Submillisecond-response and scattering-free infrared liquid crystal phase modulators

Jie Sun, Yuan Chen, and Shin-Tson Wu[*]

CREOL, The College of Optics and Photonics, University of Central Florida, Orlando, Florida 32816, USA
[*]*swu@mail.ucf.edu*

Abstract: We demonstrate a submillisecond-response and scattering-free infrared phase modulator using a polymer network liquid crystal (PNLC). The required voltage for achieving 2π phase change at $\lambda = 1.06$ µm is 70V (or 5.8 V/µm) and the measured response time is ~200 µs at 25°C and 30 µs at 70°C. Opposite to our conventional understanding, a high viscosity LC helps to achieve small domain size during polymerization process, which in turn reduces the response time and light scattering. We use Rayleigh-Gans-Debye scattering model to analyze the voltage-on state transmission spectra. When the domain size is comparable to the wavelength, the model fits with experimental results well. But when the domain size is smaller than the wavelength, the simple Rayleigh model works well.

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1. Introduction

Fast-response liquid crystal (LC) devices with a large phase change ($\geq 2\pi$) are highly desirable for photonic applications, such as spatial light modulator [1], adaptive lens [2], and dynamic film in 3D display [3]. However, to achieve a large phase shift would require a fairly thick LC layer, which dramatically increases the response time. This problem gets worse in infrared (IR) region due to longer wavelength and lower birefringence [4]. To improve response time, several approaches have been proposed. Dual frequency LC [5–7] can speed up both rise and decay times but it requires a relatively high voltage and complicated driving scheme. Moreover, dielectric heating would shift the crossover frequency and cause performance instability [8]. The emerging polymer-stabilized blue phase LC is promising for display applications because of its submillisecond response time [9–11], but its phase dynamic range is only one third of a nematic LC. Sheared PNLC shows submillisecond response time and large phase retardation, but it requires a very delicate mechanical shearing process [12–14]. In comparison to the abovementioned approaches, polymer network liquid crystal (PNLC) is relatively easy to fabricate and operate, and it exhibits fast response time and large phase change [15,16]. However, light scattering takes place in the voltage-on state as LC molecules forming multi-domains. An effective way to suppress scattering is to reduce domain sizes by increasing polymer concentration from 6 to 8% to 10-12 wt% [17,18]. The tradeoff is increased operation voltage. Some employed monomers are non-mesogenic, which reduces operating voltage but also disturbs the LC alignment. A typical response time for 2π phase change at $\lambda = 1.55$ μm of such a PNLC is around 1 ms at room temperature.

In this paper, we studied the viscosity effect of liquid crystal hosts on PNLCs and demonstrated a "scattering-free" phase modulator at 1.06 μm with only 6% reactive mesogen monomers. The on-state voltage for 2π phase change is 70V at 22°C and 90V at 70°C, and relaxation time is 220 μs at 25°C and 30 μs at 70°C. By analyzing the on-state transmission spectra, we find that high viscosity LC host tends to form small domains. Also, samples based on viscous LC host exhibit faster response time compared to those adopting less viscous LC host. This is completely opposite to what we know for nematic LCs which favors low viscosity for fast response time. Detailed mechanisms will be explained later.

2. Sample preparation

To prepare a PNLC sample cell, we first mixed LC host with 6 wt% Merck RM257 monomer and 0.5 wt% photoinitiator Irgacure 819. Lower polymer concentration was found to be less stable for certain LC hosts during electro-optic test. The prepared mixture was then filled into an empty homogeneous LC cell whose pretilt angle is ~3°. Cell gap d was 12 μm, ensured by spacer rods. An ultraviolet light source ($\lambda = 385$ nm and intensity ~200 mW/cm^2) was used to illuminate the sample cell for one hour. The curing temperature for PNLC 1-5 was 22°C (room temperature). Table 1 lists the physical properties of the five LC hosts for making PNLC 1-5 at 22 °C. The manufacturer HCCH represents Jiangsu Hecheng Display Technology.

Table 1. Physical Properties of the Five LC Hosts Used in PNLC 1-5 (22 ℃).

PNLC	LC host	γ_1/K_{11} (ms/μm^2)	γ_1 (Pa·s)	K_{11}(pN)	$\Delta\varepsilon$ (1kHz)	Δn@1.06μm
1	MLC14200 (Merck)	27.3	0.27	9.9	25	0.15
2	E44 (Merck)	27.3	0.33	12.1	16	0.22
3	BL038 (Merck)	40.7	0.56	13.8	16	0.23
4	HTG135200 (HCCH)	119.6	1.20	10.0	86	0.19
5	BP1 (HCCH)	153	1.52	9.9	50	0.15

3. Viscosity effect on PNLCs

3.1 Power-on light scattering characterization

To analyze the scattering loss of PNLC, we proposed a Rayleigh-Gans-Debye model of scattering [19,20]. This approximation is valid when the domain size is comparable to the wavelength while the phase shift caused by the scattering domains is small: $D\delta n_{eff} << 2\pi\lambda_m$. Here, D is the average domain size, δn_{eff} is the effective refractive index difference, and $\lambda_m = \lambda_0/n$ is the wavelength in the medium. If $\delta n_{eff} \sim 0.2$, $\lambda_0 \sim 500$ nm, and average refractive index $n \sim 1.6$, then D should be around ~ 1 μm to fulfill this approximation. The scattering cross section σ_s is written as $\sigma_s \sim (\delta n_{eff}/n)^2 D^4/\lambda_m^2 = (\delta n_{eff})^2 D^4/\lambda_0^2$. Taking D^{-3} as the density of scattering centers, the extinction coefficient becomes $\alpha \sim \sigma_s/D^3 = (\delta n_{eff})^2 D/\lambda_0^2$. In our case, scattering is mainly caused by the multi-domains of LCs. So δn_{eff} is proportional to the birefringence (Δn) of LC host, i.e., $\delta n_{eff} = B\Delta n$, where B is a parameter between 0 and 1 depending on the applied voltage. The extinction ratio becomes $\alpha = C\Delta n^2/\lambda_0^2$, where $C \sim DB^2$. We assume $\delta n_{eff} \sim \Delta n$ (i.e. B~1) when a voltage (V_{max}) leading to maximum scattering is applied. Then, C becomes a domain size parameter which is proportional to domain size D only. Considering scattering of PNLC is highly polarization dependent, o-ray (polarization perpendicular to rubbing direction) and e-ray (polarization parallel to rubbing direction) have different extinction ratio α, the transmittance of PNLC for a randomly polarized light at V_{max} can be written as:

$$T = \frac{1}{2}\exp\left(-C_e \frac{\Delta n^2}{\lambda_0^2}d\right) + \frac{1}{2}\exp\left(-C_o \frac{\Delta n^2}{\lambda_0^2}d\right),\qquad(1)$$

where C_e and C_o represent the domain size parameters for e-ray and o-ray, respectively.
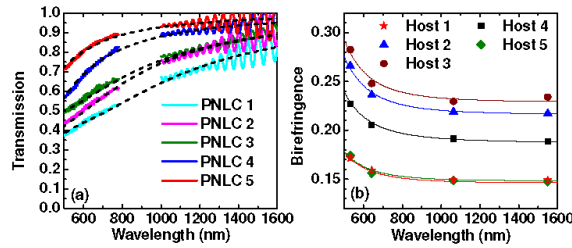

Fig. 1. (a) Transmission spectra of PNLC 1-5 for an unpolarized light with V_{max} applied. Solid lines: experimental results; dashed lines: fitting results with Eq. (1). (b) Wavelength dependent Δn of the five LC hosts.

Figure 1(a) shows the measured transmission spectra (unpolarized light) of PNLC 1-5 with V_{max} applied (solid lines). Data points between 780 nm and 1000 nm are missing because the spectrometer detectors have very low sensitivity in this region. A 12-μm cell filled with BK7 matching liquid (Cargille, refractive index: n = 1.5167 at λ = 589 nm, 25°C) was used for normalization purpose. Sample holder was set at 20 cm in front of detector with an aperture of 0.9 cm, corresponding to a collection angle ~2.6°. Such a small collection angle

ensured that light scattered by LC multi-domains was not collected by the detector. The oscillations in spectra are caused by Fabry-Perot effect, since the refractive index mismatch between indium tin oxide and liquid/liquid crystals increases as wavelengths goes up. In order to fit the experimental spectra with Eq. (1), we first measure the Δn of the five LC hosts at 532 nm, 642 nm, 1064 nm and 1550 nm and then fit the data with extended Cauchy model [21] $\Delta n = A_1 + A_2/\lambda^2 + A_3/\lambda^4$ (Fig. 1(b)). After that, we achieve a very good fitting between Eq. (1) and measured spectra. Domain size parameters are plotted against the reciprocal of rotational viscosity (γ_1) of LC hosts in Fig. 2(a). To confirm the fitting results, we measured the transmission spectra for o-ray and e-ray and fitted independently from $\lambda = 500$ nm to $\lambda = 700$ nm (spectra not shown). The extracted domain size parameters (C_{ep}, C_{op}) are plotted in Fig. 2(a), agreeing well with those extracted from Fig. 1(a). As expected, C_o (or C_{op}) is negligible as compared to C_e (or C_{ep}), because ideally there shouldn't be voltage-induced phase change for the o-ray. A linear relationship is found between domain size parameters and γ_1^{-1}, which can be explained by Stokes-Einstein theory [22]. The mean square displacement of a particle suspended in a liquid is described as:

$$\overline{x^2} = \frac{k_B T}{3\pi\eta R}t,\tag{2}$$

where k_B is the Boltzmann constant, T is the Kelvin temperature, η is the flow viscosity, R is the radius of the particle and t is the time interval. Under the same reaction rate, monomers show shorter coherence length in a more viscous LC host. Instead of aggregating into thick fibrils, monomers tend to form finer polymer networks. Since the rotational viscosity γ_1 generally has a linear relationship with flow viscosity η, the domain size parameter is proportional to γ_1^{-1}.
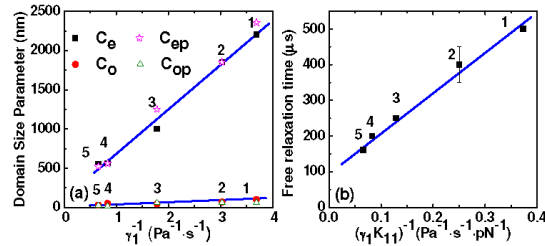

Fig. 2. (a) Plot of domain size parameters of PNLC 1-5 versus $1/\gamma_1$ of the corresponding LC hosts. (b) Plot of free relaxation time constant of PNLC 1-5 versus $(\gamma_1 K_{11})^{-1}$. Straight lines are for visual guide only.

3.2 Electro-optical response time

Under small angle approximation (i.e. small phase change), the LC director's relaxation time of a homogeneous cell can be approximated as $\tau \sim \gamma_1 d^2/K_{11}\pi^2$; where K_{11} is the splay elastic constant [23]. As viscosity increases, LC response time increases. However, for PNLCs, the characteristic lengths are much shorter than the cell gap d, because the polymer network divides the LC cell into multiple nano/micro-domains. Thus, the cell gap d can be replaced with the average domain size D. Since D is proportional to γ_1^{-1} according to our study, τ is supposedly proportional to $(\gamma_1 K_{11})^{-1}$. From this prediction, a higher viscosity LC host tends to produce a PNLC with faster response time (because of smaller domain sizes). In contrast, a nematic LC prefers low viscosity to achieve fast response.

To validate this prediction, we measured the relaxation time of PNLC 1-5. The testing cell was sandwiched between two crossed polarizers with rubbing direction oriented at 45° with respect to the polarizer's transmission axis. To minimize scattering, we used a $\lambda = 1.55$ µm laser as the probing beam. LC cell was biased with a voltage for a small initial phase change

δ_0 in order to fulfill the small angle approximation condition. Free relaxation time τ of the LC can be extracted through fitting the time-dependent phase (δ) relaxation curve with equation $\delta(t) = \delta_0 \exp(-2t/\tau)$ [24].

Figure 2(b) depicts the free relaxation time τ of PNLCs versus $(\gamma_1 K_{11})^{-1}$ for the corresponding LC hosts. We find that PNLC5 based on the most viscous LC host shows the fastest response time while PNLC 1 with the least viscous LC is the slowest. τ generally follows the linear relationship with to $(\gamma_1 K_{11})^{-1}$ as we predicted.

4. A 2π phase modulator at $\lambda = 1.06$ μm

To fabricate a 2π phase modulator at $\lambda = 1.06$ μm while eliminating light scattering, we need to choose a proper LC host. Note that the average domain sizes for PNLC 4 and PNLC 5 are quite close, but PNLC 5 shows less scattering mainly because of its lower birefringence. However, a smaller Δn would require a thicker cell gap in order to obtain 2π phase change. Since No.4 LC host (HTG 135200) has a larger $\Delta\varepsilon$ which is helpful for reducing operating voltage, we consider No.4 as the best choice among these five LC hosts.
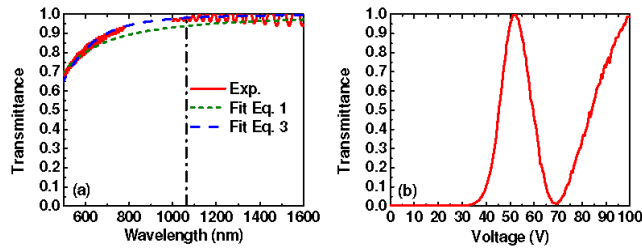

Fig. 3. (a) On-state non-polarized light transmission spectra of PNLC 6 at $V_{max} = 50V_{rms}$ (the voltage leading to maximum scattering loss). The vertical dashed lines indicate $\lambda = 1064$ nm. (b) Measured voltage dependent transmittance curve of PNLC 6 at 25°C and $\lambda = 1064$ nm.

PNLC 6 was prepared with the same precursor as PNLC 4, but cured at 11°C. From the modified Arrhenius model, rotational viscosity of nematic LC can be described by $\gamma_1 = b \cdot S \cdot \exp(E_a/k_B T)$, where b is a proportionality constant, E_a is the activation energy, S is the order parameter, and K_B is the Boltzmann constant [24]. As the temperature is reduced from 22°C to 11°C, the viscosity of LC host 4 increases from 1.2 Pas to 2.1 Pas. Thus, the prepared PNLC is expected to have smaller domain sizes. Figure 3(a) depicts the measured transmission spectrum of PNLC 6 with a bias voltage $V_{max} = 50V_{rms}$ (red solid lines). At $\lambda = 1.06$μm the transmittance exceeds 97% (c.f. the transmittance of PNLC 4 is <90% as Fig. 1(a) shows), indicating that PNLC 6 has a smaller average domain size than PNLC 4. However, Eq. (1) no longer fits well (the fitting parameters are $C_e = 330$ nm and $C_o = 10$ nm) with the experimental data, as the green dashed lines show. This is because the average domain size of PNLC 6 is much smaller than the wavelengths so that scattering starts to fall into Rayleigh region. If we replace λ_0^{-2} with λ_0^{-4} in Eq. (1), we get transmittance equation as:

$$T = \frac{1}{2}\exp\left(-C_e' \frac{\Delta n^2}{\lambda_0^4} d\right) + \frac{1}{2}\exp\left(-C_o' \frac{\Delta n^2}{\lambda_0^4} d\right). \tag{3}$$

As shown by the blue dashed lines in Fig. 3(a), Eq. (3) fits well with the measured spectra. Here, C' is proportional to D^3 ($C_e' = 7 \times 10^8$ nm^3, $C_o' = 1 \times 10^6$ nm^3). Similar results have been reported in previous studies of polymer-dispersed LCs [20] and transparent alumina [25]. The free relaxation time of PNLC 6 is measured to be $\tau = 110$ μs while for PNLC 4 it is $\tau = 200$ μs at the room temperature. This also indicates that PNLC 6 has smaller average domain size than PNLC 4. Since temperature effect may involve more complicated factors

such as change in polymerization rate and birefringence, we will not go into detailed discussion in this paper.

Figure 3(b) depicts the measured voltage dependent transmittance of PNLC 6 between two crossed polarizers for $\lambda = 1.06\mu m$. Driving frequency is 5 kHz. As the applied voltage increases from 0 to 100V, the total phase shift is 3π. The required voltage for 2π phase change is ~70 V.

Figure 4 shows the temperature dependent response time of PNLC 6 for a 2π phase shift, which is defined as the time interval for phase changes from 100% to 10%. At 25°C, the measured rise time is 207 µs and decay time is 220 µs. As the temperature increases to 70 °C, the measured decay time is decreased to 30 µs while rise time is decreased to 28 µs because of the reduced viscosity. However, the operating voltage increases to 90V mainly because of the decreased birefringence. As most polymer-stabilized LC systems have hysteresis issues [23], our PNLC 6 shows a 7.7% hysteresis at 25°C and 2% hysteresis at 70°C.
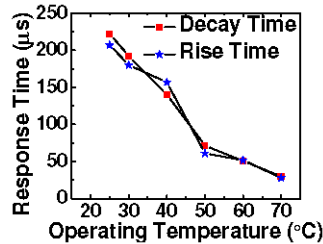

Fig. 4. Temperature dependent 2π phase response time for PNLC 6 at $\lambda = 1.06$ μm.

6. Conclusion

In this paper, we proposed a scattering model based on Rayleigh-Gans-Debye approximation to analyze the on-state scattering loss of PNLCs. With this model, we are able to extract the domain size parameter from the transmission spectra of PNLCs. We studied the viscosity effect of LC hosts on domain sizes and found that the domain size of PNLCs is inversely proportional to the viscosity of the LC host. This result is further confirmed through the response time measurement. The free relaxation time constant τ is found to be proportional to $(\gamma_1 K_{11})^{-1}$. With selected high viscosity LC host and only 6wt% reactive mesogen monomer, we demonstrated a nearly scattering-free (<3%) 2π phase modulator at $\lambda = 1.06$ μm. The operating voltage is ~70V at room temperature. The relaxation time for 2π phase shift is measured to be 220 µs at 25°C and 30 µs at 70°C. Comparing with previous PNLC phase modulator [18], the relaxation time is ~4X faster. In contrast, 2π relaxation time of traditional E7 nematic LC phase modulator (d = 12 μm) is ~200 ms (25 °C). This ~1000X faster response time is attributed to the small domain sizes [26]. If reflective mode is employed, we could lower the operating voltage by ~30% for the same amount of phase modulation [17]. To further reduce operating voltage, larger dielectric anisotropy LC hosts can be employed. Our PNLCs have potential applications in next-generation photonic devices especially for IR applications.

Acknowledgments