Influence of curing temperature and high birefringence on the properties of polymer-stabilized liquid crystals

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Abstract: We report the curing temperature effect on the performance of polymer-stabilized liquid crystals at λ=1550 nm. The curing temperature in the polymerization process is found to make a significant impact on the light scattering efficiency, hysteresis, operating voltage, and response time. Using a high birefringence liquid crystal mixture, we have improved the device contrast ratio while keeping low operating voltage, and fast response time. Potential applications of such a PSLC for light shutters, variable optical attenuators, and switchable polarizers are emphasized.

OCIS codes: (160.3710) Liquid crystals; (230.2090) Electro-optic devices

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References and links

1. R. A. M. Hikmet, "Electrically induced light scattering from anisotropic gels," J. Appl. Phys. **68**, 4406-4412 (1990).
2. R. A. M. Hikmet and H. J. Boots, "Domain structure and switching behavior of anisotropic gels," Phys. Rev. E **51**, 5824-5831 (1995).
3. H. Ren and S. T. Wu, "Anisotropic liquid crystal gels for switchable polarizers and displays," Appl. Phys. Lett. **81**, 1432-1434 (2002).
4. K. Hirabayashi, M. Wada and C. Amano, "Optical-fiber variable-attenuator arrays using polymer-network liquid crystal," IEEE Photon. Technol. Lett. **13**, 487-489 (2001).
5. K. Hirabayashi, M. Wada and C. Amano, "Liquid crystal variable optical attenuators integrated on planar lightwave circuits," IEEE Photon. Technol. Lett. **13**, 609-611, (2001)
6. F. Du and S. T. Wu, "Curing Temperature effects on liquid crystal gels", Appl. Phys. Lett. **83**,1310-1312 (2003)
7. I. Dierking, L. L. Kosbar, A. C. Lowe and G. A. Held, "Polymer network structure and electro-optic performance of polymer stabilized cholesteric textures. I. The influence of curing temperature," Liq. Cryst. **24**, 387-395 (1998).
8. T. Murashige, H. Fujikake,S. Ikehata and F. Sato, "Relationship of polymer molecular weight and cure temperature in photopolymerization-induced phase separation of liquid crystal and polymer fiber networks," Jpn. J. Appl. Phys. **41**, L 1152–L 1154 (2002)
9. J. M. Oton, J. M. S. Pena, and A. Serrano, "Light scattering spectral behavior of liquid crystal dispersions in silica glasses," Appl. Phys. Lett. **66**, 929-931 (1995).
10. S. T. Wu and D. K. Yang, *Reflective Liquid Crystal Displays*, (Wiley, New York, 2001)
11. S. Gauza, F. Du, J. R. Wu, S. T. Wu, A. Spadlo, R. Dabrowski, N. Janarthanan and C. S. Hsu, "High birefringence and low viscosity liquid crystal mixtures," Soc. Information Display, Tech. Digest **34**, 1054-1057 (2003).

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1. Introduction

Liquid crystal (LC) devices are attractive for optical network applications due to their compactness, low cost, and comparable performance to the optomechanical ones. Polymer-

stabilized liquid crystal (PSLC)[1-3] exhibits an anisotropic light scattering behavior and can be used as variable optical attenuators (VOA)[4,5], shutters, and polarizers.

In a PSLC cell, a low concentration (<10%) of diacrylate monomer is dissolved in an LC host and then injected to an empty cell with homogeneous alignment. A weak UV light is used to induce photopolymerization. In the voltage-off state, the polymer networks and LC molecules have the same orientation and thus the cell is highly transparent. With applied voltage, the polymer networks resist LC directors from being reoriented by the electric field. As a result, microdomains are formed and threshold voltage increased. The light polarization parallel to the rubbing direction is scattered and the orthogonal polarization is transmitted.

The major shortcomings of the PSLC for the abovementioned applications are inadequate contrast ratio, relatively high operating voltage, and noticeable hysteresis. Especially when a VOA is intended for λ=1550 nm, these drawbacks manifest. There is an urgent need to develop new methods for enhancing contrast ratio and reducing operating voltage.

In this article, we report a reflective-type PSLC with ~32 dB attenuation range, ~20 ms response time, and ~12 Vrms operating voltage achieved by combining a two-stage curing process and a high birefringence LC mixture. A detailed characterization of the curing temperature effects on attenuation range, hysteresis, operating voltage, and response time are presented. The high birefringence mixtures were shown to be useful, when used in combination with the temperature curing effect, for improving of the attenuation range while keeping low operating voltage and fast response time.

2. Sample preparation

To fabricate a PSLC cell, we mixed 4 wt% of bisphenol A dimethacrylate monomer in a Merck E44 LC mixture (Δn=0.26 at λ=589 nm). The LC/monomer mixture was injected into an empty cell with homogeneous alignment. The pretilt angle of the buffed polyimide alignment layers is about 3°. The sample cell was then exposed to a weak UV light (100 $\mu W/cm^2$) to induce polymerization. Being influenced by the surface rubbing effect, the polymer networks basically follow the same LC alignment direction. In the voltage-off state, the polymer networks and LC molecules have the same orientation and thus the cell is highly transparent. With applied voltage, the polymer networks resist LC directors from being reoriented by the electric field. As a result, the microdomains with disturbed LC orientation are formed. The light polarization parallel to the rubbing direction is scattered while the orthogonal polarization is not affected.

Curing process plays an important role in affecting the PSLC contrast ratio, operating voltage, hysteresis and response time in the visible spectral region [6]. In our new two-stage curing process, for the first half an hour the cell was kept at an elevated temperature during UV exposure. The elevated temperature procedure creates larger dispersion of polymer and LC [7]. At the higher cure temperature the time for polymer fibers growth is extended due to the slower polymerization. This results in formation of a coarse polymer network [8]. In fact, the coarser polymer network results in larger microdomain sizes in the voltage-on state. After the first 30 min of UV exposure at elevated temperature, the sample was moved away from the heating stage. The UV exposure continued for another 4 h at room temperature to further stabilize the polymer network.

3. Experimental results

To characterize the sample performance, we used a linearly polarized λ=1.55 μm laser beam. The experimental setup is shown in Fig. 1. During experiments, the LC rubbing direction was oriented parallel to the laser polarization. For a reflective-type device, in principle the reflector should be deposited in the inner side of the LC cell. For feasibility studies, we simply placed a dielectric mirror behind the sample cell. The laser light incidence angle is ~4° to the LC cell. Voltage-dependent reflectance was measured by a large dynamic range photodiode detector at 3° collection angle. Data were recorded by a computer-controlled LabVIEW system. In the voltage-off state, the sample is transparent. As the applied voltage increases, the laser beam is scattered by the micron-sized domains resulting in a decreased reflectance.
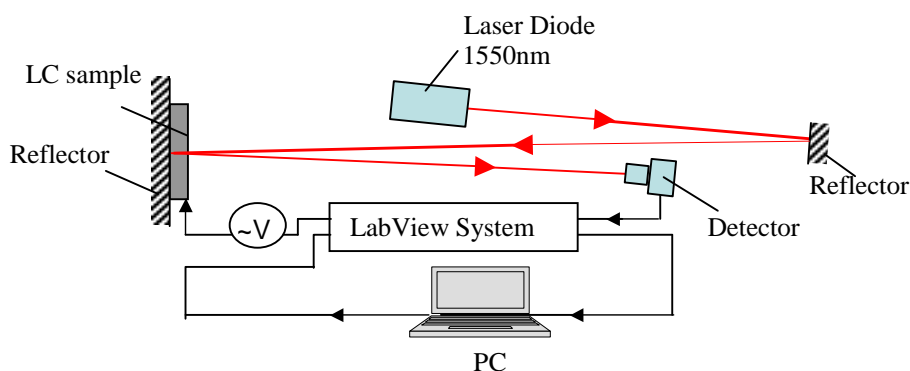
Fig. 1 The reflective experimental setup for measuring the properties of
the E44 PSLC cells

The performance of a PSLC is dependent on the LC material employed, cell gap, monomer concentration, wavelength, and curing temperature. We have studied various experimental conditions in order to optimize the device performance. A thinner cell gap and lower monomer concentration would lower the operating voltage except that its attenuation is sacrificed. On the other hand, a thicker cell gap and higher monomer concentration would result in a higher attenuation and faster response time. The tradeoff is the increased operating voltage. In our experiments, we found that a 16-μm cell gap and 4 wt% monomer concentration gave a reasonably good overall performance at λ=1.55 μm.

To investigate the curing temperature effects of the 16-μm 4 wt% PSLC samples, we measured the voltage-dependent reflectance at λ=1.55μm. The curing temperature studied ranges from 23 to 85 °C. Results are shown on Fig. 2.
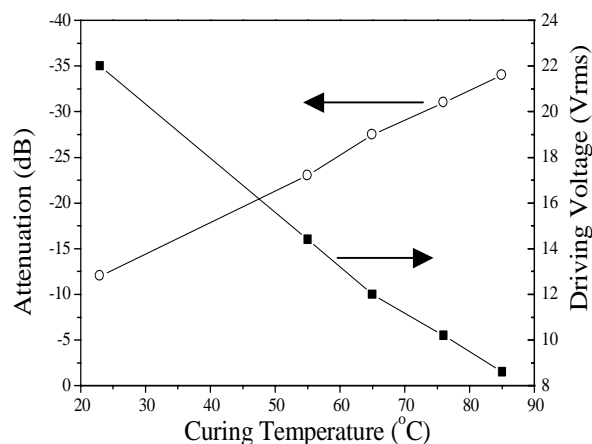

Fig. 2. The curing temperature dependent attenuation of the reflective E44 PSLC cell. Cell gap d=16μm, monomer concentration 4 wt%, laser wavelength λ=1.55μm and measurement temperature T=23 °C.

For the case of room temperature curing, the attenuation range is only ~12dB at V=22 V_{rms}. As the curing temperature increases from 23 to 85°C, the attenuation increases from 12 to 34dB and the driving (scattering state) voltage is reduced almost linearly from 22 to 9 V_{rms}.

The high temperature curing process produces coarser polymer networks and, therefore, generates larger LC microdomain sizes. If the microdomain size is comparable to the laser wavelength, the maximum light scattering efficiency occurs [9]. The measured light scattering loss for the laser polarization which is orthogonal to the cell rubbing direction for the 16μm, 4 wt % E44 PSLC cell was less than 5%. The large attenuation range and low operational voltage enables PSLCs to work at infrared as a high performance switchable polarizer, shutter, and VOA. At V=0, the cell is highly transparent and independent of polarization. In a high voltage state, the polarization parallel to the rubbing direction is scattered so that the transmitted light becomes linearly polarized. Thus by turning on/off the voltage the PSLC cell acts as a switchable polarizer. If we stack two such PSLC cells in the orthogonal directions, one can control the output polarization state of an incident unpolarized light. When there is no voltage applied to the cells, both polarizations will be transmitted and the light remains unpolarized. However if one of the cells is activated, we get linearly polarized light with polarization orthogonal to the rubbing direction of the activated cell. By activating both cells, all light is scattered.

Figures 3(a) and 3(b) plot the curing temperature dependent hysteresis and response time, respectively. From Fig. 3(a), the hysteresis decreases almost linearly as the curing temperature increases. The hysteresis width δV is defined as V_{down}-V_{up} where V_{down} and V_{up} are the voltages corresponding to 50% transmittance for the forward and reverse voltage scans. As the curing temperature increases from 23 to 85 ^{o}C, the hysteresis width is suppressed by more than 5X. For optical switch applications, the major performance criteria are high contrast ratio, low voltage, and fast response time; hysteresis is not a big concern. However, for VOA devices, hysteresis is undesirable and should be minimized.
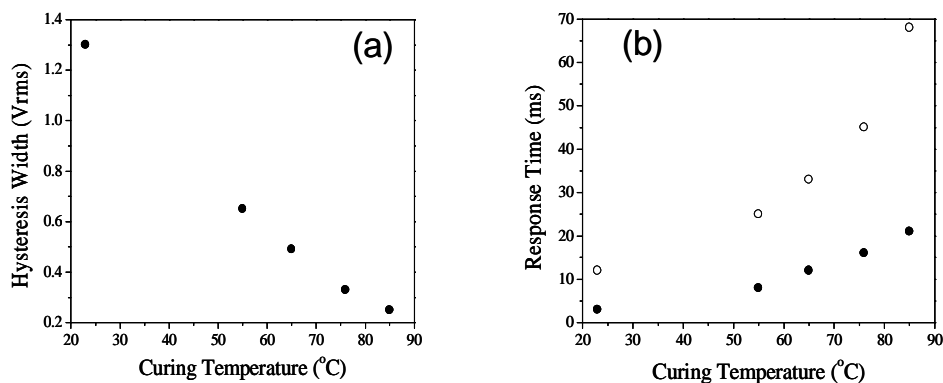

Fig. 3. Curing temperature dependent (a) hysteresis and (b) response time of the E44 PSLC cell containing 4% monomer concentration. Cell gap d=16 μm. The measurements were taken at λ=1.55μm and T=23°C. The rise (dots) and decay time (open circles) were measured between V=0 and the corresponding driving voltage shown in Fig. 2.
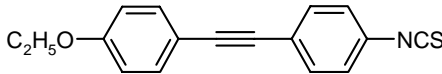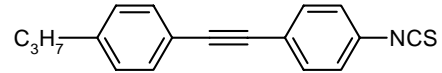
Although high temperature curing process lowers the dark state voltage, enhances the contrast ratio, and suppresses the hysteresis width, it has an undesirable effect on response time. Figure 3(b) shows the measured rise and decay time of the 16μm, 4 wt % E44 PSLC samples at various curing temperatures. Both turn-on and turn-off times increase with the increased curing temperature. In general, the response time of a PSLC is affected by the LC viscosity, cell gap, and microdomain sizes. In this experiment the decay and rise times were measured between V=0 and the corresponding driving voltages shown in Fig. 2. The rise time represents an electric field driven reorientation. Therefore the increase in the rise time is consistent with the reduced applied driving voltage observed at higher curing temperatures, as shown in Fig. 2. In addition benefiting from the driving voltage effect the rise time, as shown in Fig. 3(b), is faster than the decay time. The decay time represents an elastically driven

reorientation. At a higher curing temperature the polymer network is coarser resulting in weaker interaction between LC molecules and polymer network. Therefore the decay time is slower at the higher curing temperature (for more details on the concepts of the rise and decay times see for example [10]).

To improve response time, one could use a thinner cell gap or a higher monomer concentration. However, using a thinner cell gap would lead to a narrower attenuation range whereas using a higher monomer concentration would require a much higher operating voltage. To enhance attenuation range while keeping low operating voltage, we have taken the high birefringence LC approach.

The isothiocyanato (NCS) tolane LCs are known to exhibit a high birefringence, low viscosity, and large dipole moment [10, 11]. For feasibility demonstration, we have prepared two mixtures containing NCS tolanes (with molecular structures shown in Table 1).

Table 1. The LC molecular structures, phase transition temperatures and birefringence of the isothiocyanato tolanes used for enhancing E44's birefringence. K and I represent the crystalline and isotropic phase, respectively. Δn is the extrapolated birefringence at room temperature and λ=633 nm

	Structure	Phase Transitions (°C)	Δn
1	C_2H_5O—⬡—≡—⬡—NCS	K 128.3 I	0.41
2	C_3H_7—⬡—≡—⬡—NCS	K 97.1 I	0.38

Mixture E44-1 contains 8.6% alkoxy NCS tolane and E44-2 contains 25% alkyl NCS tolane. Some performance characteristics of these two mixtures are listed in Table 2 for comparison with E44. The birefringence of E44, E44-1 and E44-2 was measured to be 0.22, 0.23 and 0.25, respectively, at λ=1.55μm.The alkoxy NCS tolane has a relatively high melting point (128 °C) so that its solubility in E44 is limited. Owing to the increased birefringence, the dynamic range of the E44-1 PSLC sample is improved to 27dB. On the other hand, the alkyl NCS tolane has a lower melting temperature so that its solubility is up to 25 % and performance improvement is more significant. The voltage-dependent attenuation of the E44-2 cell at 55 °C curing temperature is shown in Fig. 4. From Fig. 4, the 16μm reflective E44-2 PSLC sample exhibits a 32dB attenuation range at V~12 Vrms. The rise and decay time is 7 ms and 20 ms, respectively.

Table 2. Comparisons of E44, E44-1 and E44-2 PSLC cells with 4 wt% monomer, 16μm cell gap, laser wavelength λ=1.55 µm, curing temperature T=55 °C, and measured at temperature T=23 °C

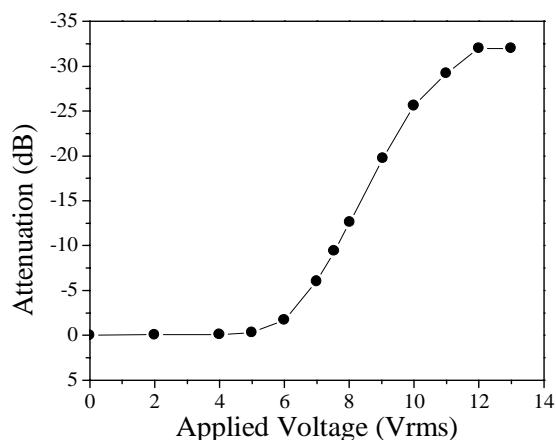|	E44	E44-1	E44-2
Attenuation Mechanism	Scattering	Scattering	Scattering
Dynamic Range (dB)	22	27	32
Control Voltage (V_{rms})	0~14.4	0~14	0~12
Hysteresis Width (V_{rms})	0.65	0.64	0.46
Rise Time/Fall Time (ms)	8/25	6/25	7/20

Fig. 4. The voltage-dependent optical attenuation of the reflective 16μm E44-2 PSLC cell containing 4 wt % monomer. Cure temperature T=55°C, operating temperature T=23 °C, and λ=1.55 μm.

4. Conclusion

Our two-stage elevated temperature curing process greatly improves the PSLC performance at λ=1.55μm. It was shown that a higher curing temperature leads to a higher attenuation range, lower operating voltage, and narrower hysteresis except for the slower response time. The slower response time results from the coarser networks generated during the elevated temperature curing process. High birefringence and low viscosity isothiocyanato tolane LCs hold promises for reducing the response time while keeping high contrast ratio and low operating voltage. These high performance PSLCs will find useful applications as variable optical attenuators, light shutters, and switchable polarizers.

Acknowledgment