Electro-optic characteristics of stabilized cholesteric liquid crystals with non-liquid crystalline polymer networks

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The selective reflection of cholesteric liquid crystals (CLCs) does not readily change to direct application of electric field. Extensive prior research has explored the stabilization of the CLC phase with polymers. These prior efforts have demonstrated both tunable and switchable electro-optic reconfiguration of the selective reflection of the CLC phase. Recently, we and other groups have detailed that polymer stabilization of the CLC phase with liquid crystalline monomers retains "structural" chirality (e.g., the chiral phase templates the morphology of the achiral polymer network). Here, we demonstrate that structural chirality can be retained in aliphatic, non-liquid crystalline monomers. PSCLCs prepared by photoinitiated polymerization of aliphatic polymer networks exhibit reversible electro-optic responses. Distinctively, facilitated by the retention of structural chirality in aliphatic stabilizing polymer networks, we explore the role of surface affinity and crosslink density in the transfer of of structural chirality to the liquid crystal media.

Introduction

Dynamic reconfiguration of optical properties has potential functional use in microscopy, machine vision, lasers, displays, and aerospace.[1–3] Several stimuli have been utilized to adjust optical properties including electric field, heat, light, and chemical exposure. Of relevance to the work presented here, liquid crystals (LCs) are widely utilized in electro-optic devices due to their anisotropic properties, the ease at which their molecular orientation can be altered to change the effective refractive index, and associated phase shift experienced by light interacting with the material.[4]

The cholesteric liquid crystal (CLC) phase is of particular interest. In the planar orientation, the CLC phase is inherently reflective. The selective reflection of the CLC phase is associated with the periodic variation in refractive index associated with the helical structure of the phase. The periodicity of the phase is defined by the pitch length, P, which is the distance over which the nematic director completes a 360-degree rotation. The CLC phase is almost always prepared by chirality transfer from chiral additives mixed into nematic liquid crystals. The pitch is inversely proportional to the concentration ([C]) and the helical twisting power (HTP) of the chiral additive/LC host mixture (equation 1).

$$P = \frac{1}{HTP * [C]} \quad (1)$$

For mixtures prepared with multiple chiral dopants, the effective HTP is the weighted average of the HTP of all dopants.[5]

The selective reflection of the CLC phase is observed when the wavelength of light is approximately equal to the pitch. For light propagating along the helical axis, the reflected wavelengths are given by Equations 2 and 3.

$$\lambda_c = n_{avg}P \quad (2)$$
$$\Delta\lambda = \Delta nP \quad (3)$$

The central wavelength (λ_c) is dependent on the average refractive index (n_{avg}) of the LC while the bandwidth ($\Delta\lambda$) is dependent on birefringence (Δn). Within the reflection band, only 50% of unpolarized light is reflected. This is due to the asymmetry of the helical twist in the CLC. Light with circular polarization will reflect if the handedness matches that of the CLC while oppositely polarized light will be transmitted, outside the Bragg regime both polarizations of light will be transmitted. Unpolarized light can be considered a mix of right and left-handed circularly polarized light. A common workaround to reflect 100% of light in a region is to stack a left-handed and right-handed CLC.[6–8] Distinctive unpolarized reflection are observed in CLC set at oblique incidence to the propagation of light.[9–12]

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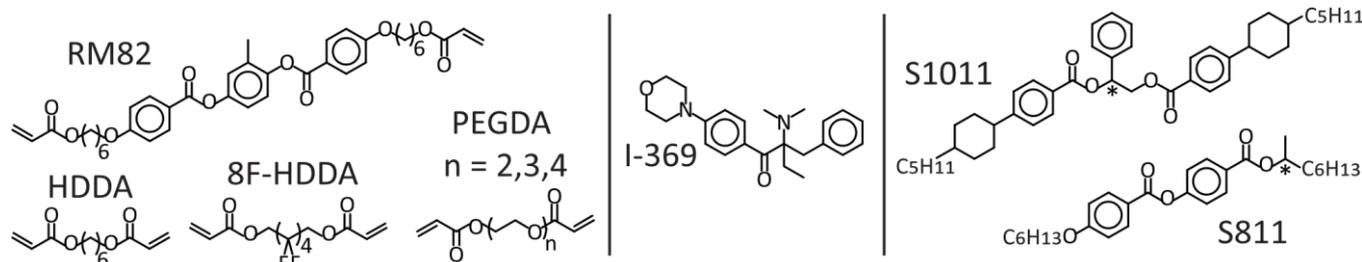
Fig. 1 Chemical structures of the monomers (RM82, HDDA, 8F-HDDA, and PEGDA), photoinitiator (I-369), and left-handed chiral dopants (S1011, S811) used in this study for preparing PSCLCs. Not shown is the nematic liquid crystal host MLC-2079.

Polymer/LC composites can have distinctive stimuli-response compared to pure LC systems. Generally, the response is dependent on the material choice as well as the ratio of monomer to non-reactive components.[13] Here, we are concerned with polymer-stabilization of the CLC phase (PSCLCs). Polymerization of small concentrations of monomer in the CLC phase can stabilize the reflective state. Stabilization is evident in an adjustment in the thermotropic character of the phase as well as differentiated electro-optic performance.[14,15] Dynamic electrical control of PSCLCs that retain the reflection notch has been intensely explored in materials with negative dielectric anisotropy ($\Delta\epsilon < 0$). LCs with negative dielectric anisotropy align with the short molecular axis perpendicular to the electric field. Therefore, when a voltage is applied across a cell the LC maintain their planar orientation.

Electrical reconfiguration of the selective reflection has been examined in PSCLCs. Responses depend on the composition and polymerization conditions and vary from bandwidth broadening[16–18], red[19,20] and blue shift tuning[21], and notch splitting.[22] Generally, when the polymer network is formed within the CLC in a planar orientation this network adopts a chirality that matches the phase in which the polymerization occurred.[23] The electrical response is a result of deformation of the polymer network under a DC field, which adjusts the structural chirality of the polymer through the depth of the cell, In turn this affects the pitch of the bulk mixture. The polymer network expands from the positive electrode and contracts near the negative electrode after double layer formation has occurred. The spatial variation in pitch distortion is affected by a number of potential variables but results strongly indicate that the basis of the deformation is ionic groups trapped within or on the polymer

stabilizing network.[18,20,24–26] This mechanism for pitch variation is not exclusive to negative dielectric mixtures, samples prepared with positive dielectric liquid crystals can also exhibit long range tuning behavior. Due to the anchoring between the polymer network and free liquid crystal the reorientation to a homeotropic alignment is prevented maintaining a planar reflective state, with the ability to enter a non-reflective state under AC voltage application.[25]

To date, electro-optic reconfiguration of PSCLCs by this mechanism have been based on difunctional LC monomers. It has been assumed that these monomers will be compatible with the phase and maintain favourable anchoring between the polymer network and LC host. A large initiator:monomer ratio is used to produce a deformable network with suppressed crosslink density. In this paper, we explore electro-optic responses of PSCLCs that have been made with non-LC monomers that allow us to explore the fundamental nature of structural chirality and assess the contribution of surface affinity and the molecular weight between crosslinks on the electro-optic response. Though non-LC monomers have lower miscibility in the mixture compared to LC monomers the wide variety of commercially available monomers allows us to readily explore these variables in PSCLCs.

Results and Discussion

This study explores the translation of chirality from the cholesteric liquid crystal (CLC) phase to stabilizing polymer networks prepared from aliphatic, non-liquid crystalline monomer. The molecular structures (except for the proprietary liquid crystalline mixture MLC-2079 ($\Delta\epsilon$ = -6.1, Δn = 0.15)) of the
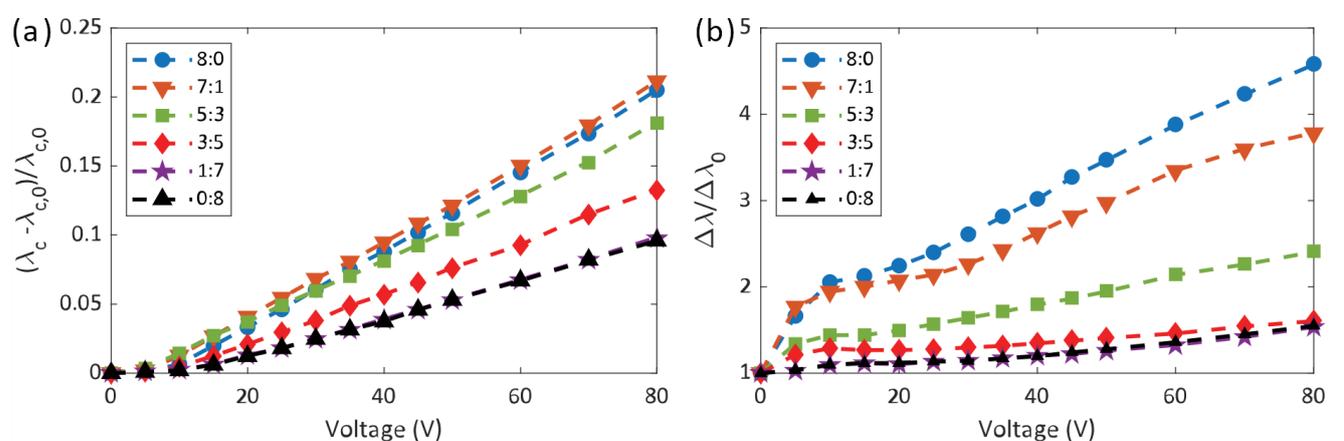
Fig. 2 (a) Change in the position of center of the selective reflection (λ_c) normalized against the original spectral position ($\lambda_{c,0}$). (b) The ratio of the electrically-induced bandwidth ($\Delta\lambda$) and the original bandwidth ($\Delta\lambda_0$) of the selective reflection of PSCLC as a function of voltage. Samples were prepared with 8wt% monomer, 5wt% S1011, 5wt% S811, 1wt% I-369 in MLC-2079. The weight ratio of RM82:HDDA was changed between each sample as indicated in the legends. Polymerization was initiated by UV light (365nm, 50
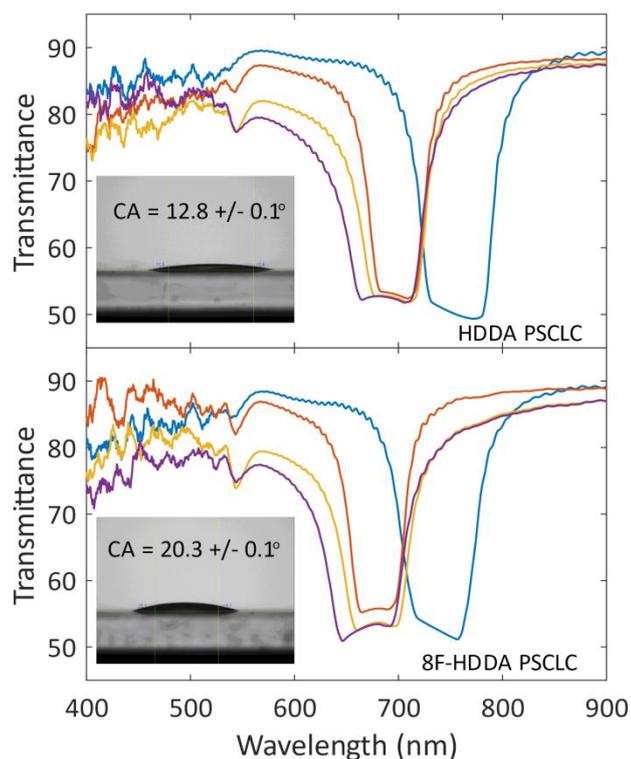
Fig. 3 Anchoring behavior between the host liquid crystal and HDDA (top) and 8F-HDDA (bottom) are shown. Transmission spectra were obtained from samples with 1wt% I-369 with a monomer: initiator molar ratio of 13:1. (Blue) Unpolymerized sample at room temperature, (orange) unpolymerized sample at 60°C, (yellow) polymerized sample at 60°C, (purple) polymerized sample at room temperature. Inset are contact angle measurements between solid polymer films made with a monomer: initiator molar ratio of 13:1 with a drop of MLC-2079.

Fig. 4 (a,b) Change in the reflection notch center normalized against the original notch position versus time while an electric field is applied on and off. The molar ratio of HDDA to 8F-HDDA are shown in the legend. Samples were prepared with differing initiator concentrations, (a) 0.5wt% I-369 (b) 1.0wt% I-369 and constant monomer:initiator molar ratio (a) 13:1 (b) 6.6:1. DC voltage was cycled every 3 min, voltages applied were (a) 7.5, 15, 22.5, 30 (b) 5, 10, 15. All samples contained 5wt% of each chiral dopant, S1011 and S811.

components used in this study are shown in Fig. 1. From these constituents, we first examine the retention of structural chirality in compositions containing non-LC monomers. Towards this end, we mix the LC monomer RM82 with HDDA at concentrations ranging from 0-8wt%. All samples were prepared with 8wt% monomer total, with a varying weight ratio between RM82 and HDDA. As can be seen in both the tuning of reflection notch center position (Fig 2a) and the bandwidth of the notch (Fig 2b), as the RM82 is replaced by HDDA the change in the reflection at a given voltage is reduced. However, it is notable that the PSCLC prepared with a completely aliphatic polymer network (e.g., non-LC) tuning is still observed. This indicates that the aliphatic polymer network can retain structural chirality and that the anchoring is strong enough between the polymer network and the LC host to facilitate this mechanism. Two factors may contribute to the reduction in tuning in this experiment. First, in choosing to keep the monomer weight percent constant, with the reduced molecular weight of HDDA, there is commensurate increase in the molar ratio of the monomer to the initiator when more HDDA is present in the mixture. Accordingly, the kinetic chain length will increase and deformability of the polymer stabilizing network may decrease for the 8wt% HDDA sample. Furthermore, generally the shorter length of HDDA should affect the crosslink density. It appears as the polymer network becomes stiffer there is less broadening that occurs for a

given degree of tuning, this can be more easily seen in Fig. S1. At lower voltages, the samples prepared with RM82 show a significant increase in bandwidth before exhibiting red-shift, in the stiffer HDDA samples this is not as pronounced with very little increase in bandwidth even at higher voltages. This seems to imply that a stiffer network promotes a more uniform deformation in the polymer network and pitch, though some non-uniformity is exhibited through the non linear relationship seen in all samples in Fig. S1, previous studies have shown this non-uniform deformation in red-shifting PSCLC samples.[20] Due to significant differences in their structures, it is not possible to investigate how the intermolecular interactions between the LC host and the polymer network affect the tuning capabilities. However, with the ability to create electro-optically active PSCLCs with non-LC polymer systems, we can use the extensive range of commercially available monomers to investigate polymer-LC interactions and the results contribution to response.

Again, prior studies have conclude that the polymerization of the stabilizing polymer network in the CLC phase retains structural chirality. Accordingly, upon application of an electric field, the polymer stabilizing network deforms. Thus, the coupling between polymer network and LC host is critical in facilitating the electro-optic response. Accordingly, we devised experiments that we report in Fig. 3 to access the role of surface affinity on the electro-
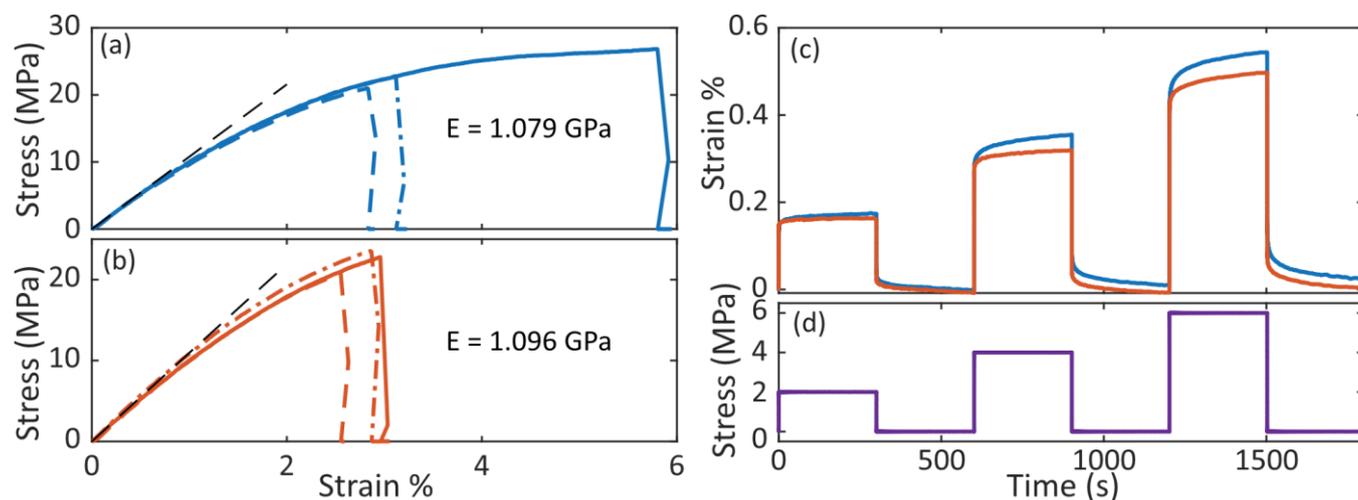
Fig. 5 Mechanical tests performed on solid HDDA (a) and 8F-HDDA (b) films at room temperature. (a,b) Tensile tests performed with a strain rate of 0.1%/min, the monomer used is shown in the inset. Creep recovery tests (c) performed with the stress applied shown in (d), the blue line is an HDDA film and the orange line is for an 8F-HDDA film. The solid films were made with a monomer: initiator molar ratio of 13:1 and were 100μm thick.

optic response of these materials. Towards this end, neat polymers were prepared from HDDA and 8F-HDDA. In contact angle measurements, a lower angle indicates a stronger interaction strength between the liquid and the solid. The contact angle measurements inset in Fig. 3 shows a stronger interaction between our liquid crystal host (MLC-2079) and a HDDA polymer film compared to an 8F-HDDA film. However, the contact angle measurements for both polymers generally show a strong affinity. Not shown, contact angle measurements with an RM82 film exhibited a contact angle of ~0°. To determine if the non-LC monomers were capable of forming templated networks and if the anchoring between the network and liquid crystal is sufficient thermally responsive samples were prepared by using only a single chiral dopant (S1011) was used to prepare the mixture. Before polymerization, the samples were heated to 60°C, to shift the reflection notch to lower wavelengths. After temperature
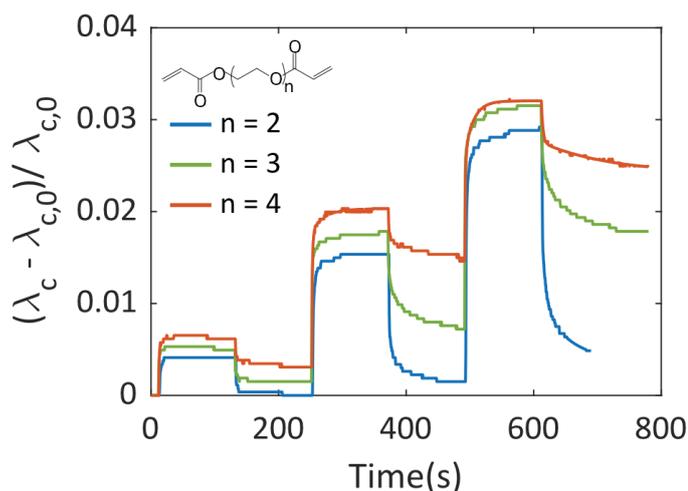
Fig. 6 Change in the reflection notch center normalized against the original notch position vs time while an electrical field is applied on and off. These samples were formulated with a constant monomer: initiator molar ratio of 6.8:1 with 1.0wt% I-369. DC voltage was cycled every 2 min, voltages applied were 5, 10, 15.

equilibration the sample was polymerized by UV light exposure, this results in a small shift in the notch and a mild increase in the haziness of the samples. When the sample is cooled to room temperature the PSCLC prepared with HDDA as well as 8F-HDDA maintain the relative reflection they exhibited after polymerization rather than their original reflection. This result is further evidence the non-LC polymer networks exhibit a structural chirality and have a significant surface interaction strength with the LC host.

In Fig. 4, we compare the electro-optical response of PSCLCs prepared with varying degrees of fluorination in the polymer network. All samples were prepared with the same weight percent of initiator and the monomer to initiator ratio was kept constant for each series to promote equal crosslink density and mechanical properties. PSCLC samples were prepared with three different polymer network compositions, a pure HDDA network, a pure 8F-HDDA network, and a network with a 1:1 molar ratio of HDDA to 8F-HDDA. A constant voltage was applied and held to tune the sample followed by a return to 0V. This cycle was repeated with increasing voltages and spectra collected throughout. It can be seen that independent of the voltage applied, the samples with only HDDA tuned farther regardless of the monomer to initiator ratio. We also observed that samples prepared from the mixture of HDDA and 8F-HDDA exhibited the best recovery of any samples. The inclusion of 8F-HDDA promoted faster dynamic behavior, samples containing this monomer recovered their initial spectral properties faster than the pure HDDA network, even when tuned to a similar position using different voltages. We hypothesize that the inability of these and other samples to return to the original reflection position is due to a permanent deformation in the polymer network.

While we cannot measure the mechanical properties of the polymer network in the PSCLCs, we examine the properties in fully solid polymer films. Fig. 5 plots stress-strain deformation of neat polymerization of HDDA network and an 8F-HDDA network. All mechanical tests were performed on 100μm thick films with the same monomer:initiator molar ratio used to prepare the PSCLC. Tensile tests and creep recovery are presented in Fig. 5 for both

materials. Both films were glassy and exhibited almost identical values for Young's modulus. In the creep recovery tests, the 8F-HDDA samples deformed slightly less at given stress values compared to the HDDA film. However, we conclude from the data presented in Fig. 5a-c that these polymer networks have effectively identical mechanical properties.

To investigate how a change in the mechanical properties of a polymer stabilizing network would affect the response of PSCLCs prepared with aliphatic polymer networks, we utilize polyethylene glycol diacrylate monomers. The comparative electro-optic responses can be seen in Fig. 6. All samples were prepared with a constant monomer:initiator molar ratio so that the only difference affecting the mechanical properties would be the monomer chain length. As the length of the monomer increases, it would be expected that the polymer network would become softer. As evident in Fig. 6, increasing the MW of the PEGDA monomer increases the magnitude of tuning. However, with the increase in tuning range, the optical recovery worsens. Thus, future efforts to realize functional devices based on PSCLCs must optimize mechanical properties of the polymer network as well as surface affinity to maximize tuning rate and recovery.

Conclusions

The electro-optic response of PSCLCs were investigated in stabilized polymer networks prepared with non-LC precursors. The retention of structural chirality in the aliphatic polymer networks allowed the electrical response of the materials (rate, optical properties) to be correlated to the surface affinity and mechanical properties of the stabilizing polymer network. While the magnitude of the electro-optic response is reduced compared to PSCLCs prepared with LC monomers, this examination of aliphatic PSCLC samples amplify the important contribution of mechanical properties in ensuring the ion-mediated electromechanical deformation of structurally chiral, polymer stabilized networks is reversible.

Methods

Cell Preparation

ITO coated glass slides (100Ω/sq) (Colorado Concepts Coatings LLC) were washed with acetone and isopropyl alcohol then treated with air plasma for 10 min. The slides were spin-coated with a 0.025wt% Elvamide (Dupont) solution at 1500 rpm for 10 s followed by 3500 rpm for 50 s. The slides were held under vacuum overnight then rubbed with a cloth to produce a planar alignment layer. The cell was finished by placing two slides together in anti-parallel alignment with the cell gap controlled by 20μm glass spacers (Nippon Electrical Glass Co.) mixed with an optical adhesive (Norland Optical Adhesive 68) which was exposed to a UV lamp for 3 min.

Sample Preparation

Mixtures were prepared from a negative dielectric nematic liquid crystal mixture MLC-2079 (Merck) with a monomer, left-handed (S1011, S811) chiral dopants (Merck), and photoinitiator Omnirad 369 (IGM Resins). Different monomers were used including RM82 (Willshire Technologies), 1,6-Hexanediol diacrylate

(Alfa Aesar), 2,2,3,3,4,4,5,5-Octafluoro-1,6-hexanediol diacrylate (Monomer-Polymer and Dajac Labs), and di/tri/tetra (ethylene glycol) diacrylate (Sigma Aldrich). The mixtures were melt-mixed and capillary filled into on a hot plate below their isotropic temperature and allowed to cool to room temperature before polymerization under a UV lamp (365nm).

Measurements

Transmission spectra were taken with STS-VIS and STS-NIR spectrometers (Ocean Insight) operating concurrently with unpolarized light as the probe beam. Spectra were captured with OceanView software while a DC electrical field was applied. Contact angle measurements were measured with an angle goniometer (Ramé-Heart) with 100μm thick polymer films. Mechanical tests were performed on TA Instruments' RSA-G2 Solids Analyzer. Solid polymer films (2mm x 10mm x 100μm) were loaded into the tensile grips along the long axis and tested at room temperature. Tensile tests were performed with a strain rate of 0.1%/min, creep recovery tests were performed by applying constant stress for 5 min after which the stress was removed and the sample was allowed to relax for another 5 min before repeating the cycle at a higher stress level.

Acknowledgments

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