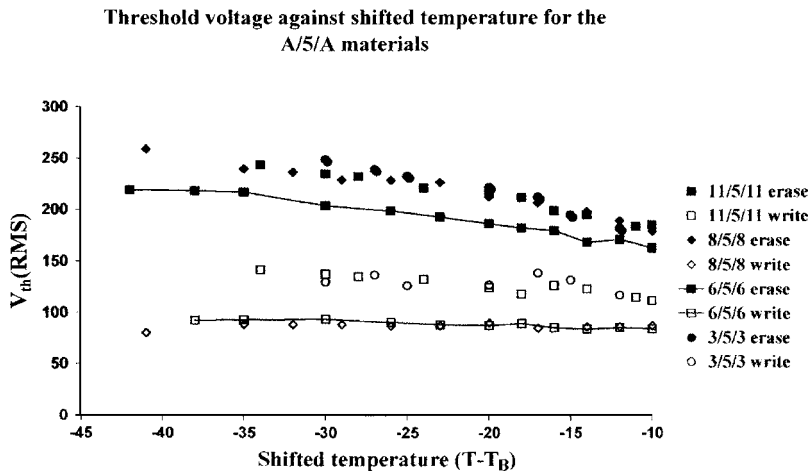


FIG. 4. Threshold voltage for the write and erase modes against shifted temperature for the A/5/A series.

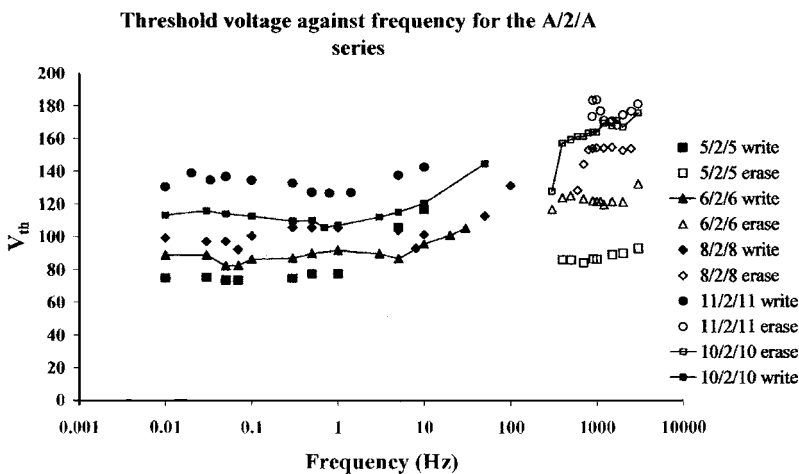


FIG. 5. Threshold voltage for the write and erase modes against frequency for the A/2/A series at a shifted temperature of -10°C .

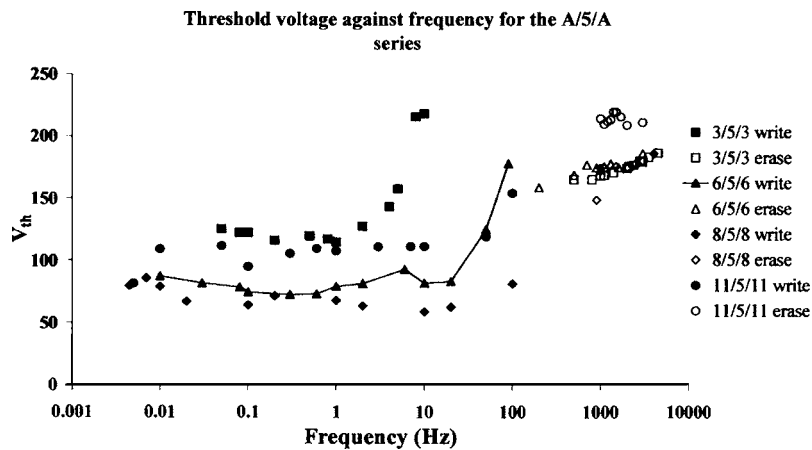


FIG. 6. Threshold voltage for the write and erase modes against frequency for the A/5/A series at a shifted temperature of -10°C .

response times as a function of applied voltage. The shifted temperature is defined as $T - T_B$, where T_B is the onset of the biphasic region of the sample on heating.

IV. RESULTS AND DISCUSSION

A. Threshold voltage as a function of temperature

The threshold voltages for the write and erase modes against shifted temperature, for the A/2/A and A/5/A series, are shown in Figs. 3 and 4. From the data one can see that the erase threshold is greater than, or equal to, that of the

write for all the compounds. This is opposite behavior to that found in non-siloxane-containing mesogens.¹ The 5/2/5 material showed an equivalence in the write and erase thresholds ($\sim 5 \text{ V}/\mu\text{m}$). The threshold voltages follow a similar trend to that seen in monomeric organosiloxane compounds,^{4,5} showing a large variation close to the biphasic region of the material before tending to a regime of very weak temperature dependence. This would be very important for practical devices since the electronic drive schemes would not need to include temperature compensation. For

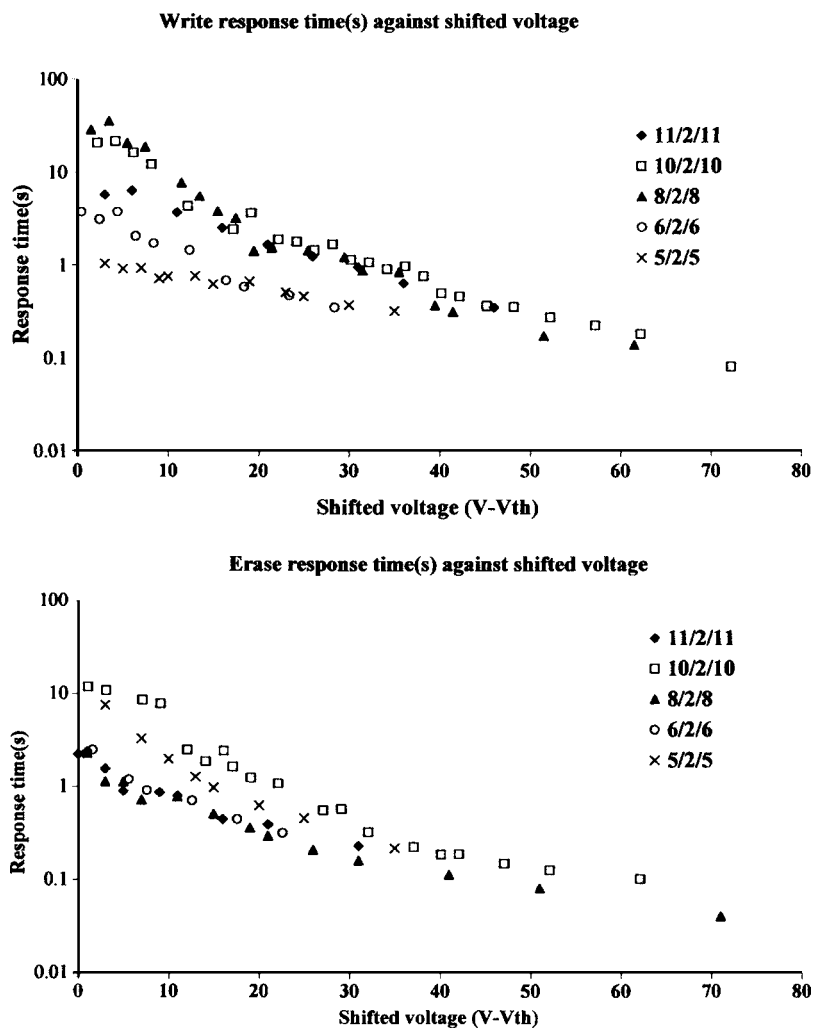


FIG. 7. Response times (s) as a function of shifted voltage from the threshold voltage at a shifted temperature of -10°C for the A/2/A series.

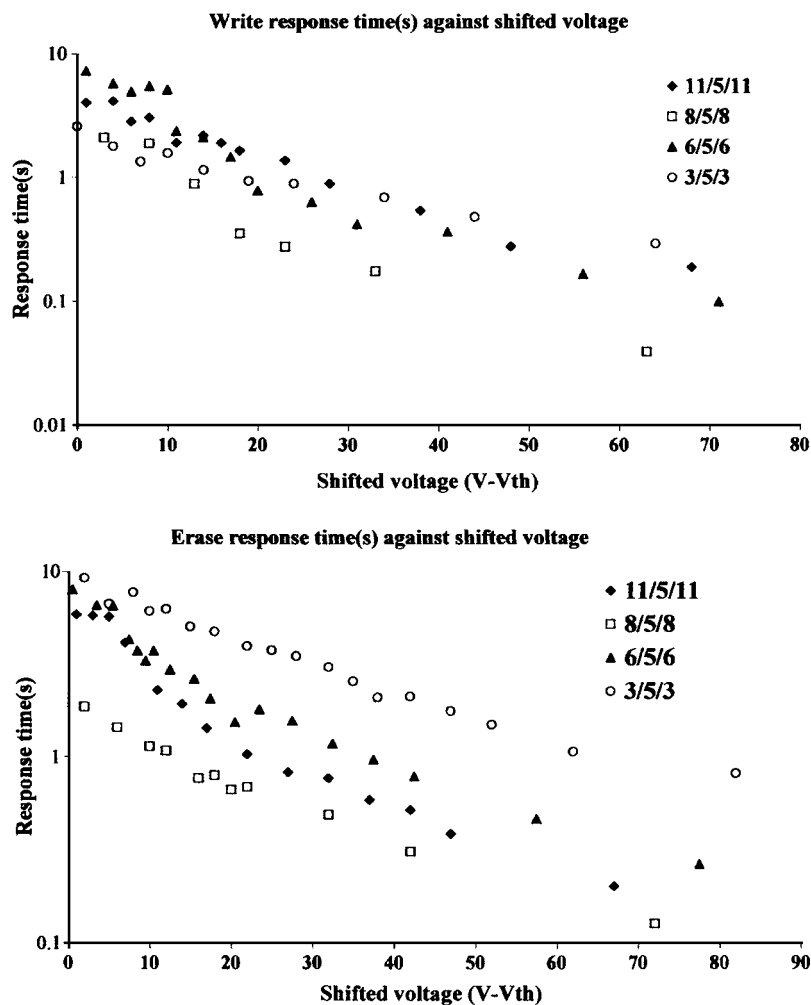


FIG. 8. Response times (s) as a function of shifted voltage from the threshold voltage at a shifted temperature of -10°C for the $A/5A$ series.

clarity, only the weak temperature dependent regime is shown. For the $A/2/A$ materials, both of the threshold voltages increased with increasing n , tending toward a saturation value. This supports the x-ray data for the $n=10$ and 11 homologs which show the same $2d/L$ values, indicating similar decoupling of the mesogenic and siloxane moieties. The $A/5/A$ results show a clear odd-even effect for the write threshold, with the 8/5/8 and 6/5/6 materials showing lower values than the 3/5/3 and 11/5/11 homologs; however, this split is not seen in the erase threshold. The difference between these materials is the number of methylene units in the flexible spacer and according to the two-conformer model proposed by Ferrarini *et al.*¹⁰ the shape of the molecule differs depending on whether there is an even or odd number of units. Conventionally, semiflexible molecules with an odd number of units exhibit a bent shape in the *all-trans* conformation of the spacer chain whereas an even-spaced molecule exhibits a more elongated linear shape. In this case, the situation is complicated by the siloxane moiety and two spacer chains. According to Eq. (1) the lower write thresholds that are observed for the even compounds suggest that in these compounds the ratio $\sigma_{\parallel}/\sigma_{\perp}$ is greater than the odd. Further measurements are being made to confirm this.

In order to explain the difference in the write thresholds between the $A/2/A$ and $A/5/A$ series, one must consider the

smectic structure formed in each case. From the x-ray data given in Table II, the $A/2/A$ homologs adopt a more interdigitated layer structure than the $A/5/A$, as evidenced by lower $2d/L$ values. This would suggest that there is greater impairment to ionic flow along the smectic layer. This hypothesis is supported by a σ_{\perp} value of $1.1 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$ for 8/2/8 compared with $4.4 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$ for 8/5/8, with similar σ_{\parallel} data for both materials ($2.3 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$).

B. Threshold voltage as a function of frequency

The threshold voltages as a function of frequency, at a fixed shifted temperature of -10°C , are shown in Figs. 5 and 6. In general, the bimesogenic liquid crystals show lower write and erase thresholds than the monomesogenic compounds⁴ due to their enhanced dielectric coupling. The values of $\Delta\epsilon$, measured at $T-T_B=-15^{\circ}\text{C}$, for 5/2/5 and the BA material 5/2 are 3.5 and 0.8, respectively. The difference between the magnitudes of the threshold for both write and erase is small and indeed less than that for the monomesogens. This is an important result from a device perspective since dual frequency operation could be readily achieved, e.g., by switching the drive field from 500 to 50 Hz. All the curves show similar responses: increasing write voltages as the critical frequency is approached, then a transition to the

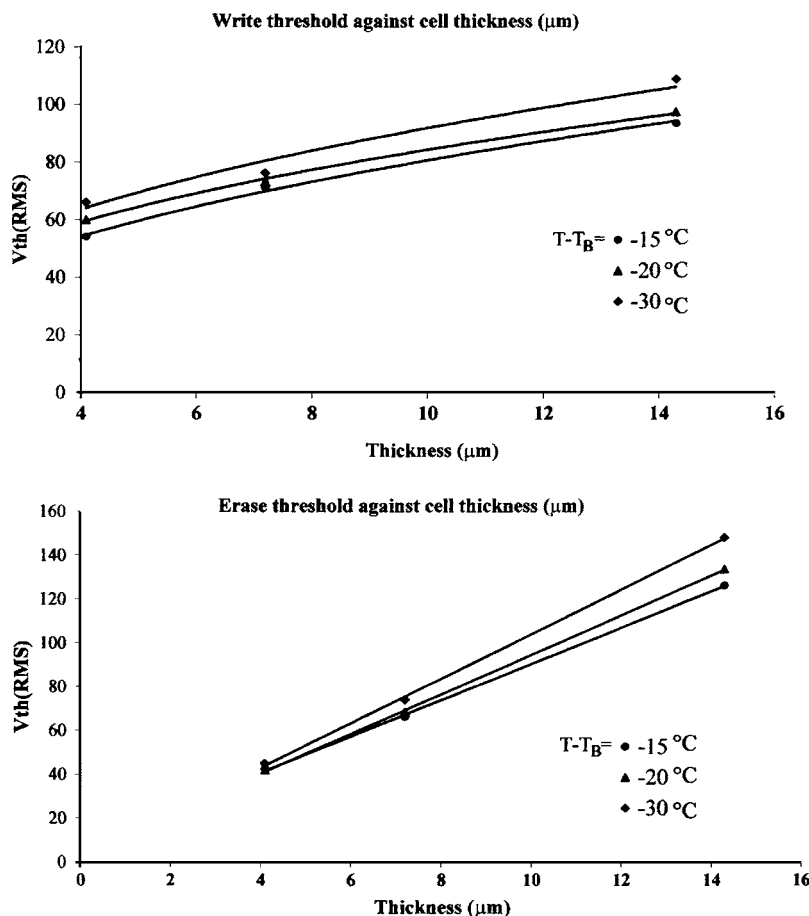


FIG. 9. Threshold voltages against cell thickness for the 6/2/6 mesogen.

higher erase threshold. For clarity the behavior in the critical frequency region is omitted, but in this regime it is possible to obtain both types of switching at a single frequency, depending on the initial state of the system. From the data, one can see several structural dependencies. For the $A/2/A$ materials the threshold at a given frequency appears to be a function of the alkyl chain length, with the $5/2/5$ homolog showing particularly low thresholds (~ 5 V/ μm) across the whole frequency range. This is a similar threshold to that reported for the nonsiloxane material¹ 4'-*n*-octyl-4-cyano-biphenyl (8CB) but without the superior mechanical resistance of the siloxane materials.⁴ This can be qualitatively demonstrated by greater resistance of the siloxane liquid crystals to applied mechanical shear than 8CB in the clear (homeotropic) texture.

For the $A/5/A$ series, one again sees a pronounced odd-even effect, with the 6/5/6 and 8/5/8 materials showing reduced write thresholds across the lower frequency range, but there is no discernible effect in the erase data.

C. Response time as a function of voltage

The response times as a function of shifted voltage from the threshold voltage, measured at a shifted temperature of -10°C , are shown in Figs. 7 and 8. As can be seen from all the data, the response time shows a strong dependency on applied voltage (V_{app}) for both switches. Typical values for the $A/2/A$'s are >10 s for $V_{\text{app}}=V_{\text{th}}$, falling to ~ 100 ms for $V_{\text{app}}=V_{\text{th}}+50$ V. For the $A/5/A$'s the data show much less spread; typical values are less than 10 s for $V_{\text{app}}=V_{\text{th}}$ and

100 ms for $V_{\text{app}}=V_{\text{th}}+50$ V. Further work is required to establish a response time-voltage relationship—for the above data no consistent correlation between materials could be found. However, there is widespread discrepancy in the literature regarding the power law dependency: Coates *et al.*¹ report $\tau_{\text{write}} \propto V^{-2.5}$ and $\tau_{\text{erase}} \propto V^{-5}$ for 8CB in a $20\ \mu\text{m}$ cell, while for the same material Hareng *et al.*¹¹ give $\tau_{\text{erase}} \propto (V - V_{\text{th}})^{-2}$.

Comparison of these data with polysiloxane polymers shows that the low molar mass materials used in this work switch much faster—typical values for polymer systems are minutes rather than seconds.³ On the other hand these materials switch slightly slower than 8CB and the monomesogen siloxane materials.⁴ Additionally, one finds that the write switch in the monomesogen compounds is much faster than the erase. It is suspected that this is due to greater restriction on ionic flow in the bimesogenic materials due to the partially interdigitated layer structure.

D. The role of cell thickness

Threshold voltages for the write and erase modes as a function of cell thickness for the material 6/2/6 are presented in Fig. 9. The data are shown for three shifted temperatures of -15 , -20 , and -30°C . A fit of these data reveals that for the write mechanism $V_{\text{th}} \propto \sqrt{d}$ and for erase $V_{\text{th}} \propto d$. Comparison with the literature shows agreement for the erase switch with Coates, *et al.*,¹ which is counter to the theoretical predictions, i.e., Eq. (2). It is suspected that the assumptions used in this model—that of modeling the scattering to clear

switch as a planar to homeotropic transition—are insufficient. For the write threshold the \sqrt{d} dependency is in agreement with theory but not with Coates *et al.*;¹ however, the difference could be due to the more limited range of cell thicknesses used in the present study (20–60 μm in Ref. 1). However, the cell thicknesses used herein were sufficient to give good on/off optical contrast, an effect noted before for organosiloxane based S_A scattering displays.⁴

V. CONCLUSION

We have presented the key electro-optic characterization parameters of two homologous series of bimesogenic organosiloxane liquid crystals. These materials have enantiotropic smectic A phases of wide temperature ranges, especially for the series with a five siloxane spacer which typically exhibits a phase range of $\sim 50^\circ\text{C}$. For each stable mode, write and erase, the threshold voltage was measured as a function of temperature and frequency. It was found that the magnitude of the write and erase thresholds was similar, such that dual-frequency devices can be readily achieved, and that the thresholds were almost temperature independent. For the 5/2/5 material equivalence in the write and erase thresholds was observed ($\sim 5\text{ V}/\mu\text{m}$). An odd-even effect in the write thresholds for the A/5/A series was seen and explained in terms of molecular conformation. In addition, response times were found to depend strongly on applied voltage (50 ms $\leq \tau \leq 10$ s). The extent of the partial bilayer structure that the materials adopt was used to explain the variation in electro-optic performance between the series. The thickness dependencies of the write and erase threshold voltages were found to be \sqrt{d} and d , respectively. In conclusion, it has been dem-

onstrated that siloxane-containing liquid crystals have much potential for use in electro-optic storage/display devices and simple mixtures of these materials should lead to broad temperature phase ranges. This work is in progress.

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