Nanohybrid Materials with Tunable Birefringence via Cation Exchange in Polymer Films

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In this work, a nanohybrid material based on a freestanding polymeric liquid crystal network capable of postmodification via cation exchange to tune birefringence is proposed. The smectic liquid crystal films can be infiltrated with a variety of cations, thereby changing the refractive indices ($n_e$ and $n_o$) and the effective birefringence ($\Delta n$) of the nanohybrid material, with reversible cation infiltration occurring within minutes. Birefringence could be tuned between values of 0.06 and 0.19, depending on the cation infiltrated into the network. Upon infiltration, a decrease in the smectic layer spacing is found with layer contraction independent of the induced change in birefringence. Potential applications are in the field of specialty optical devices, such as flexible, retunable reflective filters.

1. Introduction

Nanohybrid materials have gained significant attention over the past decade.[1] The interplay between the organic and the inorganic phases generally gives rise to remarkable properties, providing a wide range of potential applications, including biomedical, catalytic, and sensory but also in electrical and optical devices.[2] Many nanohybrid materials display extraordinary mechanical and/or optical properties, often arising from alternating organic–inorganic layers.[3] Of particular interest is the optical property birefringence, which is widely exploited to realize waveplates, optical fibers, and reflective filters.[4] Production of adjustable optical gratings could also find use in flexible optical beam steering and light intensity modulation.[5] To extend toward even more advanced optical applications, including displays and smart windows, we are aiming for a nanomaterial with tunable birefringence.[6]

Birefringence is known for nanohybrids and polymeric materials and such materials are often used in sophisticated optical applications, such as flexible waveguides.[7] Although the optical properties of these materials typically can be adjusted during synthesis of the material to meet specific requirements,[8] it is uncommon that these materials display tunable birefringence after manufacturing.

Liquid crystal networks (LCNs) have been previously used to adsorb silver ions, which could then be reduced to form silver nanoparticles inside the liquid crystalline matrix.[9] Due to their polymeric nature, these LCNs are excellent frameworks for the selective and reversible adsorption of cations.[10] Here, we propose a novel postmodification strategy of a LCN to reversibly tune the birefringence through infiltration with cations. In this way, we can set and maintain the birefringence at desired value without the need of a constant external stimulus. It is subsequently possible to reverse the modification and alter the birefringence in the freestanding polymerized film over a range of values.

2. Results and Discussion

2.1. Preparation of the Liquid Crystal Network and Cation Infiltration

The polymerizable LC mixture used in this work consisted of a hydrogen bonded acid dimer (6OBA, 4-(6-acryloyloxy)hexyloxy) benzoic acid) and a liquid crystalline crosslinker (C6H, 1,4-phenylene bis(4-(6-acryloyloxy)hexyloxy) benzote). 6OBA and C6H were mixed in a 50/50 w/w ratio to minimize swelling of the material and maintain the network integrity upon base treatment (Figure 1A).[11] The LC films were formed in rubbed...
polyimide-coated glass cells with 20 µm spacers. The mixture was photopolymerized in the smectic A phase at 95 °C to fix the layered smectic structure.[12] Upon photopolymerization, the smectic A structure changes to form a smectic C phase (Figure 1B1).[13] Upon photopolymerization, the smectic A structure changes to form a smectic C phase (Figure 1B1).[13] which could be observed as a chevron-like pattern in polarized optical microscopy images (Figure S1, Supporting Information). The cells were opened, and the films carefully removed from the glass plates using a razor blade to form planarly aligned, freestanding polymer films ≈ 2.5 cm × 2.5 cm × 20 µm in size.

The hydrogen bonds between the acid dimers were broken by immersing the freestanding polymer film in a 0.5 M KOH solution for 15 min, leading to potassium ion infiltration and the formation of a polymer salt (Figure 1B2). The breaking of the hydrogen bonds and the formation of the carboxylate salt were followed using transmission Fourier transform infrared (FTIR) (Figure 1C). After base treatment, the peak indicative of acid dimers at 1680 cm⁻¹ in the pristine film[14] (Figure 1C1) disappeared, while two new peaks appeared at 1550 and 1390 cm⁻¹ (Figure 1C2). These latter peaks are associated with the asymmetric and symmetric COO-stretch for carboxylate salts, respectively.[14] After this base treatment, which we will from here onwards refer to as K⁺ cation infiltration, the polymeric network is
accessible for the infiltration of other cations (Figure 1B3).[10] By immersing the liquid crystalline network in a 10 × 10⁻³ m salt solution, the potassium ions were exchanged for Cs⁺, Na⁺, Mg²⁺, Ca²⁺, Ba²⁺, or Zn²⁺. The cation exchange relies on ionic interactions between the metal ion and the carboxylate. For bivalent ions, binding to two carboxylate groups instead of one, the binding of the metal ion inside the LCN is stronger and therefore favored over monodentate binding. We expect that the potassium ions could be exchanged for other monovalent ions due to a large excess of cations in the exchange solution, competing out the potassium ions over time.

It is known that the IR frequencies for carboxylate salt stretching vibrations are highly dependent on the coordinating metal ion.[14,15] Indeed, infiltration of cations led to ion-specific peak shifts of the carboxylate peaks in the FTIR spectrum (Figure 1C3 and Figure S2, Supporting Information). In some cases, like for Cs⁺, the shift in IR signal compared to the potassium carboxylate signal is minimal. In those cases, cross-sectional scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM-EDX) was used to confirm successful cation infiltration (Figure S3, Supporting Information).

Both transmission FTIR and SEM-EDX suggest a homogeneous distribution of cations throughout the film. Moreover, in thermogravimetric analysis (TGA), inorganic fractions of 21.7% and 8.6% were observed, for potassium and calcium ion infiltrated films, respectively (Figure S4, Supporting Information). These values are close to the theoretically calculated inorganic fractions of 22.8% and 12.2%, assuming that all carboxylic acids are converted to carboxylate anions with potassium or calcium counter ions, respectively.[9,10,16] This suggests full occupation of the carboxylate groups for both monovalent and bivalent cations.

2.2. Tunable Refractive Index and Birefringence upon Cation Infiltration

The Brewster angle (θB) was used to calculate the refractive indices of the LCN films before and after cation infiltration. The angle of minimal surface reflection, θB, was determined by measuring the reflection intensity of the incoming light beam (400–750 nm) over varying incident angles. The refractive index was calculated via Equation (1)

\[
\tan(\theta_B) = n_2/n_1
\]  

with n₁ the refractive index of air and n₂ the refractive index of the LC film.

The reflection of light polarized perpendicular to the optic axis is determined by the ordinary refractive index, n₀, and the reflection of light polarized parallel to the optic axis is determined by the extraordinary refractive index, nₑ. Once nₑ and n₀ were determined, the birefringence (Δn) could be calculated via Equation (2)

\[
\Delta n = n_e - n_o
\]

In Figure 2, the refractive indices and birefringence of the pristine LC film are shown. Over the wavelength range of 400–750 nm, n₁ and n₀ were relatively constant, ≈1.69 and 1.50, respectively. The deviations around the mean value for the full spectral range are comparable for all LC films (Figure S5, Supporting Information). The averaged values for the refractive indices and birefringence at 590 nm for the pristine and infiltrated LC films are listed in Table 1.

Compared to the pristine LC film, n₀ decreased to ≈1.58 for all infiltrated LC films. For barium and zinc ion infiltration, n₀ increased with respect to the pristine film, while infiltration of potassium or calcium led to a decrease. The changes in both the nₑ and the n₀ resulted in different birefringences for all infiltrated LC networks. The pristine film has the highest birefringence (0.19 ± 0.03); calcium (0.15 ± 0.03) and potassium (0.12 ± 0.03) infiltrated LC films show a somewhat lower birefringence compared to the pristine film. In contrast, the barium and zinc infiltrated films showed the lowest birefringence with a value of 0.06. Thus, upon cation exchange, the birefringence of the freestanding LC films (Figure S6, Supporting Information) can be tuned between values of 0.06 and 0.19. The birefringence of the polymeric LCN films is comparable to values found for nematic LCs commonly used in LC displays, which have a Δn generally between 0.05 and 0.12.[17] The birefringence of the LC network nicely falls in the range between quartz (Δn = 0.009) and rutile (titanium dioxide, Δn = 0.287), two well-known inorganics that are often employed for their birefringent properties.[18]

Previous work demonstrated that the cations could be removed from such an infiltrated LC network via acid treatment, thereby restoring the hydrogen bonds between the benzoate monomers,[16a,19] with high efficiency (over 60%) during multiple adsorption–desorption cycles.[18] Indeed, when exposing infiltrated LCNs to an acidic solution, the hydrogen bonds are successfully restored between the 60BA acid dimers, for both K⁺ and Ca²⁺ infiltrated films (Figure S7, Supporting Information). Furthermore, after acid treatment, the hydrogen bonds can be broken again by immersing the films in a KOH solution to facilitate infiltration of cations.[16b]
Cation infiltration-driven changes in birefringence occur simultaneously with a structural rearrangement in the LC film (see Section 2.3). In situ small angle X-ray scattering (SAXS) experiments (Figure 3) show that K\(^+\) infiltration throughout the bulk of the LC network and structural rearrangement occur rapidly (300 s initiation and 200–300 s rearranging). Thus, cation infiltration allows refractive index tuning of the films under 10 min.

### 2.3. Structural Rearrangements upon Cation Infiltration

A decrease in the layer spacing in smectic LC networks upon base treatment has been observed previously.\(^{[20]}\) To further investigate the influence of cation infiltration on the network, transmission electron microscopy (TEM) analysis on microtomed cross sections and SAXS measurements were performed (Figures 1 and 4). In contrast to what was previously hypothesized,\(^{[13]}\) the pristine film itself provided sufficient contrast in TEM to visualize the striping pattern associated with the layered smectic LC structure (Figure 1D1). An assignment of the bright and dark stripes to either the benzene rings close to the cation binding site or the alkyl backbone could not be established. When imaging the striping pattern throughout the film, the smectic C orientation proposed in Figure 1B1 is clearly visible (Figure S8 and Movie S1, Supporting Information).\(^{[21]}\)

Analysis of the TEM images by fast Fourier transform (FFT) showed that sharp peaks are present which indicates highly directional layers with uniform layer spacing both before and after cation infiltration. The layer periodicity was accurately measured from the position of the peaks in the FFTs, with a layer spacing of 3.8 nm found in pristine LCN. For potassium and calcium infiltrated films (Figure 1D2,D3), the layer spacing decreased to 3.6 and 3.4 nm, respectively. Using SAXS, the layer spacing and orientation throughout the bulk of the liquid crystalline films were also determined (Figure 4 and Figure S9, Supporting Information) and matched well to the layer spacings determined with TEM. All tested cation exchanges led to decreases in the smectic layer spacing, while maintaining the smectic C structure (Figure S10, Supporting Information).

Surprisingly, the decreases in layer spacings upon cation infiltration appear unrelated to the size or charge of the ions. Zinc, for example, has the smallest ionic radius (0.68 Å)\(^{[22]}\) but does not result in the smallest layer spacing. One must consider that the size of the ions is not fixed in aqueous environments, as the ions are surrounded by coordinating water molecules. This hydration shell depends on the size, charge, and chemical environment of the ion, and the carboxylic acid binding to metal ions is influenced by the hydration layers around the cation.\(^{[23]}\) Therefore, it is difficult to predict the ionic radii or the binding geometry of the infiltrated cations in general, nor their effect on the smectic layer spacing.\(^{[24]}\) Nevertheless, it can be argued that for Ca\(^{2+}\) ions, which are known to favor a bidentate binding to the carboxylate group,
a planar carboxylate-calcium complex may be formed,[16a,25] which would explain the pronounced decrease in layer spacing to 3.38 nm (Figure 4).

2.4. Linking LC Morphology/Structure to Birefringence

The changes in the effective refractive index and birefringence of the films could be caused by several structural/morphological changes: i) the variation of smectic layer thicknesses, ii) the tilt angles of the LCs in the smectic layers, iii) the formation of inorganic crystals within the LC pores, or iv) are simply related to the nature of the infiltrated metal itself. Each possibility will be discussed in detail next.

When comparing the variations in layer spacing with changes in birefringence, it becomes clear that they are not directly related. For example, the pristine LC film has the largest layer spacing (3.8 nm) and the highest birefringence (0.19), while the barium infiltrated film has the second largest layer spacing (3.6 nm) but the lowest birefringence (0.05). The calcium infiltrated film, on the other hand, has the smallest layer spacing (3.4 nm) but the second highest birefringence (0.15). Similarly, there appears to be no relation between the changes in refractive indices and the decreases in layer spacing upon cation infiltration. Thus, variations in birefringence and refractive indices seen in the infiltrated films are not the result of the decreased layer spacing in the LC network.

The decrease in layer spacing is potentially associated with a changing tilt angle of the LC monomers. The molecular order in the LC-based nanohybrid materials was monitored using wide angle X-ray scattering (WAXS): upon breaking the hydrogen bonds with potassium hydroxide, we observe that the WAXS angle X-ray scattering (WAXS) may be formed, [16a,25] which would explain the pronounced decrease in layer spacing to 3.38 nm (Figure 4).
(Ca²⁺, Mg²⁺, Ba²⁺, Cs⁺, and Zn²⁺) by immersing the film in 10 × 10⁻³ M salt solutions (CaCl₂, MgCl₂, BaCl₂, NaCl, Cs₂CO₃, Zn(NO₃)₂) for 24 h, to ensure that all K⁺ ions were exchanged. After infiltration, the films were dried on filter paper. The infiltration of ions was checked using FTIR in transmission mode on a Varian 670 IR spectrometer over a range of 4000–650 cm⁻¹ with a spectral resolution of 4 cm⁻¹ and 100 scans per spectrum.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

birefringence, cation infiltration, liquid crystals, nanohybrid materials, tunable optical properties

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