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First Published on: 01 January 2008

To cite this Article Tork, Amir, Dumont, Dany, Zohrabyan, Armen, Birabassov, Rouslan and Galstian, Tigran(2008)'Composite Liquid Crystalline Mixtures for Guided Wave Electro-Optic Applications'.Molecular Crystals and Liquid Crystals,488:1,74 — 87
To link to this Article DOI: 10.1080/15421400802240284
URL: http://dx.doi.org/10.1080/15421400802240284

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Composite Liquid Crystalline Mixtures for Guided Wave 
Electro–Optic Applications

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A low refractive index multifunctional composite liquid crystalline mixture is
proposed to address the issues of in-guide tuning of optical properties. As the standard optical telecommunication line is made of fused silica, signal phase and amplitude modulation using liquid crystal requires that its refractive indices match the
refractive index of silica, which is low compared to the majority of commercially
available mixtures. In the present work, low molecular mass liquid crystals are mixed
with fluorinated additives to adjust refractive index below a critical limit (n < 1.4584
at D-line) without impacting significantly on the nematic temperature range
(TCN = −24°C and TNI = 68°C). A method of reducing the surface anchoring energy
of liquid crystals to glass surface is also proposed as a non contact alignment method
around the reduced diameter optical fibers. The bulk elastic energy around the fiber
acts as an alignment mechanism when LC-fused silica molecular interactions are
minimized. The combination of these two properties makes possible the in-guide modulation of the light phase and amplitude with the liquid crystal used as an
outer-cladding electro-controllable medium, significantly improving insertion losses.

Keywords: electro optic modulator; liquid crystals; variable optical attenuator;
waveguides

1. INTRODUCTION

The energy budget control in optical telecommunication networks is a
key issue to reduce overall implementation costs, optimize the

This work has been done in the research and development laboratories of Photintech inc.
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network’s performance and decrease the number of components and consequently the size of systems. These challenges encourage network designers to choose optical components (e.g., variable optical attenuator (VOA), add/drop filter, etc.) that are introducing a minimal level of losses when operating in their transparent state (insertion losses). Traditionally, telecommunication signal processing components are built using semiconductor, mechanical or micro mechanical technologies that are usually well-adapted for free-space applications, i.e. where light is brought out from the fiber, transformed and coupled back into the telecommunication line. However, it is well known that when the light is coupled out of a fiber to be transformed (filtered, attenuated, dropped, dispersion compensated, etc.) then the coupling losses are always higher than if the light remains in the original communication fiber. Typically, insertion losses can differ on the order of 1 dB.

In-guide tuning of optical properties appears thus to be an intuitive solution to address the issue [1,2]. The challenge however is the material and design that will transform an ordinary telecommunication waveguide (especially an optical fiber) into a dynamically reconfigurable waveguide capable of altering the optical properties of the optical signal during its propagation. Recent developments of composite organic materials provide innovative possibilities to address this paramount problem. This class of materials often provides low-cost fabrication techniques requiring relatively easy manipulation in comparison with complex and costly operations needed to fabricate inorganic semiconductor components (vacuum deposition, very high curing temperature, fragile solid crystal growth, etc.).

Among the most interesting organic materials, liquid crystal (LC) materials have demonstrated high reliability, excellent performance and cost-effectiveness. LCs are now considered as promising materials for the development of intelligent (i.e., dynamically reconfigurable) optical telecommunication networks [3–8]. For example, LC micro displays (LCD's), which consist of LC planar cells capable of changing the polarization state of light, may be used as a part of VOAs, optical switches, optical routers, tunable filters and polarization control devices. This technology benefits from the huge amount of knowledge and know-how developed during the past decade. Most of the LC light transformation devices developed for telecommunication applications so far are mainly designed in free space geometry where the light propagates in the direction perpendicular to the cell substrates. This geometry suffers however from reflection losses at the multiple interfaces during the free space propagation and from coupling losses. In addition, micro LCD’s do not provide an appropriate solution in terms of compact integration. Using LCs in wave guiding geometries then appears to be a better
way to combine the advantages of the LC (low cost, low loss, low power consumption, strong electro-optic effect, short response time, high reliability, etc.) with the specific needs for integration (miniaturization, heatless operation, etc.). It implies that LC is used as tunable medium within which a certain portion of the signal is propagating. The architecture we will focus on in this paper is the one described in Refs. [1,2]. Figure 1 presents a schematic drawing of the waveguide geometry. A segment of an SMF-28 optical fiber is etched to reduce its diameter using hydrofluoric (HF) acid. This segment is then sandwiched between two glass plates with electrodes treated to form a planar alignment in a direction parallel to the fiber. This geometry allows the LC material to interact with the evanescent part of signal propagating in the fiber core. The transparent state would be reached for an alignment parallel to the fiber where the LC refractive index, seen by the light, is minimal. When a voltage is applied between the cell plates, the molecules reorient, increasing the refractive index and thus inducing leaky modes. To achieve that mode of operation, the molecules must be aligned parallel to the fiber when no voltage is applied. This is traditionally realized using surface treatments such as mechanical rubbing or ionic deposition which are simply not applicable in our case, where 1 to 10 μm diameter (etched or tapered) fibers are used. The relative fragility of these structures makes it impossible to use standard LC aligning techniques. Planar waveguides are better adapted to conventional aligning methods, but are not easily adaptable to communication networks using optical fibers of circular cross section.

**FIGURE 1** A segment of reduced diameter optical fiber is inserted in a liquid crystal cell where the substrates are treated to impose a uniform planar alignment parallel to the fiber. The thickness of the cell is 25 μm, significantly greater than the 10 μm fiber diameter.
The present work aims to develop a composite material [9] allowing overcoming two major issues for the design of wave-guided electro-optic applications. Namely, we propose a LC mixture that has refractive indices suitable for modulating the signal propagating in an optical fiber and that aligns in a preferred orientation around the same optical fiber without applying additional surface treatments. The desired liquid crystal mixture optical properties are discussed in section 2 while section 3 addresses the anchoring issue. The mixture composition and measurements are presented in sections 4 and 5.

2. Optical Properties

As pointed out in the previous section, LC refractive index and birefringence are key parameters to be set in order to achieve light phase and amplitude modulation within waveguiding geometry as the one described in Figure 1, where the LC forms an electro-controllable cladding. For the light to remain in a guided mode, the refractive index of the LC must be lower than the refractive index of the fiber core, which is \( n_g = 1.4584 \) at \( \lambda = 589 \text{ nm} \). In fact, as described in Ref. [2], the refractive index of the outer electro-controllable cladding must be tuned below or above to the effective refractive index of the waveguide to obtain, respectively, phase or amplitude modulation. The amount of the phase shift or attenuation of the signal depends also on the interaction length, i.e. the part of the fiber where light interacts with the electro-controllable cladding, typically in the range of millimeters to centimeters, many orders of magnitude greater than the typical thickness of a LCD cell. The difference between the core and cladding refractive indices \( \delta n = n_{\text{core}} - n_{\text{cladding}} \) being very small (in the order of \( 10^{-3} \)), an optimal LC would have a birefringence in the same order of magnitude. Given the interaction length, an extraordinary refractive index, only a slightly larger than the core refractive index, would lead to significant leaking. On the other hand, LC materials may have a birefringence value as high as \( \Delta n = 0.3 \).

Figure 2 presents a collection of nematic liquid crystal refractive index data measured at D-line and at room temperature from commercially available mixtures (mainly from Merck) and other scientific literature. The correlation between the extraordinary refractive index \( n_e \) (or the ordinary refractive index) and the birefringence \( \Delta n \) is clearly seen and suggests that low refractive index LCs also implies low birefringence. An empirical relation can be deduced from the regression \((R^2 = 0.995)\).

\[
n_e = 1.4537 + 0.3012 \Delta n
\]
On the same graph is plotted the curve that relates the birefringence that a liquid crystal must have for a given $n_e$ in order to be able to provide a guided mode, i.e. having $n_o$ less than $n_g = 1.4584$. We can therefore hypothesize that the synthesis of new mesogenic materials suitable for our target application must have refractive indices near the crossing point of the two curves (regression and limit curve), meaning low refractive index and low birefringence. A significant progress, for the development and use of low refractive index LC materials, has been done by the Poland group (Ref. [8] and references therein).

A low birefringence $\Delta n = n_e - n_o$, comparable but greater than $\delta n$, has the additional benefit of minimizing the difficulties related to the fine electro-optic tuning (variation of the external controlling field amplitude required to induce a corresponding refractive index variation) of the optical propagation properties. This requirement is also in agreement with the preceding hypothesis. Figure 3 describes the working principle of the in-guide phase tuning or signal attenuation when using electro-optic liquid crystal materials where, in particular, the response time (the time required to reorient the molecules from the elastic equilibrium to the prescribed orientation) depends on the applied electric field. The anisotropic behavior of the device is not described here, but is certainly presenting other challenges and advantages.

FIGURE 2 Extraordinary refractive index survey of 227 pure nematic liquid crystal and mixtures commercially available or characterized in the literature as a function of birefringence. A strong correlation is observed ($R^2 = 0.995$, dash line). Liquid crystal lying at the left of the solid line may be suitable for electro-optical in-guide modulation applications.
3. LIQUID CRYSTAL ALIGNMENT IN A CYLINDRICAL GEOMETRY

Liquid crystal surface anchoring still represents a great challenge for LCD fabrication and it is obvious that existing mechanical rubbing techniques cannot be adapted to the surface of a reduced diameter optical fiber. Figure 6 shows different possible alignments around a cylindrical rod. Each of these configurations is characterized by a certain amount of elastic energy that must be balanced by anchoring energy for this configuration to be stable in time, except for the case where this energy is minimized. If we assume that the surface anchoring energy is zero, the orientation state that minimizes the elastic energy is the planar-parallel (Fig. 6a) orientation. The two other orientation states (Fig. 6b and 6c) contain more elastic energy because of the spatial variation of the director orientation. The difference of elastic energy between these two states and the planar-parallel act as a potential well encouraging the molecules to align parallel to...
the fiber axis. This represents a *bulk* anchoring mechanism related to the geometry of the liquid crystal cell boundaries. The value of the potential well is proportional to $K \ln(1/R)$ where $R$ is the radius of the optical fiber and $K$ is the elastic constant of the LC. When $R$ is sufficiently small (typically 5 $\mu$m), the elastic energy density of the perpendicular (Fig. 6b) or circular (Fig. 6c) configuration become significant in comparison with the surface anchoring induced by molecular interactions. If the surface anchoring is less important than the bulk anchoring due to geometrical factors, the latter one will predominate. The maximum bulk anchoring remains however relatively weak compared to anchoring induced by traditional methods such as polymer rubbing. This is prescribing another key property of a suitable LC mixture: it must minimize the LC-glass surface anchoring energy due to molecular interactions in order to let the geometrical anchoring to predominate.

To summarize, the composite liquid crystalline mixture must simultaneously comply with the following requirements: 1) the nematic

![Diagram](image-url)

**FIGURE 4** a) Surface hydrogen bonding of a generic reagent. b) Two types of chemical bonding that may occur between the glass surface and the reagent.
range, which defines the main operation condition, must preferably comprise a well-defined temperature interval (e.g., between $-10$ to $+70^\circ C$); 2) the optical properties of the mixture must be adjusted to have at least one of the refractive indices below the refractive index of the silica; 3) the anchoring energy of the mixture due to molecular interactions at the silica waveguide surface must be negligible so the director could align following the bulk anchoring defined above; 4) the anchoring properties at other aligning interfaces, such as rubbed polymer should remain reliable; and 5) the mixture has to be chemically and thermally stable, and must not degrade when submitted to electromagnetic radiation.

To address these objectives, we first created low refractive index LC mixtures having a reasonable nematic range by mixing multiple two or more mesogens. Low refractive index additives are introduced to further decrease the refractive index of the mixture, following Ref. [3]. The concentration is adjusted so that the ordinary refractive index is lower than the refractive index of silica, while making sure that the nematic range is still adequate. Finally, we used reagent additives recognized as interacting with silica glass and shielding the LC from surface anchoring. The chemical shielding of the glass surface by the reagent compound results into the significant reduction of the anchoring energy that is mainly attributed to the various chemical bonds of the LC molecules with interfaces (see Fig. 4).

4. MIXTURE PREPARATION AND CHARACTERIZATION

4.1. Composition

As aforesaid in the previous section the material used is a composite liquid crystalline mixture having a low refractive index and a chemical reactive power that makes it capable of minimizing the surface anchoring energy when in contact with silica. This mixture comprises two key components:

a) low ordinary refractive index nematic liquid crystals;
b) a reagent compound capable of reducing the anchoring energy via a chemical shielding process leading to the reduction of surface anchoring energy;

The host mixture is prepared using low refractive index liquid crystals usually formed of small molecules such as cyclohexyl carboxylic acid (CHCA) or bicyclohexyl (CCH) mixed to their eutectic point that maximize the nematic range.
The reagent compounds used as component (b) can be selected from the group consisting of organic silanes, siloxane copolymers, and polysiloxane polymers. The organic silane can be represented by

\[ R_n Si - X_{(4-n)} \]  

wherein R is an organic non-functional group, such as an alkyl, which must not react with the mixture of low ordinary refractive index nematic liquid crystals. X is a functional group selected from group consisting of OH, OCO, OCONH\(_2\), OCONH, OCON, CN, SCN, OR, OCONHR, COOR, -CH=CH-, an epoxy group, and OSi(CH\(_3\))\(_2\) OSiH(CH\(_3\))\(_2\) and n is 0,1,2 or 3. This functional group is introduced to react with inorganic material by forming hydrogen bonds and/or covalent bonds (Fig. 4). Basically, an alkoxysilane molecule reacts on a glass surface and forms a siloxane bond (Si-O-Si). An example of the corresponding chemical reaction is described by the following equation

\[ Si - OR + HO - Si \rightarrow Si - O - Si + R - OH \]

Due to the strong proton donor and acceptor role of the Si-OH group, the molecular interaction between alkoxysilanes and silanol is higher than with the liquid-crystal molecules. The molecules attached on the glass surface, having non-functional remaining groups, such as alkyl groups, have virtually no interactions with each other or with the LC molecules of the mixture.

Finally, a low refractive index (n < 1.4584) fluorinated additive such as 1,1,1,3,3,3-hexafluoro-2-propanol is added in small proportion in order to further decrease the refractive index and the viscosity without impacting too much on the nematic range.

To test the reactive effect, we realized two mixtures which are described in Table 1. Mixture A has 5% of 1,1,3,3,5,5-hexamethyltrisiloxane as a reagent compound and mixture B has none. Two cells were built according to Figure 1 with the substrates treated to induce a uniform planar alignment with the director aligned along the fiber. This cell contained an optical fiber of reduced cladding diameter which was centered with respect to the substrates. For this purpose, a segment of a standard optical fiber was etched down to a diameter of 4 \( \mu \)m using HF acid. No special treatment was made to the fiber other than rinsing with distilled water. The cells were filled with the two mixtures and observed with a polarizing microscope. Figure 5a shows the cell without reagent with crossed polarizer and analyzer. The alignment is planar homogeneous throughout the cell except in the vicinity of the fiber where the director is thought to make a strong pretilt angle at the silica surface. Figure 5c shows the cell in unpolarized light to compare the size of the actual fiber with the liquid crystal pattern.
Figure 5b shows a uniform alignment even at the fiber surface where the director is aligned parallel to the fiber axis. Light was injected in the fiber and no significant losses were noticed due to propagation in the etched fiber segment, meaning that the ordinary refractive index of the mixture is lower than the silica refractive index. Leaky modes were observed in the first case where the extraordinary refractive index is higher.

**TABLE 1** Composition of Mixtures A and B

<table>
<thead>
<tr>
<th></th>
<th>Mixture A</th>
<th>Mixture B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Merck 18523</td>
<td>70%</td>
<td>73%</td>
</tr>
<tr>
<td>trans-4-pentylcyclohexane carboxylic acid</td>
<td>18%</td>
<td>20%</td>
</tr>
<tr>
<td>1,1,3,3,5,5-hexamethyltrisiloxane</td>
<td>5%</td>
<td>0%</td>
</tr>
<tr>
<td>1,1,1,3,3,3-hexafluoro-2-propanol</td>
<td>7%</td>
<td>7%</td>
</tr>
</tbody>
</table>

**FIGURE 5** Optical fiber with reduced diameter in a LC cell observed with a polarizing microscope (25X) between crossed polarizers. a) The cell is filled with mixture B, where no reagent was added. b) The cell is filled with mixture A with 5% of reagent. c) The cell observed in natural light that show the size of the actual fiber.
It is thought that the bulk reagent proportion is lower than what was put in initially because it bonds to surfaces like a surfactant. In fact, no significant change in the refractive index of the mixture B were observed compared with mixture A, meaning that the reagent compound is not forming a significant part of the mixture volume after a certain stabilization time.

Tables 2 and 3 present other mixtures prepared following the mentioned above principle. Table 2 below gives the composition of two LC mixtures (C) and (D) of negative dielectric anisotropy at low frequency. In this composition, the initial host mixture is a LC mixture of negative dielectric anisotropy containing CCH, CCN, CH and BCN types of LC compounds. The mixture ZLI-2806 is commercially available from E. Merck, Darmstadt.

Table 3 below gives the composition of two LC mixtures (E) and (F) of positive dielectric anisotropy at both low and optical frequencies. In this composition, the host mixture forming the principal constituent is a LC mixture with positive dielectric anisotropy, containing cyclohexylcarboxylic acid and phenylcyclohexyl types of mesogens. The composition also contains organic compounds that are added to the host to obtain the final specific composition.

**FIGURE 6** Different possible liquid crystal alignments at the surface of a cylindrical waveguide: a) parallel alignment (along the waveguide axis); b) perpendicular alignment (parallel to the waveguide radius); c) circular alignment (tangential to the waveguide surface and perpendicular to the waveguide axis).

**TABLE 2** Composition of Mixtures C and D

<table>
<thead>
<tr>
<th></th>
<th>Mixture C</th>
<th>Mixture D</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZLI-2806</td>
<td>86%</td>
<td>92%</td>
</tr>
<tr>
<td>1,1,1,3,3,3-hexafluoro-2-propanol</td>
<td>10%</td>
<td>5%</td>
</tr>
<tr>
<td>1,1,3,3,5,5-hexamethyltrisiloxane</td>
<td>4%</td>
<td>3%</td>
</tr>
</tbody>
</table>
Figure 7 presents the extraordinary refractive index and birefringence values of mixture A, C, D, E and F, measured using prism total reflection. The values are compared to the limit curve of wave-guided applications (solid line) and the regression where most of the liquid crystal mixtures are likely to be found.

**4.2. Nematic Range**

Differential scanning calorimetry (DSC) was used to detect the phase transitions of the proposed liquid crystalline mixtures (crystal-nematic/\(T_{CN}\) and nematic-isotropic/\(T_{NI}\)) and measure the temperature at which they occur. Heating scan was employed to determine the

![Graph showing refractive index and birefringence values](image)
transition sequence. A Perkin Elmer DSC-7 was used with heating scans of 10°C/min. An average of 8 mg of LC compounds was packed into a standard aluminum crucible with an empty crucible being used as a reference. Before each experiment, the temperature was held at 500°C for 10 minutes in order to clean the DSC head and a background scan was obtained. Table 4 shows the crystal-nematic and nematic-isotropic transition temperatures.

5. CONCLUSION

As aforementioned, the obtained composite liquid crystalline mixture can be used in optical waveguide tuning applications. This mixture has a low refractive index as compared to silica, low surface interaction energy with silica, a broad thermal range of mesogenic phase and a positive or negative dielectric anisotropy at low frequency. All of these properties enable the mixture to easily align liquid crystalline molecules and corresponding electro-optic applications with guiding optical devices made of silica, such as fibers, planar or arrayed waveguides. The alignment around a reduced diameter optical fiber is guaranteed by the minimization of the bulk elastic energy when the molecular interactions between the mesogens and the surface are shielded with a proper reagent compound added to the mixture.

REFERENCES


<p>| TABLE 4 The Transition Temperatures for Different Mixtures |
|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>TCN (°C)</th>
<th>TNI (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture A</td>
<td>–24</td>
</tr>
<tr>
<td>Mixture B</td>
<td>–30</td>
</tr>
</tbody>
</table>

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