

SYMPOSIUM CC

Liquid Crystal Materials and Technology

November 29 - December 2, 2004

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* Invited paper

8:30 AM *CC1.1

Thermo/Electro-Mechanical Instabilities in Confined Samples of Nematic Gels. Robert B. Meyer and Guangnan Meng; Physics Dept., MS057, Brandeis University, Waltham, Massachusetts.

Nematic gels and elastomers are soft solids in which a nematic liquid crystal is orientationally coupled to a polymer gel. This results in an interdependence of sample shape and orientation of the nematic orientation axis, and in an interdependence of the local anisotropy of the gel network and the degree of orientational ordering in the nematic phase. For a positive coupling between gel and nematic, as the nematic becomes more highly ordered, the gel tends to become more elongated parallel to the nematic alignment axis (the director). In a confined sample, for instance with rigid boundaries to which the gel is attached, this tendency to change shape can lead to buckling instabilities, in a number of geometries. Addition of an electric field that couples to the director can modify the geometry and threshold conditions for these instabilities. Studies of this subject carried out at Caltech and at Brandeis will be discussed.

9:00 AM *CC1.2

Liquid Crystal Elastomers with Dispersed Nematogenic Molecules. Slobodan Zumer^{1,2}, Andrija Lebar², Bostjan Zalar², Zdravko Kutnjak² and Heino Finkelmann³; ¹Department of Physics, University of Ljubljana, Ljubljana, Slovenia; ²Jozef Stefan Institute, Ljubljana, Slovenia; ³Institut für Makromolekulare Chemie, University of Freiburg, Freiburg, Germany.

Temperature dependence of the orientational order in a monodomain side-group liquid crystalline elastomer poses questions. It is characterized by a continuous evolution of the nematic order as opposed to a weakly first order transition to a nematic phase in a simple liquid crystal. We decided to investigate whether it is possible to distinguish between a supercritical transition induced by an internal mechanical field of the polymer backbone and a smeared transition due to local random fields caused by cross linking the polymer. The deuteron nuclear magnetic resonance (NMR) study is complemented by a high resolution calorimetric study. A polysiloxane type conventional nematic side-group liquid crystalline elastomer (EC4OCH3) is mixed with low molecular weight nematogenic probe molecules of alpha-deuterated octylcyanobiphenil (8CB). The deuteron line splitting originating from the probe molecules is used to determine the average orientational order of mesogenic units of the elastomer. The addition of mesogenic molecules reduces the net effect of the local internal mechanical field of the backbone on the liquid crystalline component of the elastomer. With increasing concentration of low molecular weight component the system becomes closer to an ordinary low molecular weight liquid crystal. Therefore the nematic isotropic transition of the mixture becomes weakly first order. The order was checked also directly using deuterium in natural concentrations. The modeling based on the Landau-de Gennes free energy expansion by including the coupling of the orientational order parameter to the internal mechanical field is used in a critical discussion of the polymer induced orientational ordering and disordering effects dominating experimental results obtained by NMR and calorimetric studies.

9:30 AM CC1.3

When Liquid Crystallinity Meets Actuation. Ingrid A. Rousseau and Patrick T. Mather; Polymer Graduate Program and Chemical Engineering Department, University of Connecticut, Storrs, Connecticut.

Soft actuators are now preferred over hard actuators in a multitude of applications, in particular in biomedical applications where stiffness matching with biological tissue as well as high strain production are necessary to optimize mechanical coupling. Toward this end, we have been developing low-stiffness liquid crystalline elastomers that combine the low glass transition temperatures of silicones and the tailorable phase behavior of liquid crystals. Here, the synthesis and actuation behavior of new main-chain liquid crystalline elastomers (LCEs) exhibiting various mesophases are presented. Low transition temperature LCEs were formed with easily tunable transition temperatures dictated by their chemical composition. We explain the different actuation mechanisms observed in light of previously established rheological behavior intrinsic to liquid crystalline polymers of varying nature. Interestingly, we have found that smectic-C LCEs exhibit shape memory properties - shape fixing and recovery - for which we attribute the maintenance of an arbitrary strain at room temperature for long times to the formation of smectic "transient network" superimposed on the permanent crosslinked network structure. While such a transient network is apparently able

to resist the entropic elasticity of a deformed polymer network to allow fixing, a rapid shape recovery event is possible upon heating to the isotropic rubber state - above the smectic-to-isotropic transition temperature - where the transient network disappears and entropy elasticity drives recovery. Measurements of both shape fixing and shape recovery characterizing the overall shape memory capabilities of our new LCE materials were conducted, revealing admirable values (>98%) relative to other common shape memory polymers (SMPs). In addition, high compliance of the new LCEs was observed, with values ranging from less than 1 MPa to a few 10 MPa, depending on the external temperature and LCE composition.

9:45 AM CC1.4

Tandem Shape Memory Effect in a Polydomain Nematic Network. Haihu Qin and Patrick T. Mather; Polymer Graduate Program and Chemical Engineering Department, University of Connecticut, Storrs, Connecticut.

A family of main chain, thermotropic, unsaturated nematic polyesters has been prepared by Acyclic Diene Metathesis (ADMET) polymerization of 2-t-butyl-1,4-phenol(bis(4-pentenloxybenzoate)), here termed P5tB. By peroxide crosslinking of P5tB, a nematic network with a broad window of liquid crystallinity and unique thermomechanical behavior was obtained. Specifically, this material simultaneously exhibits two distinct shape memory effects, stemming from the coexistence of a fine nematic texture and a polymeric network. The crosslinked nematic structure allows exceptional two-way shape memory effect: on cooling the material under an applied tensile stress, the material undergoes a sharp and large elongation event (~100%), interpreted as the polydomain-monodomain transition, that is completely reversed upon heating through the nematic-isotropic transition (T_{NI}). This thermal actuation persists even against a load of approximately 500 times the sample weight. At the same time, as a polymeric network, the material also demonstrates one-way shape memory at lower temperatures and triggered/fixed by its glass transition (T_g). Here, deformations above T_g can be set, or fixed, by cooling below T_g and then recovered completely by reheating. Interestingly, the two types of deformation and recovery are quite independent. We have studied this aspect by deforming the samples, on cooling, first through the polydomain-monodomain transition and then through network strain, finally vitrifying the entire deformation below T_g . On heating, the strains derived from the distinct deformation mechanisms selectively recover at different temperatures. As a result, simple continuous heating leads to tandem shape recovery events.

10:30 AM *CC1.5

Dynamics of Liquid Crystal Elastomers. Peter Palfy-Muhoray¹, Luis Carlos Malacarne² and Michael Shelley³; ¹Liquid Crystal Institute, Kent State University, Kent, Ohio; ²Departamento de Fisica, Universidade Estadual de Maringa, Maringa, Brazil; ³Courant Institute, New York University, New York, New York.

Because of the strong coupling between orientational order and mechanical strain, liquid crystal elastomers can exhibit large and fast responses to external stimuli. Modelling the dynamic response is an interesting and challenging problem; accurate and efficient modeling is also requirement for device development. The system dynamics can be characterized by the motion of the conserved crosslinks, and the time evolution of non-conserved orientational order parameter. We have developed a fully non-local free energy for nematic elastomers, which includes the effects of incident light, applied electric and magnetic fields, temperature and mechanical stress. We have also constructed the corresponding Rayleigh dissipation function. From the free energy and the dissipation function, we have derived the equations of motion for the displacement and nematic order parameter fields. We discuss these equations, boundary conditions, approaches to providing a numerical solution, and the current status of our numerical efforts. We give a quick overview of experimental results to date, and compare these with the preliminary results of computation.

11:00 AM *CC1.6

Thermal mechanical responses of liquid-crystalline networks with splayed molecular organization. Dirk J. Broer^{1,2}, Titie Mol¹, Ken Harris² and Cees Bastiaansen²; ¹WAG 1230, Philips Research Laboratories, Eindhoven, Netherlands; ²Eindhoven University of Technology, Eindhoven, Netherlands.

Various groups have demonstrated dimensional changes in liquid crystal elastomers induced by temperature[1-3]. The mechanism is based on changes in molecular organization, which becomes particularly large at the transition to isotropic. To allow large amplitudes, the molecular rotational mobility must be sufficiently high. Therefore polymers are selected with a flexible backbone and consequently relatively low elastic modulus. The selection of a low modulus allows for large dimensional changes, though prohibits supply of mechanical work. We demonstrate a polymer, based on a densely

crosslinked liquid crystal obtained by photopolymerization of reactive mesogens, that combines large temperature-stimulated amplitudes with a high modulus. We used the difference in thermal expansion of the LC network measured parallel to the molecular alignment opposite to the orthogonal alignment direction [4]. Perpendicular to the alignment of the mesogenic units the thermal expansion has a normal behavior although somewhat larger than for an isotropic network of the same material. Parallel to the alignment the thermal expansion is low and becomes negative when the temperature exceeds the glass transition. This is explained in terms of the reversible variation of the order parameter. To utilize these thermal expansion differences, we made polymer films with a gradient in the molecular orientation over their cross-section. This generates a difference in thermal expansion and consequently bending of the films. There are two options to make this orientation gradient. Firstly we used the so-called TN mode where the mesogenic units are oriented in the plane of the film but rotate over 90 degrees. The top and the bottom of the film will now have orthogonal thermal expansion behavior in two directions tending to form saddle-like shapes when being heated. More favorable, giving a well-controlled mechanical deformation, are films that contain a splayed molecular alignment. Here the mesogenic units are aligned parallel to one surface and perpendicular to the opposite surface. The transition between the two states occurs gradually and is controlled by the molecular elastic behavior of the LC monomer. The splayed structure gives a large and two-dimensionally isotropic expansion at the surface with perpendicular alignment. At the opposite surface with planar alignment the thermal expansion is large in the in-plane direction perpendicular to the director but small in the in-plane direction parallel to the orientation. As a result the bending deformation of the film with increasing temperature proceeds smooth and with a large amplitude. [1] A. Greve and H. Finkelmann, *Macromol. Chem. Phys.* 175 (14), 2926 (2001) [2] P. Stein, N. Afsal and H. Finkelmann, *Eur. Phys. J. E.* 4(3), 255 (2001) [3] W.E.P. Palffy-Muhoray, *J. Nonlin. Sci.* 9, 417(1999) [4] D.J. Broer and G.N. Mol, *Polymer Engineering and Science* 31 (9), 625(1991)

11:30 AM CC1.7

Dynamics of Nematic Gels Self-Assembled from Block Copolymers. Rafael Verduzco, Neal R. Scruggs and Julie Kornfield; Chemical Engineering, Caltech, Pasadena, California.

We report the behavior of novel liquid crystalline materials that consist of a physically crosslinked polymer network swollen by a small molecule LC. The network is formed by the association and microphase separation of nematophobic endblocks, but the network is solubilized due to the presence of a nematogenic midblock, which is a side group liquid crystalline polymer. We report on the alignment, phase behavior, electro-optic behavior, and stripe phenomena in the resulting gels. Using very long side-group liquid-crystalline (LC) midblocks (>800 kg/mol), single phase gels can form at lower concentrations than permitted by prior approaches. At low polymer concentration (3-5%), the gel switches quickly (milliseconds) under modest electric fields. (Switching is associated with a threshold field, rather than the usual threshold voltage, because the network acts throughout the volume.) The speed at which the gel switches and relaxes depends on the amplitude of the applied AC field. Just above the threshold field, the switch on time is slow while the relaxation back to the initial state (driven by the polymer network) is faster than for conventional TN displays. At high voltages, the switch on time is fast but the switch off time is extremely slow. At intermediate voltages, both times are comparable to those for commercial displays, but contrast is reduced. The various regimes arise from the response of the network to the applied field.

11:45 AM CC1.8

Molecular Architecture of Nematic Gels Self-Assembled from Block Copolymers. Neal R. Scruggs¹, Rafael Verduzco¹, Jyotsana Lal² and Julie Kornfield¹; ¹Caltech, Pasadena, California; ²Argonne National Laboratory, Argonne, Illinois.

Block copolymers with side-group liquid crystalline (LC) midblocks and LC-phobic end-blocks form a physical network that swells readily in a small molecule LC to form nematic gels. Ultralong (800 kg/mol) side-group liquid crystal polymers (SGLCP) are used for the midblock to enable gelation at relatively low concentration (~5% polymer). The materials provide model systems in which the molecular weight between crosslinks is well defined and determined by the length of the polymer midblock. Similar to LC elastomers, an initially unaligned, polydomain gel aligns under applied strain. The optical uniformity of the resulting monodomain is excellent - sufficient to generate clear conoscopic figures. Small-angle neutron scattering (SANS) is used to measure the sense (parallel vs. perpendicular) and degree of orientational coupling between the backbone of the SGLCP and surrounding mesogens. The alignment tendency of the gel is dictated by the inherent properties of the SGLCP: in a shear cell, gels with prolate-type SGLCP midblocks align along the flow direction, while gels with oblate-type midblocks align homeotropically. Birefringence

and NMR measurements (deuterium quadrupolar splitting) show that the homopolymer SGLCP weakly perturbs the order parameter, S , of the host; however, the triblock polymer reduces S significantly. Self-assembly of coil-LC block copolymers should also extend to gels exhibiting higher-order LC phases, such as ferroelectric gels.

SESSION CC2: Dye-Doped and Lyotropic LC Materials

Chairs: Dick Broer and Allan Guymon

Monday Afternoon, November 29, 2004

Room 313 (Hynes)

1:30 PM *CC2.1

Photoalignment Effect in Dye-doped Liquid Crystal Films.

Andy Y. G. Fuh, ¹Physics, National Cheng Kung Univ., Tainan,

Taiwan; ²Institute of Electro-optics, National Cheng Kung University, Tainan, Taiwan.

This study examines the surface-assisted photo-alignment effect of azo dye-doped liquid crystal (DDLC) films having a homogeneous alignment. Observations made using a polarizing optical microscope (POM), a scanning electron microscope (SEM) and an atomic force microscope (AFM) confirm that the morphology of laser-induced surface-adsorbed dyes at the command surface strongly affect the orientation of liquid crystals (LCs) in a manner that depends significantly on the intensity and duration of the green-blue pumping light. In weak intensity regime, homogeneous and fine layer of adsorbed dyes competes with the layer of ripple structure in reorienting LCs. These two effects dominantly cause LCs to reorient perpendicular and parallel to the polarization direction of the pump beam in the early and late stage, respectively. In high intensity regime, rough and inhomogeneous ribbon-like adsorbents produced by rapid and random aggregation and adsorption form on the top of the pre-formed microgrooves, reorienting LCs irregularly. This surface morphology does not enable photoalignment. The adsorption of the dyes induced by the green-blue pumping light is through the strong dye absorption and then the trans-cis isomerization. The adsorption is found to be inhibited by the simultaneous irradiation of red light on the sample with the green-blue light. The red light induces the cis-trans inverse-isomerization. Thus, the biphotonic effect allows us to fabricate the micropatterning of LC alignment. Using such a biphotonic effect, the fabrication of an electrically-switchable and thermally-erasable biphotonic grating is demonstrated. The author would like to thank the National Science Council (NSC) of the Republic of China (Taiwan) for financially supporting this research under the Contract No. NSC 91-2112-M-006-019.

2:00 PM *CC2.2

New Developments in Photo-Aligning with Azo-Dye Layers.

Vladimir G. Chigrinov¹, Hoi Sing Kwok¹, Hirokazu Takada² and Haruyoshi Takatsu²; ¹Hong Kong University of Science and Technology Clear Water Bay, Kowloon, Hong Kong, Hong Kong, Hong Kong; ²Corporate R&D Division, Dainippon Ink and Chemicals Inc., Japan, Tokyo, Japan.

The paper presents the new developments of the liquid crystal photoaligning technology by using azo-dyes. We proposed the model of the rotational diffusion of azo-dye molecules under the action of a polarized UV-light to explain the formation of the photo-induced order in azo-dye layers. Diffusion mechanism does not involve any photo-chemical or structural transformation of azo-dye molecules. The model uses the diffusion equation with the specific potential, which characterizes the interaction of the molecule and the activated light. A good agreement with the observed experimental value was found. We have shown, that azo-dye materials can provide a perfect uniform alignment with a sufficiently high polar and azimuthal anchoring energy and appropriate pretilt angles. The Voltage Holding Ratio (VHR) is high enough to enable the application of these materials in TFT-LCDs. The azo-dye materials are thermostable and UV-stability can be considerably improved after thermo-polymerization. Both bistable ferroelectric mode and Vertical Aligned Nematic (VAN) mode can be produced using the azo-dye photoaligned liquid crystal cells. Recently we have also shown, that the azo-dye photo-aligning materials can be very helpful for p-bistable nematic twisted LCD and silicon microdisplays. The photo-aligned azo-dye materials are promising candidates for the new generation of high resolution TFT-LCDs.

2:30 PM CC2.3

Optical and Electrical Switching of Diffraction Gratings

Based on Azo Polymer/Liquid Crystal Composites. Xia Tong¹,

Guang Wang¹, Artashes Yavrian², Tigran Galstian² and Yue Zhao¹;

¹Chemistry, University of Sherbrooke, Sherbrooke, Quebec, Canada;

²Physics, Laval University, Quebec, Quebec, Canada.

A mesogenic azobenzene-containing dimethacrylate monomer was

synthesized and dissolved in a nematic liquid crystal (BL006) in large amount (20 wt%). When the mixture containing also a visible light photoinitiator was filled in a parallelly rubbed, ITO-coated electrooptical cell (10 mm gap) and exposed to visible light, both through a grating photomask and using an interference pattern, photopolymerization induced segregation of the azo polymer from the LC occurred under appropriate conditions, which resulted in the formation of a diffraction grating. The diffraction efficiency of such gratings could be switched not only by an electric field, but also by light at two wavelengths. The control of light diffraction by light was based on the reversible trans-cis photoisomerization of the azobenzene chromophore incorporated in a LC polymer network.

2:45 PM **CC2.4**

Photo-optic Properties of Patterned, Polymer Stabilized LC Materials. Augustine M. Urbas¹, Vincent Tondiglia¹, Lalgudi Natarajan¹, Richard Sutherland¹, Haiping Yu², J.-H. Li² and Timothy Bunning¹; ¹AFRL, WPAFB, Ohio; ²KOI, Kent, Ohio.

Dynamic optical materials will be the basis of a wide range of technologies including sensing and communications. A variety of strategies will be used to enable practical and useful changes in the optical properties of bulk material and nanostructured optical systems. In this presentation, the details of a photo-optic holographically prepatterned polymer stabilized liquid crystal (LC) optical structure will be explored. A 'reverse-mode' or normally transparent, nanopatterned optical device has been fabricated which, when exposed to light, becomes reflective for a range of wavelengths, as a Bragg reflector. The optical properties of this passive dynamic system will be explored in relation to the patterning geometry and material composition. In addition, the dynamic properties of the polymer stabilized structure will be compared to those of a bulk liquid crystal and polymer stabilized LC system. This will further refine the technology for application and provide some insight on the physical properties of photo-optic LC systems.

3:30 PM ***CC2.5**

Control of Polymer Nanostructure in Photopolymerization of Lyotropic Liquid Crystalline Systems. Allan Guymon and Michael DePierro; Chemical and Biochemical Engineering, University of Iowa, Iowa City, Iowa.

Photopolymerization within lyotropic liquid crystalline (LLC) media is a promising method for the controllable synthesis of nanostructured polymers. The nanoscale morphology of various LLC phases has been preserved in numerous organic materials with full retention of structure. Polarized light microscopy (PLM) and small angle x-ray scattering have been employed to examine the structure evolution during polymerization. The degree to which original LLC structure is preserved appears highly dependent on the polymerization kinetics. Excellent retention of various LLC phases occurs with relatively fast polymerizations. When polymerization occurs more slowly, phase separation is manifest by blurring of the optical texture observed with PLM as well as changes in x-ray diffraction, indicating less retention of original LLC order in the polymerized material. To understand the factors influencing the polymerization behavior in LLC media, the polymerization kinetics of monomers with different polarity in several LLC phases have been monitored using photo-differential scanning calorimetry (PDSC). Polar and nonpolar monomers segregate to different regions of the LLC, and as a result, display remarkably different trends in the rate of polymerization with respect to LLC order. Segregation of photoinitiator also plays an important role in the polymerization kinetics in LLC domains despite its low overall concentration in the system. The polymerization behavior with highly mobile photoinitiators depends primarily on the segregation of monomer, while that with relatively bulky, less soluble initiators is governed by the rate of initiation in the different phases.

4:00 PM ***CC2.6**

Self-Assembled Nanostructures of Novel Liquid Crystals Containing Amphiphilic Phenyl- α -D-Glycopyranoside group. Chain-Shu Hsu, Applied Chemistry, National Chiao-Tung Univ., Hsinchu, Taiwan.

A novel class of organic nanostructure with an intriguing diverse aggregate morphologies, that exhibit mesomorphic properties as well, were prepared by a simple precipitation method. The salient features of these newly developed amphiphiles include an imine as spacer between sugar and lipid as well as a convenient procedure for the Schiff-base preparation. All compounds show smectic liquid crystal phase. The amphiphile nanostructures were prepared by a simple precipitation method. Distilled water was added dropwise to a phenyl glucoside solution in THF as well as various other organic solvents, and then heated to give a clear solution. Interestingly, the morphology of the prepared materials produced variation from tubular, twisted ribbon, helical ribbon to vesicle when the length and the number of the long flexible alkoxy tether altered.

4:30 PM **CC2.7**

Interfacing Liquid Crystals with Mammalian Cells.

Nathan Lockwood¹, Yan-Yeung Luk¹, Sean Campbell², Christopher Murphy² and Nicholas Abbott¹; ¹Chemical and Biological Engineering, University of Wisconsin, Madison, Wisconsin; ²Department of Surgical Sciences, School of Veterinary Medicine, University of Wisconsin, Madison, Wisconsin.

Our work explores the use of the liquid crystalline state to create interfaces between synthetic materials and cells. Cell-compatible liquid crystals could lead to a means of imaging, for example, dynamic reorganization of cell surfaces. Mechanical cues could also be delivered to cells using liquid crystals. A prerequisite to using liquid crystals for whole-cell experiments, however, is the identification of nontoxic liquid crystals. We have investigated the toxicity of several liquid crystals using mammalian fibroblast and human corneal epithelial cell lines. Using dual fluorescent staining assays, we measured the number of viable and dead cells following immersion of the cells under the liquid crystals. We found that most of the liquid crystals, such as commonly used 5CB and E7, caused cell death after contact with cells for four hours. However, we identified two classes of liquid crystals, one being cholesteric liquid crystals and the other a class containing fluorophenyl groups, that possess minimal or no toxicity to cells over four hours. Following immersion in cholesteric and fluorophenyl liquid crystals for four hours, we observed the cells to subsequently proliferate normally in cell culture medium. Immersion of the cells under the liquid crystals for 24 hours resulted in cell death due to the lack of essential nutrients in the liquid crystals (i.e., cell starvation, not toxicity). During these studies, toxic liquid crystals were observed to cause leakage of cell contents through damaged cell membranes. Based on the hypothesis that toxic liquid crystals act by disrupting the cell membrane, we investigated liquid crystal interactions with a cell-mimetic liposome system. After incorporating liquid crystals into lipid bilayers, we used dynamic scanning calorimetry to measure changes in the thermal properties of lipid bilayer as an indication of liquid crystal-lipid bilayer interactions. Perturbations in the lipid phase transitions were found to be much greater for toxic liquid crystals incorporated into liposomes than for non-toxic liquid crystals in the same lipid system. Further, neat toxic liquid crystals were taken up in bilayer vesicles of pure lipid, whereas neat non-toxic liquid crystals were not.

4:45 PM **CC2.8**

Swollen Liquid Crystals as new nanoreactors. Eric P. Prouzet¹, Hynd Remita² and Laurence Ramos³; ¹I.E.M., C.N.R.S., Montpellier Cedex 05, France; ²L.C.P., C.N.R.S., Orsay Cedex, France; ³G.D.P.C., C.N.R.S., Montpellier Cedex 05, France.

Since 90's, one observes a huge development in the synthesis processes of nano- or meso-structured materials. Following the first developments of mesoporous oxides by assembly processes between inorganic precursors and micellar solutions, the concept of "nanocasting" by binary Liquid Crystals (LC) was developed for the synthesis of silica or metals [1, 2]. However, these syntheses referred always to binary systems and did not provide an extreme versatility in the final structure. We developed a similar approach, but with the help of Highly Swollen Liquid Crystals (SLC) that exhibit hexagonal, cubic or lamellar symmetry. The hexagonal shape of these mesophases, which are formed by a quaternary mixture combining a surfactant, an aqueous solution of inorganic salt, an alkane as a hydrophobic swelling solvent and a linear alcohol as a co-surfactant, was discovered in the 90's but they were only used for the insertion of nanoparticles inside, not as true nanoreactors [3, 4]. They displayed at room temperature a direct hexagonal phase constituted of infinite nonpolar cylinders swelled by cyclohexane and stabilized by a monolayer of SDS surfactant plus pentanol as co-surfactant, arranged in a hexagonal array in water, and whose diameter ranges usually between 3 and 30 nm. We demonstrated that various compounds including metals, polymers and oxides could be synthesized, either in the aqueous phase or in the organic one. If one wishes to use these mesophases as actual nanoreactors whose characteristics (nature of solvents, pH...) could be monitored as a function of the physico-chemical properties required for any desired synthesis, the concept of SLC had to be extended to a broader range of compositions than those reported previously. To this purpose, after a brief description of the different materials that can be obtained by this method, we will demonstrate that this concept can be extended to the whole range of surfactants (nonionic, anionic, cationic) and in a wide range of pH (from -0.6 to 11). The influence of the SLC structure on the final nanomaterial structure will be also discussed. [1] G. S. Attard, J. C. Glyde, C. G. Goltner, *Nature*, 378 (1995) 366 [2] G. S. Attard, P. N. Bartlett, N. R. B. Coleman, J. M. Elliott, J. R. Owen, J. H. Wang, *Science*, 278 (1997) 838 [3] L. Ramos, P. Fabre, *Langmuir*, 13 (1997) 682 [4] L. Ramos, P. Fabre, R. Ober, *European physical journal B*, 1 (1998) 319

CC3.1
Abstract Withdrawn

CC3.2
Effect of the U.V. Power on the Morphology and Electro-optical Properties of Reverse Mode Polymer-Dispersed Liquid Crystal Films. Giovanni De Filipo, Luana Tortora, Roberta Cassano, Fiore P. Nicoletta and Giuseppe Chidichimo; Chemistry, University of Calabria, Arcavacata di Rende, COSENZA, Italy.

The aim of this work was to investigate the effect of the U.V. irradiating power on polymer-dispersed liquid crystal films (PDLC) working in reverse mode operation. Films have been obtained by mixtures of a low molecular weight nematic liquid crystal and a photo-polymerizable liquid crystal monomer, homeotropically aligned between rough conductive surface. IR spectra and conductivity measures demonstrate that U.V. exposition induces a degradation of the nematic liquid crystal. The morphological and electro-optical properties of the reverse-mode PDLC films have been related to the polymerization conditions: samples polymerized at 1mW/cm² had a morphology and an electro-optical response typical of the reverse-mode PDLC, while samples obtained polymerizing at high UV power showed a droplet morphology and were characterized in the ON state by a dynamic scattering.

CC3.3
Colored Cholesteric Emulsion. Giovanni De Filipo, Luana Tortora, Roberta Cassano, Fiore P. Nicoletta and Giuseppe Chidichimo; Chemistry, University of Calabria, Arcavacata di Rende, COSENZA, Italy.

We present a new RGB colored electro-optical film obtained by means an oriented cholesteric liquid crystal confine in droplets dispersed in an organic monomer matrix. The pitch of the cholesteric liquid crystal was adjust by using a photosensitive chiral material in order to produce the three reflected colors (red, green, and blue) for a multicolor reflective cholesteric display. Confining the cholesteric liquid crystal in droplets solve the problem related of color diffusion between two different colored areas. We report the reflection spectra of such films irradiated at different U.V. energy and the their morphology.

CC3.4
Effect of Varying the Thiol and Ene Functionalities on the Formation and Performance of H-PDLC Gratings. Lalgudi V. Natarajan^{1,3}, Vincent P. Tondiglia^{1,3}, Richard L. Sutherland^{1,3}, Pam Lloyd^{2,3} and Timothy J. Bunning³; ¹Science Applications International Corporation, Dayton, Ohio; ²UES, Dayton, Ohio; ³Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio.

A systematic study of varying the functionality of the aliphatic thiol component and the ene component in the thiol-ene photopolymerization leading to the formation of holographic polymer dispersed liquid crystal gratings was made. Electrically switchable reflection gratings in the visible region were made using the 363.8 nm line of Argon ion laser. Commercially available (Merck) nematic crystal BL038 was used in the pre-polymer syrup. The thiols studied were: 1,6-hexane dithiol, trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tertakis(3-mercaptopropionate). The enes were: tris(ethylene glycol) divinyl ether, trimethylol propane diallyl ether, pentaerythritol triallyl ether. The diffraction efficiencies of the reflection gratings increased with functionality. Optical, electro-optical and morphology studies were made.

CC3.5
Morphological Characterization of Polymer/LC Composites Using Ultra Small Angle X-ray Scattering (USAXS). Ryan S. Justice¹, Timothy J. Bunning², Richard A. Vaia² and Dale W. Schaefer¹; ¹Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio; ²Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright Patterson Air Force Base, Dayton, Ohio.

Polymer dispersed liquid crystals (PDLCs) are of technological importance in the development of switchable windows, electro-optic shutters, displays, and switchable gratings. Using photo-initiated

polymerization of an initially homogenous mixture containing reactive monomers and liquid crystal molecules, a two-phase product is produced whose optical properties depend on the composition and polymerization protocol. Using ultra small angle x-ray scattering (USAXS), we find nanoscale domains whose morphology depends on 1) the liquid crystal concentration, 2) the components of the initial monomer syrup, or 3) the intensity of the curing radiation. We find that the domain size depends strongly on the liquid crystal concentration but weakly on the other processing parameters. In some cases, two length scales are observed in the morphology. From the limiting Porod slope, we observe a crossover from mass to surface fractal character with liquid crystal concentration. Because of the fractal character of the domains, invariant analysis proved inconclusive.

CC3.6
Synthesis and Characterization of Fluoroazobenzene Side Chain Liquid Crystal Diblock Copolymers. Fengxiang You, Marvin Young Paik and Christopher K. Ober; Materials Science & Engineering, Cornell University, Ithaca, New York.

Liquid crystalline side chain block copolymers have received growing attention in recent years since these polymers can simultaneously self-assemble on different length scales, thereby providing a new approach to tailoring material properties. Fluoroazobenzene side groups were prepared with different lengths of CF₂ segments and then attached to the isoprene block of poly(styrene-*b*-isoprene) diblock copolymers which were synthesized via anionic polymerization. These fluoroazobenzene side chains can organize into a well-ordered surface layer due to their combination of low surface energy and liquid crystallinity. We have investigated the effects of UV irradiation on surface properties and the reorientation of the fluorinated side chains as a result of the trans-cis photoisomerization of the azobenzene unit. Block copolymers with 2-arm and 3-arm monodendron azobenzene side groups have also been synthesized and their surface and bulk properties were studied.

CC3.7
Cholesteric Stacking as the Predominant Contributor to Chiroptical Activities in Oligofluorene Films. Anita Trajkovska¹, Yanhou Geng¹ and Shaw H. Chen^{1,2}; ¹Chemical Engineering, University of Rochester, Rochester, New York; ²Laboratory for Laser Energetics, University of Rochester, Rochester, New York.

Glassy chiral oligofluorenes were synthesized for an investigation of the origin of chiroptical activities in neat films. Thermal annealing of 4-micron-thick sandwiched films and of 90-nm-thick spin-cast films on surface-treated substrates produced monodomain glassy films characterized as a right-handed cholesteric stack with a helical pitch length ranging from 180 to 534 nm and from 252 to 1151 nm, respectively. The observed strong circular dichroism and circularly polarized fluorescence as functions of helical pitch length in single-substrate monodomain glassy cholesteric films were quantitatively interpreted with a CPF theory accounting for light absorption, emission, and propagation in a cholesteric stack. Although intertwined molecular helices are likely to be present, cholesteric stacking of rod-like molecules seems to be the predominant contributor to the strong chiroptical activities. All the cholesteric stacks comprising a polydomain glassy film on an untreated substrate contribute to circular dichroism and circularly polarized fluorescence largely to the same extent as in a monodomain film. A light-emitting diode containing a nonafluorene film resulted in a high degree of circularly polarized emission.

CC3.8
Polarized OLEDs Using Monodisperse Glassy-Nematic Oligofluorenes. Andrew Chen¹, Sean W. Culligan¹, Yanhou Geng¹, Shaw H. Chen^{1,2}, Kevin Klubek³, Kathleen Vaeth³ and Ching W. Tang³; ¹Chemical Engineering, University of Rochester, Rochester, New York; ²Laboratory for Laser Energetics, University of Rochester, Rochester, New York; ³Eastman Kodak Company, Rochester, New York.

Polarized OLEDs were constructed using heptafluorene lightly doped with monodisperse conjugated oligomers for an efficient emission of green, red and white light. This is the first demonstration of polarized OLEDs by way of the intermolecular Forster energy transfer. At a current density of 20 mA/cm², an emission peak polarization ratio up to 26, an integrated polarization ratio up to 19, and a luminance yield up to 6.4 cd/A have been accomplished. Compared to previously reported polarized green and red OLEDs, the donor-acceptor approach resulted in superior polarization ratio and luminance yield. The first ever polarized white-light OLED has been achieved with an integrated polarization ratio of 16 and a luminance yield of 4.5 cd/A. All the CIE coordinates were found to be essentially independent of current density up to 100 mA/cm². Highly polarized OLEDs are

potentially useful as an efficient light source for liquid crystal displays, for electroluminescent displays with improved viewing quality, projection displays, and stereoscopic imaging systems. In addition, efficient electroluminescence via energy transfer using monodisperse conjugated oligomers could lead to low threshold solid-state organic lasers with an added advantage of high polarization.

CC3.9

Mechanical Properties of Polystyrene Ionomers Blended with two Different Liquid Crystalline Polyesters. Joon-Seop Kim, Yu-Ri Park and Ju-Myung Song; Polymer Engineering Dept., Chosun University, Gwangju, South Korea.

The dynamic mechanical properties of thermotropic liquid crystalline polyester copolymers of 2-(phenylisopropyl)hydroquinone, 2,6-dihydroxynaphthalene and terephthalic acid (PIDHN) blended with non-ionic polystyrene (PS) and Li-sulfonated polystyrene ionomer (LiSPS) (10.1 mol% of ions) were studied dynamic mechanically. It was found that the PS homopolymer was not miscible with PIDHN. In addition, it was seen that the modulus values increased upon the addition of PIDHN to the PS, indicating that the PIDHN acted as filler particles for the PS homopolymer below its glass transition temperature. In the case of LiSPS/PIDHN blends, it was also observed that the modulus values increased and the cluster Tg of ionomer increased. These results suggested that the LCP copolymer also acted as filler. However, it should be mentioned that the level of the increase in modulus values was higher for the ionomer blend system, compared to the PS blend system, which was due to the difference in the natures of un-blended PS and ionomer properties. In a second study, the sulfonated random copolymer of the rigid moiety terephthaloyl bis(4-oxybenzoyl) with butylene terephthalate flexible unit was prepared (NaS-TLCP), and the dynamic mechanical properties of its blends with PS and NaSPS ionomer (containing 4.2 mol% of ions) were investigated dynamic mechanically. It was found that the non-ionomer form TLCP in the blend of PS acted just as filler, and, thus, shifted the Tg of PS to higher temperatures. In the case of NaSPS blends with TLCP and NaS-TLCP, it was seen that the TLCP molecules disrupted the formation of multiplet of NaSPS ionomer. However, the addition of the NaS-TLCP ionomer to the NaSPS decreased the cluster Tg of blends, but shifted the modulus plateau related with ionomer clustering to higher values, indicating NaS-TLCP acted as filler strongly.

CC3.10

Monodisperse Glassy Liquid Crystalline Conjugated Oligomers for Organic Field-Effect Transistors. Feng Yan¹, Sean W. Culligan¹, Shaw H. Chen^{1,2}, Ching W. Tang³ and David Levy³; ¹Chemical Engineering, University of Rochester, Rochester, New York; ²Laboratory for Laser Energetics, University of Rochester, Rochester, New York; ³Eastman Kodak Company, Rochester, New York.

Organic semiconductors comprising conjugated molecules or polymers are promising for use in plastic electronics with potential applications in flat-panel displays, electronic paper, solar cells, and chemical sensors. One major motivating factor is that organic semiconductors can be readily processed into thin films on flexible substrates at substantially lower temperatures than traditional silicon-based materials. Molecular order and pi-stacking are conducive to charge transport. Most organic field-effect transistors reported to date consist of polycrystalline semiconductive films in which carrier mobility varies with chemical impurities, crystal grain size and boundaries, crystallographic defects, and the orientation and order of pi-stacks. These extrinsic parameters are difficult to control or reproduce in polycrystalline films. Amorphous films have no grain boundaries but possess a much lower mobility than polycrystalline films in the absence of molecular order or pi-stacking. Through molecular self-assembly, liquid crystals can form ordered fluid films with no grain boundaries; however, solid films are preferred for practical application. Characterized by structural regularity and uniformity, chemical purity, solubility, and ease of processing into well-ordered solid films, glassy liquid crystalline conjugated oligomers are uniquely suited to furnish high mobility across a large area without grain boundaries. In this presentation, we will present the molecular design concept illustrated with a series of novel materials.

CC3.11

Synthesis and Characterization of Photopolymerizable Liquid Crystalline Compounds with Two Photoreactive Sites. Suk Hoon Kang and Ji Young Chang; Seoul National University, Seoul, South Korea.

The highly ordered polymer networks are of great interest because they exhibit anisotropic mechanical and optical properties. The physical properties of such networks can be optimized by long range ordering, e.g. a uniaxial or a biaxial orientation of the polymer chains. Liquid crystalline (LC) anisotropic network can be obtained by cross-linking polymerization of reactive mesogenic compounds in LC

states. One of the most practical methods for obtaining highly ordered LC network is photo-polymerization of liquid crystals in an oriented mesomorphic state. The LC state polymerization can be also employed to make LC gels, side chain liquid crystal polymers, and LC elastomers. In this study, we prepared a novel liquid crystal having two photoreactive sites. A acrylate and a diacetylene group were used as photoreactive sites. The reaction of symmetric 1,4-bis(4-hydroxyphenyl)butadiene with acryloyloxyhexyloxy benzoic acid was carried out to give an LC compound (1). A DSC thermogram exhibited an endotherm at 110 °C for a crystal-to-nematic transition without melt transition, and a strong exotherm around 280 °C which was attributable to the thermal polymerization. Patterned images were produced by two step photopolymerization. A solution of 1 and 4 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA) in toluene was spincoated on a rubbed polyimide film, dried in vacuum oven, and annealed at 150 °C. The partial photopolymerization of diacrylates with a 365 nm UV lamp was carried out to make uniform film for 5 min and then crosslinked reaction of diacetylenic units using 254 nm UV lamp was carried out for 60 min through a photomask. Patterned images were observed by POM.

CC3.12

Photochromic Glassy Liquid Crystals for Non-destructive Rewritable Optical Memory. Philip H. M. Chen¹, Chunki Kim¹, Shaw H. Chen^{1,2}, Steve D. Jacobs^{2,1} and Ken L. Marshall²; ¹Chemical Engineering, University of Rochester, Rochester, New York; ²Laboratory for Laser Energetics, University of Rochester, Rochester, New York.

Morphologically stable glassy liquid crystals comprising a dithienylethene core have been successfully designed and synthesized to achieve elevated phase transition temperatures. It appears that both the type and the number of nematic pendant per molecule are critical to the desired thermotropic property and stability against thermally induced recrystallization. One of the salient features of this material class is its ability to form a macroscopically ordered solid film in which the photoresponsive core's electronic transition moment is spontaneously aligned with the nematic director. As a result, refractive indices and optical birefringence can be modulated to a large extent by photochemical means. The selected dithienylethene core is characterized by thermal stability, fatigue resistance, high quantum yields, and a fast response. Therefore, glassy-nematic liquid crystals present new opportunities for nondestructive rewritable optical memory and high-speed photonic switches, including spatial light modulators, filters, polarizers, and beam splitters for optical communication and image processing.

CC3.13

Deterministic Synthesis of Glassy Cholesteric Liquid Crystals. Philip H. M. Chen¹, Chunki Kim¹, Jason U. Wallace¹ and Shaw H. Chen^{1,2}; ¹Chemical Engineering, University of Rochester, Rochester, New York; ²Laboratory for Laser Energetics, University of Rochester, Rochester, New York.

Three distinct approaches were explored for the deterministic synthesis of glassy chiral-nematic liquid crystals: monohydrolysis of the trimethyl ester of 1,3,5-cyclohexanetricarboxylic acid and that of 1,3,5-benzenetricarboxylic acid as well as using 5-hydroxyisophthalic acid as the central core. Each chiral-nematic molecule consists of two nematic groups and one chiral group chemically bonded to a benzene or cyclohexane core. Specifically, 4-(3-hydroxy-propoxy)-benzoic acid 4'-cyanobiphenyl-4-yl ester and 3-(4'-cyano-p-terphenyloxy)-1-propanol were used as nematogenic precursors, and (S)- and (R)-1-(phenylethyl)-4-[[4-(2-hydroxyethoxy)-benzoyl]oxy]benzamide and (+)-estrone as chiral precursors. A high-temperature glassy nematic was also prepared with three 4-cyano-4'-biphenylbenzoate groups to cyclohexane. The resultant glassy liquid crystals were characterized by differential scanning calorimetry, hot-stage polarizing microscopy, transmission and reflection spectrophotometry, and scanning electron microscopy. Key findings are recapitulated as follows: (1) The glassy chiral nematics showed a glass transition temperature from 67 to 82 C and a cholesteric fluid temperature range over 100°C due in part to the high clearing temperatures of the nematic precursors. A glassy nematic showed a glass transition temperature at 67 C and a clearing point at 310 C, an unusually broad nematic fluid temperature range; (2) The chiral pendant containing (R)- and (S)-1-phenylethylamine resulted in a helical pitch length from 188 to 210 nm, yielding a selective reflection band in the UV-region. In contrast, (+)-estrone as the chiral pendant led to a selective reflection in the near infrared region; and (3) Selective reflection wavelength can be tuned across the visible to the infrared region by mixing a pair of enantiomeric chiral nematics at varying ratios for the fabrication of high-performance circular polarizers, optical notch filters and reflectors. Alternatively, tunability can be accomplished by mixing a chiral nematic with a nematic at varying ratios.

CC3.14

Fluorine Controlled Liquid Crystalline Mesophases of Calamitic Organic Semiconductors for Organic Thin Film Transistor. Ghim Jieun¹, Noh Yong-Young¹, Azumi Reiko², Goto Midori³, Yoshida Yuji⁴, Yase Kiyoshi⁴ and Kim Dong-Yu¹; ¹Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea; ²Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; ³Research Facilities Department, Technical Service Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; ⁴Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

To apply organic thin-film transistors (OTFT) in logic circuits or pixel switching display devices high charge carrier mobility above 0.1 cm²/Vs would be required. Carrier trapping at grain boundaries leading to reduced mobility was hard to avoid in common organic crystalline small molecules or polymers. Therefore liquid crystal materials could be excellent candidates in OTFT due to their self assembling properties and supramolecularly ordered monodomain formation from their mesophases. We designed and synthesized a series of thiophene and fluorinated arylene based organic semiconductors because fluorine substitution at benzene rings could effectively control the energy band gap and molecular packing. Moreover, the molecular design of organic semiconductors having asymmetric electron withdrawing C-F bonds would induce more favorable packing through dipole interactions as well as hydrogen bonding between C-H and C-F bonds. Interestingly, these organic semiconductors having partially fluorinated aryl groups showed liquid crystal phases with focal-conic fan texture above 160 °C. The reason why such rigid organics showed LC mesophases even without any alkyl type flexible unit might be due to the fluorine effect. In this presentation, we will discuss the effect of fluorination at such rigid rod-like structured organics, especially on the formation of liquid crystalline phases, and the effect of this liquid crystallinity on electronic properties for OTFT.

CC3.15

Numerical Simulation of Nucleation and Coarsening of Nematic Textures Under Shear Flow. Tomohiro Tsuji¹, Shigeomi Chono¹ and Alejandro Rey²; ¹Mechanical Engineering, Kochi University of Technology, Kamigun, Kochi, Japan; ²Chemical Engineering, McGill University, Montreal, Quebec, Canada.

Three-dimensional computations of the nucleation and coarsening of nematic defect structures during and in the absence of flow are performed using a tensor type equation. The tensor type evolution equation for nematic molecular configurations includes the short and long range elasticity effects and the viscous flow effects, and thus can predict the evolution of the nematic phase during isotropic-nematic phase transition. The nematic textures, such as point defects, lines, and loops, are naturally arisen during the isotropic-nematic phase transition through the conflict of the molecular orientations between nematic domains. It is found that during the phase transition there are three stages, which are the nucleation, the re-organization, and the coarsening of the nematic textures. The effects of shear flows on the nematic textures are to decrease the nucleation density of the textures for the texture nucleation stage, and to elongate the line and loop textures for the texture coarsening stage. Finally, the way to produce the texture-free material will be proposed.

CC3.16

Effect of Magnetic Field on the Molecular Orientation of Nematic Liquid Crystalline Polymers Under Shear Flows. Shufang Fu, Shigeomi Chono and Tomohiro Tsuji; Mechanical Engineering, Kochi University of Technology, Kamigun, Kochi, Japan.

Computational investigation of effect of magnetic field on the molecular orientation of nematic liquid crystalline polymers under shear flows is achieved using the Doi theory. The evolution of orientation probability density function of the LCP molecules is directly solved without closure approximations. When the magnetic field is imposed in the flow direction, the effect of the magnetic field on well-known flow-orientation modes, which are tumbling, wagging, and aligning modes, are: (1) for the tumbling mode, the effect is to increase the period of the rotation of the major orientation direction, (2) for the wagging, the effect is to increase the period and to decrease the amplitude of the oscillation of the major orientation direction, and (3) for the aligning, the effect is to increase the molecular orientation order. For low magnetic field strength, aligning-tumbling-wagging-aligning orientation mode transitions occur with the shear rate. For intermediate magnetic field strength, aligning-wagging-aligning transitions occur, and above a certain critical magnetic field strength only the aligning mode is appeared for any shear rates.

CC3.17

Oblique Micropores Filled with Liquid Crystals for Photonic Applications. Vladimir Presnyakov, Isabelle Chabot, Emile Knystautas and Tigran Galstian; Center for Optics, Photonics and Lasers, Laval University, Quebec, Quebec, Canada.

Micro- or submicro-metric cylindrical pores traversing the polymer film normally were employed in previous work to study the elastic properties and surface-induced order of liquid crystals [1]. We studied the polymer films prepared with uniaxially tilted oblique pores and then filled with nematic liquid crystals. It has been found that spectral and electro-optical characteristics of such structures strongly depend on the direction of polarization of the incident light [2]. We optimized the pore preparation technique for a polyethylene terephthalate matrix [3] - a polymer which permits precise control of the pore diameter by chemical methods. The samples thus obtained are characterized by a narrow distribution of pore sizes as well as a gradual variation of pore density across the surface of the film and can be considered as an attractive anisotropic polymer/liquid crystal composite material for various photonic applications. For example it can be used to develop colour filters with tunable spectral characteristics or flexible displays. || [1] G.P.Crawford, S.Zumer, Liquid Crystals in Complex Geometries, Taylor&Francis Publ., 1996. || [2] V.V.Presnyakov, V.R.Oganessian, T.V.Galstian, Proc. SPIE 4833, pp.562-567, 2003. || [3] I.Chabot, V.V.Presnyakov, T.V.Galstian, E.Knystautas, Proc. SPIE 5260, pp.404-410, 2003.

CC3.18

Computational Modeling of Texture Formation in Mesophase Pitch-Based Carbon-Carbon Composites. Gaurav Gupta and Alejandro D. Rey; Chemical Engineering, McGill University, Montreal, Quebec, Canada.

Carbon-carbon composites based on dispersing carbon fibers in a liquid crystalline mesophase pitch are important materials for structural and heat transfer applications. Property optimization requires a fundamental understanding of structure evolution. Insertion of fibrous particles in a liquid crystalline matrix leads to the nucleation of topological defects which control the global structure and properties of the composite. In this work we present a computational study of structure formation on random carbon-carbon composites that describes the emergence of topological defects due to the distortions in the oriented matrix. Dynamical and structural features of texture formation are characterized using gradient elasticity and defect physics.

CC3.19

Surface Anchoring Phenomena of Liquid Crystals Modified by Ligand-Receptor Binding Events. Yoonseuk Choi¹, You-Gyoung Park², Hoonjeong Kwon² and Sin-Doo Lee¹; ¹School of Electrical Engineering, Seoul National University, Seoul, South Korea; ²Department of Food and Nutrition, Seoul National University, Seoul, South Korea.

In the area of liquid crystals (LCs), interfacial phenomena of the LC molecules at various surfaces have been extensively studied for understanding fundamental physics as well as a number of device applications such as information displays, optical gratings, and biosensors. Since surface anchoring properties of the LC are very sensitive to subtle changes at the surface, a well-controlled technique for aligning the LC at the surface is extremely important to design LC-based devices. In this work, we study surface anchoring phenomena of the LCs on biologically treated surface substrates. We first examine how the specific binding events of biological ligand-receptor pairs on treated surfaces modify the LC orientation. Such surface modification by the ligand-receptor pairs is expected to change the surface morphology and the surface anchoring energy of the LC. This means that the binding events will disturb the orientational order and the anchoring properties of the LC at the modified surface. Since the LC is highly birefringent, it can be used as an optical transducer to observe the degree of the surface modification which directly results from the number of the biological binding events. As for an example, the anchoring transition characteristics of avidin-biotin pairs from the homeotropic to the homogeneous LC alignment can be easily observed and distinguished by a simple optical detection scheme under crossed polarizers. In summary, we studied surface anchoring phenomena of the LC on various biologically treated substrates where biological binding events occur. Such anchoring phenomena of the LC would be utilized for devising a versatile optical detection scheme of biological events which does not require labeling.

CC3.20

Static and dynamic light scattering in confined liquid crystals. Sarmistha Basu and Fouad M. Aliev; Physics, University of Puerto Rico, San Juan, Puerto Rico.

Static and dynamic light scattering (DLS) were applied to investigate

the influence of confinement of liquid crystals on N-I and N-SmA phase transitions, and the dynamics of director relaxation under different confinement conditions. Under extreme confinement then 2.5 nm pore diameter is less than the correlation length of LC we did not observe the N-I transition in either static or dynamic light or scattering experiments that indicates quasi-one-dimensional behavior under this confinement. For 8CB confined in pores of sufficiently large size in the nematic phase two well-defined relaxation processes were observed in DLS experiments for both axial and radial orientations of the liquid crystal in pores. The first process is qualitatively associated with bulk-like nematic director fluctuations. The second relaxation process (with relaxation time slower than the first one) is most likely due to the fluctuations in layers nearest the wall surface. In samples with homeotropic boundary conditions we observed the onset of smectic-A phase order forming on the pore wall even though the rest of the liquid crystal could be in the nematic phase. The slow decay is more pronounced in the samples with radial boundary conditions than in samples with axial orientation of liquid crystal. We found that for homeotropic boundary conditions of confined liquid crystal, the pore wall-liquid crystal interactions influence on the properties of the surface layer is stronger than in the case of axial orientation, particularly, and the influence of boundary conditions on N-SmA phase transition in confined 8CB is stronger than on isotropic-nematic phase transition. The relaxation times of the first process (bulk-like) decrease with the decrease of the pore size, however for each pore size it is almost temperature independent in a wide temperature range corresponding to nematic phase. The separation between the first and the second (slow) process is clearer and the amplitude of slow process is greater for smaller pores. This suggests that the slow process is surface related relaxation.

CC3.21

Computational Modeling of Light Propagation in Textured Liquid Crystals based on the Finite-Difference Time-Domain (FDTD) Method. Dae-Kun Hwang and Alejandro D. Rey; Chemical Engineering, McGill University, Montreal, Quebec, Canada.

Light propagation through uniaxial rod-like nematic liquid crystal films containing singular (thin) and non-singular (thick) line disclinations is computed using the finite-time domain-method (FDTD), which is based on accurate and rigorous numerical solutions to the governing Maxwell equations. The results obtained by the FDTD method are compared with classical matrix-type methods, including the aggregate model and Berreman method. It is found that the optical signals for singular and non-singular defects predicted by the matrix methods deviate significantly from the FDTD method because director gradient effects on the plane normal to the incident light are not properly taken into account. It is also found that the FDTD optical signal for singular thin lines has a characteristic length scale associated with the wave-length of the incident light, while for non-singular thick lines the scale is associated with the defect escaped core dimensions. The FDTD method offers an accurate quantitative tool of use in new applications including liquid crystal-based biosensors and rheoptical characterization of liquid crystalline polymers where strong lateral gradients in the director field are present.

CC3.22

A Polarized Infrared Technique to Obtain Optically Uniform Domains of Highly Ordered Liquid Crystals. Yo Shimizu¹, Hirosato Monobe¹, Hironobu Hori¹, Manabu Heya², Kunio Awazu², Benoit Heinrich³ and Daniel Guillon³; ¹Research Institute for Ubiquitous Energy Devices, Natl. Inst. Adv. Ind. Sci. Tech., Ikeda, Osaka, Japan; ²Institute of Free Electron Laser, Osaka University, Hirakata, Osaka, Japan; ³Groupe de Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg, Strasbourg, Alsace, France.

New phenomenon of reorientation of liquid crystalline molecules under polarized infrared laser irradiation was recently found for a columnar mesophase. This phenomenon is initiated by the photonic excitation of a vibration mode of a chemical bond in the molecules which leads to the thermal energy injection by the relaxation process. In this work, discussions are shown on a possible novel technique to control the liquid crystalline alignments for highly ordered mesophases such as columnar ones with some evidences of letter-shaped uniform domains obtained by the laser scanning. More recent studies indicate that this technique is good even for highly ordered smectics.

CC3.23

Surface Modified Liquid Crystal Lens. Dong Wang¹, L. C. Chien¹ and Robert Batchko²; ¹Liquid Crystal Institute, Kent State University, Kent, Ohio; ²Holochip Corporation, San Francisco, California.

Single-electrode liquid crystal cell lenses with the modified substrate were fabricated. The patterned polymer layer on the substrate was

obtained by contact printing of the commercial plastic Fresnel lens mold. We matched the refractive indices of the polymer and the liquid crystal filled inside so that the whole cell will act like a Fresnel lens. Furthermore, we optimized the Fresnel lens structure by designing the Fresnel lens mold and obtained the desired focal length by using liquid crystal with appropriate properties. We will present the optical responses such as the response time and focal length change with the applied voltage.

CC3.24

Liquid Crystal Alignment on Glass by Sputter-Induced Substrate Corrugation. Chunhung Huang and Christopher Cutler Umbach; Materials Science & Eng., Cornell University, Ithaca, New York.

The conventional process by which liquid crystals (LC's) are aligned for display applications relies on mechanical rubbing of the organic coating that is in contact with the LC molecules. A variety of considerations, including increasing process cleanliness and using coatings more compatible with high-temperature processing or applications, have resulted in the development of alternative, "non-contact" methods for aligning LC's. Off-normal sputter erosion of carbonaceous or polymer films is one such method; the anisotropy of the ion beam interaction with the surface is thought to induce a directionality in the local bonding of the film with the individual LC molecules. Off-normal sputter erosion affects the shape of the surface as well as the surface chemistry, and the formation of quasi-periodic surface corrugations is often observed during sputtering. Here we report on the alignment of LC's on a sputter-eroded glass surface, where the chemical effect of the ion beam on alignment is minimal, in contrast with sputter-eroded surfaces with a high density of carbon bonds. The surface of a commercial display glass (Corning Code 1737) was sputtered with 500 eV Ar ions to produce corrugations with a wavelength of 50 nm and amplitude of 1 nm. The nematic liquid crystal E7 blend was sandwiched between glass substrates subjected to sputtering and other surface treatments. The anchoring strength of these surface treatments was probed by observing the effect of the aligned LC on the transmission of polarized light. The anchoring strength of the sputtered glass is less than that achieved by the conventional rubbing method; the alignment induced by the surface corrugations is nonetheless sufficient for some applications. The anchoring strength also shows a dependence on the corrugation wavelength, amplitude, and the chemical surface termination of the glass.

CC3.25

Fabrication and Performance of LC Filled Fabry-Perot Resonators Integrated in Rectangular Waveguides.

Regor Pucker¹, Michele Crivellari¹, Constantinos Kompocholis¹, Alberto Andrioletti¹, Pierluigi Bellutti¹, Alberto Lui¹, Nicola Daldosso², Francesco Riboli², Mirko Melchiorri², Francesca Sbrana² and Lorenzo Pavesi²; ¹Microsystem Division, ITC-IRST, Povo-Trento, Italy; ²Department of Physics, University of Trento, Povo - Trento, Italy.

One of the difficulties in the realization of integrated optical devices such as modulators, switches and addressable routers is the very low electro-optical effect observed for Si. Different strategies exist to address this problem, among others the integration of materials with more attractive electro-optical properties. We describe here first results regarding the use of nematic dielectric liquid crystals in integrated optical circuits based on Si-photonics. Aim of our approach is to benefit from the large birefringence of nematic liquid crystals without losing all the advantages of integrated circuit fabrication methods. Therefore all the processing regarding the application of LCs (e.g. surface treatment for alignment) is done as post-processing step. The idea is to fill the spacer of a Fabry-Perot resonator with the LC to obtain a very large tuning range of the resonator. This concept similar to the one used in LC shutters was tested on stand alone devices: The microcavities were produced by chip bonding technique, which allows one to infill LC between two [SiO₂/Si]n 1/4 (l = 1.55 mm) Dielectric Bragg Reflectors (DBRs) grown by a series of LPCVD deposition and thermal oxidation steps, and separated by 950 nm thick SiO₂ posts. Liquid crystals with positive and negative dielectric anisotropy were used, i.e. Merck-E7 and Merck-6608 LC. Mirror-integrated electrodes allow an external bias to induce an electrical field and to tune the LC refractive index and, hence, the microcavity resonance. Electric-field-induced shifts of the second-order cavity modes of 120 nm and 50 nm were obtained for Merck-E7 and Merck-6608 LC, with driving potentials of 5 V and 10 V, and a threshold voltage about 2 V and 3 V, respectively. Both switch-on and switch-off times were measured as function of applied fields and were found to be lower than 5 ms. Similar microcavities integrated in planar-waveguides (based on Si₃N₄ or SOI) are currently realized. We will present results regarding the simulation of optical properties, fabrication and optical performance of both stand-alone test-devices and integrated devices.

8:15 AM *CC4.1

Photoinprinting spatially-ordered polymers in a cholesteric liquid crystal and electro-optical devices containing them.

Sang Hwa Kim and L. C. Chien; Liquid Crystal Institute and Chemical Physics Interdisciplinary Program, Kent State University, Kent, Ohio.

The paper presents the imprinting of spatially-ordered polymer network obtained by photopolymerization of a diacrylate monomer at a pattern-forming state of a cholesteric liquid crystal (LC) host, and the effect of the ordered polymer network on the performance of electro-optical devices. For example, a prismatic-like polymer structure can be stamped onto one of the substrates of an electro-optical cell, formed by oblique UV light irradiation and photopolymerization-induced localization of polymer network at a one-dimensional pattern-forming state of a cholesteric host. One of the applications is to use the polymer-liquid crystal composite materials for electrically-switchable liquid crystal blazed gratings. The optical diffraction measurements of a sample prepared with a 45-degree slanted UV irradiation, at the zero voltage condition (grating-on state), reveals a light diffraction with an asymmetrical light intensity between among the -1, 0, and +1 orders. Further increase the electric field, the device can be switching to a zero-order only (grating-off) state.

8:45 AM CC4.2

Liquid Crystal Controlled Polymer Morphologies. Xiaoli Zhou¹

and Liang Chy Chien¹; ¹Liquid Crystal Institute, Kent, Ohio; ²Polymer Technology Laboratory, Eindhoven, Netherlands; ³Philips Research Laboratories, Eindhoven, Netherlands.

Interest in the structurally controlled functional materials is growing rapidly. This is fueled by applying such ordered materials in broad range of applications. In this paper, the polymer morphologies controlled by liquid crystal is demonstrated. We used a system composed of a mixture of a liquid crystal as the host and a fixed low concentration of a thio-ene mesogenic monomer and small quantity of photoinitiator as the guests. We used different type of liquid crystals such as cholesteric, nematic and smectic as the hosts for comparison. The polymers are formed by photo-induced polymerization in liquid crystal, in which the liquid crystal is either aligned by the rubbed surface alignment layers or by an applied electric field. After the polymerization and removal of liquid crystal we can see immense difference in polymer morphology from different hosts. We will discuss the control mechanism and polymer morphologies in this paper.

9:00 AM CC4.3

Extra-Large Birefringence Mode of Stressed Liquid Crystals.

Anatoliy V. Glushchenko, Ke Zhang and John L. West; Kent State University, Kent, Ohio.

Stressed liquid crystals (SLCs) are new fascinating materials that produce a large shift in phase retardation at sub-millisecond speeds. The SLCs consist of interconnected micro-domains of a liquid crystal dispersed in a tiny, well developed, interpenetrating polymer structure that bridges substrates of a cell. Uniform deformation of the micro-domain structure imposes unidirectional orientation on the liquid crystal through the entire bulk of the cell. A 350 micrometers thick SLC film switches more than 35 microns of phase retardation within a couple of milliseconds with the driving voltage less than 1 V/micron. The system has a linear voltage response with no hysteresis. SLC cells are simple to fabricate and reliable, the active area of the film may be relatively large, and the films do not require any liquid crystal orientation layers. We demonstrate successful use of the thick SLC layers in a large angle beam steering devices and IR light modulators.

9:15 AM *CC4.4

Polymer Dispersed Liquid Crystal Gratings for Pressure Sensing Applications.

Adam K. Fontecchio and Michael Ermold; Electrical and Computer Engineering Department, Drexel University, Philadelphia, Pennsylvania.

Polymer dispersed liquid crystal (PDLC) Bragg gratings have been experimentally shown to alter their reflection properties, including intensity and wavelength, in response to environmental pressure variations. The optical wavelength shift has been observed as high as 1nm/psi, and exhibits a hysteresis effect that can be employed to determine whether the pressure variation is increasing or decreasing. Read with a fiber spectrometer, these films can be used as remote,

powerless sensors of absolute or relative pressure, even providing pressure gradient information using time-resolved measurements. The sensitivity of these films can be related to the composition and morphology of the polymer matrix. Preliminary results indicate that the sensitivity of the pressure sensors is correlated to both the viscosity of the monomer and the tensile strength of the cured film. This study examines PDLC formulations of bi-functional, tri-functional, and hexa-functional acrylated urethane resin; tri-functional and hexa-functional polyester-based aliphatic urethane acrylates; and blends of these monomers. Current work focuses on simultaneously optimizing the optical properties and the pressure sensitivity of the films. In addition, long-term stability tests in saline environments will be reported to determine the feasibility of biological applications. These results, as well as potential applications, will be discussed. This work was supported of the State of Pennsylvania and the National Aeronautics and Space Administration (NASA).

9:45 AM CC4.5

Photopolymerization Kinetic Contribution of Additives in the Formation of Holographic Polymer Dispersed Liquid Crystals (HPDLCs).

Timothy John White and Allan Guymon; Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City, Iowa.

Holographic polymer dispersed liquid crystals (HPDLCs) enable the creation of dynamic diffraction gratings in both reflection and transmission modes. The sequence gelation, phase separation and vitrification are critical to the formation of these materials and largely determine the electro-optic (EO) performance of the HPDLC. Thus, understanding the role that a component plays in the polymerization kinetics can serve as a means to understand its influence in polymer evolution during HPDLC formation thereby determining the mechanism by which the component dictates altered grating morphology and EO performance. The HPDLC formulation examined is based on a pentaacrylate (PA) monomer, LC (E7), surfactant (octanoic acid - OA), reactive solubilizer (n-vinyl pyrrolidinone - NVP) and photoinitiator. Examination of the photopolymerization kinetics in HPDLC formulations as a function of the concentration of OA, E7 and NVP reveal that the kinetics and consequently polymer development in HPDLCs are highly dependent on composition. Interestingly, increasing OA concentration increases the rate of polymerization $R(p)$ as the surfactant delays phase separation. This delay in phase separation allows a more plasticized reaction environment at higher conversions in the polymerization thereby delaying monomer diffusion limitations and allowing faster reaction rates. NVP increases $R(p)$ by altering network elasticity and plasticizing the polymer matrix. Finally, increasing the content of E7 decreases $R(p)$ due to degradative chain transfer reaction between polymer radicals and the LC. Additional critical information regarding the influence of polymerization kinetics on HPDLC formation has been obtained by examining the termination step during polymerization. Study of HPDLC termination kinetics shows that a majority of termination is bimolecular until the latter stages of polymerization. These results are surprising in light of the incorporation of the PA monomer that induces almost instantaneous gelation and a high crosslink density. Further examination of the propagation and termination kinetic rate parameters reveal that the termination mechanism for most of the polymerization is based on reaction diffusion. Reaction diffusion termination (RDT) implies that the polymer formed is immobile and unable to diffuse in the reaction environment. Therefore, the only means by which two radicals are able to terminate bimolecularly is through propagation. RDT is aided by high prevalence of unreacted double bonds of the PA monomer but may also be aided by the chain extending ability of NVP. Understanding the contribution of additives to the photopolymerization kinetics in concert with examination of polymer radical termination has yielded insight into the evolution of HPDLC morphology and subsequent EO performance, knowledge necessary for continued optimization of these materials for widespread device application.

10:30 AM CC4.6

Crystal Structure in Multi-Phase Polymer-Liquid Crystalline Materials.

Susanta Kumar Das and Alejandro D. Rey; Chemical Engineering, McGill University, Montreal, Quebec, Canada.

This paper presents the computational modeling of phase separation, phase ordering, and texture formation for polymer-liquid crystal mixtures. It is found that spinodal decomposition driven by liquid crystal order fluctuations can lead to colloidal crystals, where the matrix is the liquid crystalline phase and the droplets consist of the isotropic polymer phase. The positionally ordered droplets display a square symmetry, while the matrix is characterized by a disclination line network. The topological charge of the crystal colloid is shown to be zero. The driving force for crystal ordering is the local interaction between phase separation and phase ordering. The driving force for the defect network formation is the couplings between gradient

orientation elasticity and mass flux. Structure and formation processes are characterized using structure factors, Fourier spectra and extent of phase separation.

10:45 AM **CC4.7**

Nano-Structured Materials Based on Discotic Liquid Crystals. Stephan Holger Eichhorn¹, Anupama Adavelli¹, Nicholas Fox¹, Scott Dufour¹, Seyed Tadayyon² and Peter Norton²;
¹Chemistry, University of Windsor, Windsor, Ontario, Canada;
²Physics, University of Western Ontario, London, Ontario, Canada.

Two concepts for molecular patterning of materials that contain mixtures of discotic liquid crystals will be discussed. Potentially n-type and p-type semi-conducting discotic liquid crystals are linked together to star-shaped heptamers which self-organize into super-columns of p-type and n-type columnar stacks. Their synthesis, mesomorphism, and electronic properties will be discussed. Discotic liquid crystals are converted into surfactants in a small-molecule based approach towards molecular layer-by-layer deposition onto charged substrates. Tetraazaporphyrins and phthalocyanines containing either eight carboxylic acid or eight amine groups that are attached via aliphatic spacers of different length will be presented. Their differences in mesomorphism and surface coating behaviour will be discussed along with their preparation.

11:00 AM **CC4.8**

Additives for Improved Polymer Dispersed Liquid Crystal Properties. Chris Snively,¹ Department of Materials Engineering, University of Delaware, Newark, Delaware; ²Department of Chemical Engineering, University of Delaware, Newark, Delaware.

The electrooptical properties of polymer dispersed liquid crystal (PDLC) systems are highly dependent upon the nature of the interface between the polymeric and liquid crystalline regions of the system. The specific interactions between the two components can have a pronounced effect on the off-state orientation of the LC molecules and the anchoring energy at the interface. Here, the implementation of additives to PDLC systems for the control of these properties is explored. It has previously been demonstrated that the addition of common long-chain surfactants to a thermoplastic PDLC was able to slow the droplet coalescence, thus prolonging the lifetime of these systems. Here, we extend this idea in order to explore the influence of additive structure on PDLC properties and performance. A variety of common surfactants were employed, along with several tailored additives. These tailored additives were chosen because they possess moieties that are designed to specifically interact with both the polymer and the liquid crystal. A comparison of all incorporated additives, including influence on droplet textures, system morphology, and electrooptical switching speed will be presented. It was found that the tailored additives slowed the droplet coalescence in a similar manner as the surfactants, while having the added benefit of broadening the nematic temperature range of the liquid crystal.

11:15 AM **CC4.9**

Holographic Formation of Photonic Band Gap Structures with High Refractive Index Modulation. Vincent K.S. Hsiao, G.S. He, A.N. Cartwright and P.N. Prasad; Institute of Lasers, Photonics and Biophotonics, University at Buffalo, Buffalo, New York.

A novel way of creating a high index contrast of periodic structures by using a modified holographic polymer dispersed liquid crystal photopolymer system will be introduced. The resulting high index contrast (0.2) was provided by the index difference created by the resulting stacks consisting of alternating layers of nanostructured voids and layers containing the polymer that are easily written using holographic interferometry. The size of the nanostructured voids can be changed by controlling the amount of liquid crystal and through a post-cure process. The optical properties of the resulting photonic band gap structure showed 80% reflection efficiency with 80 nm wide bandwidth. The desired peak reflection wavelength can be easily tuned from visible to IR wavelengths by using different writing wavelengths, interference angle, and photoinitiator in the photopolymer system. In addition to the nanofabrication of these structures, applications of these porous photonic bandgap structures in lasing and chemical sensing will be discussed.

11:30 AM **CC4.10**

Supramolecular assembly of MJLCP rod-coil block copolymers. Christopher Y. Li and Kishore Tenneti; Materials Sci. & Eng., Drexel University, Philadelphia, Pennsylvania.

Liquid crystalline (LC) block copolymers play a major role in creating hierarchical self-assembled structures in different length scales. Most of the LC block copolymer studies focus on side chain LC polymers, in which one end of the LC mesogens are attached to the polymer backbones through soft spacers, such as methylene groups. By laterally linking the waist of LC mesogens directly to polymer

backbones (without spacers), mesogenic jacketed LC polymers (MJLCP) can be achieved. Because of the semi-rigid nature of the polymer chains induced by the strong interaction between the side chain mesogens and the polymer backbone, MJLCPs could serve as rod to form rod-coil block copolymers, which represent a new category of self-assembling polymers that combine microphase separation of coil-coil block copolymers and orientational ordering of rod segments. Recently, using MJLCP as the rod segment, a new series of rod-coil block copolymers, poly(styrene-block-(2,5-bis[4-methoxyphenyl]oxycarbonyl)styrene) (PS-b-PMPCS), have been synthesized and their solution self-assembly behavior has been investigated. Morphology and rheological behavior of rod-coil poly(styrene)-block-poly(2,5-bis-(4-butyl-benzoyl)oxystyrene) (PS-b-PBBS) has also been reported. In this presentation, we report, the hierarchically ordered rod-coil polymer structure with MJLCP as the rod segments. The confined LC phase behavior within the microphase separated block copolymers will be discussed. Using SAXS and WAXD techniques, it has been found that symmetric PS-b-PMPCS possess lamellar microphase structure and the d-spacing increases with increasing the molecular weight. PMPCS rigid columns are formed due to the strong interaction between the side chain mesogens and the polymer backbone. The macromolecular columns possess orientational order and columns are parallel to the lamellar normal. The packing of the rod coil block resembles a bilayer smectic A molecular structure observed in small molecular liquid crystals and rod coil oligomers. Self-assembly behavior of asymmetric PS-b-PMPCS has also been studied and the perforated layered structures have been observed.

11:45 AM **CC4.11**

In-situ Reorientation of Conjugated LC Polymer via μ s Blue Laser Irradiation - Polarized Fluorescence for Optical Data Storage. Tzenka Miteva¹, Akio Yasuda¹, Gabriele Nelles¹, Stanislav Balushev², Ullrich Scherf³ and Dieter Neher⁴;
¹MSL, SONY International (Europe), Stuttgart, Germany; ²Max-Planck-Institute for Polymer Research, Mainz, Germany; ³University of Wuppertal, Wuppertal, Germany; ⁴University of Potsdam, Potsdam, Germany.

Control of the orientation of liquid crystalline (LC) molecules by light has long been of great interest, especially for enabling their utilization in displays, optical switching devices and data storage applications. An already common approach for optically switching the orientation in LC cells is using alignment layers with photosensitive azobenzene or stilbene moieties [1]. Similarly, it has been possible to use azobenzene containing polymers as alignment layers for conjugated LC polymers of relatively low molecular weight [2]. In our previous work we demonstrated multiple reversible reorientation of low molecular weight LCs mixed with anisotropic fluorescent dyes. This was realized by illuminating LC cells, which contained thin layers of an azobenzene photoaddressable polymer (PAP), with polarized light. Multiple-switching between two orientation states for times of down to 0.1 s was achieved [3]. In this work we demonstrate, for the first time, reversible photoinduced in-situ reorientation of a conjugated main chain LC polymer - polyfluorene - by means of PAP alignment layers. The polyfluorenes (PFs) are highly-efficient and thermally-stable blue emitting LC polymers. The used photoaddressable polymers contain mesogenic azobenzene side-chains optimized to reorient cooperatively and effectively upon illumination with polarized light. We relied on the interplay of well-optimized materials - varying side-chain patterns and transition temperatures - with designed surfaces. This optimization enabled us to achieve macroscopic orientation and light-induced microscopic reorientation of relatively high molecular weight PF on top of PAP layers. Pre-alignment was done by irradiating the PAP layer with linearly polarized light of 532 nm and subsequently heating the PAP/PF system up to temperatures well below the crystalline-to-LC transition temperatures of the PFs. Multiple and reversible in-situ microscopic reorientation of the PAP/PF system was achieved via repeated irradiation with polarized light of 405 nm in 1 to 2 μ m spots for irradiation (writing) times as short as 10 μ s. To our knowledge, this is the fastest reorientation of conjugated main-chain LC polymers reported so far. The system gave us the opportunity to investigate the limits of this reorientation process with respect to irradiation times and power densities for applications in data storage media. 1. K. Ichimura, Chem.Rev. 100, 1847 (2000). 2. D.Sainova, A.Zen, H.G.Nothofer, U.Asawapirom, U.Scherf, R.Hagen, T.Bieringer, S.Kostromin, D.Neher, Adv.Funct.Mater. 12, 49 (2002). 3. S.Lucht, D.Neher, T.Miteva, G.Nelles, A.Yasuda, R.Hagen, S.Kostromin, Liq.Cryst. 30, 337 (2003).

SESSION CC5: Inorganic/Rod LC Materials
Chairs: Patrick Davidson and Jean-Christophe Gabriel
Tuesday Afternoon, November 30, 2004
Room 313 (Hynes)

1:30 PM ***CC5.1**

Magnetic-Field-Induced Phase and Alignment Transitions in

Liquid-Crystalline Suspensions of Goethite (FeOOH) Nanorods. Patrick Davidson¹, Bruno J. Lemaire¹, Jacques Ferre¹, Jean-Pierre Jamet¹, Pierre Panine², Ivan Dozov³, Daniel Stoiculescu³ and Jean-Pierre Jolivet⁴; ¹Laboratoire de Physique des Solides, Orsay, France; ²ESRF, Grenoble, France; ³Nemoptic, Magny-les-Hameaux, France; ⁴LCMC, Université Paris 6, Paris, France.

Colloidal aqueous suspensions of lath-shaped goethite nanorods form isotropic, nematic and columnar phases, depending on volume fraction. Although bulk goethite is a typical antiferromagnetic material, the nanorods bear a longitudinal remanent magnetic moment, most probably due to uncompensated surface spins, which gives rise to quite unexpected behaviors. (1,2) Goethite nanorods have a negative anisotropy of magnetic susceptibility that favors perpendicular alignment of the nematic phase when submitted to a magnetic field, conflicting with the parallel alignment favored by the remanent magnetic moment. This results in a crossover from parallel alignment at low field intensities to perpendicular alignment at high field intensities, both in the isotropic and nematic phases. Because of the remanent magnetic moment, the Fredericks threshold in the nematic phase is lower (20 mT for a 20 microns thick sample) than observed with organic liquid crystals and the isotropic phase acquires a very large birefringence when submitted to a magnetic field. Moreover, the combination of dipolar and quadrupolar orders leads to original symmetries compared to those of ferrofluids and classical liquid crystals. Finally, we observed in this system a reversible magnetic-field-induced transition from the nematic phase to the columnar one. Single domains could be produced by applying a magnetic field, which allowed us to determine the structure of the columnar phase. 1 B.J.Lemaire et al, Phys. Rev. Lett., vol 88, 125507 (2002) 2 B.J.Lemaire et al, Eur. Phys. J. E, vol 13, 291 (2004) ; idem, vol 13, 309 (2004).

2:00 PM *CC5.2

Mineral Liquid Crystals Based on the Self-Assembly of One and Two-Dimensional Nanosystems: Structure and Applications. Jean-Christophe P. Gabriel, Nanomix, Emeryville, California.

In this presentation, we will report findings on the mesogenic properties of the mineral liquid crystals (MLCs) based on nanotubes from the coiling of the flexible polymer $\text{NaNb}_2\text{PS}_{10}$ as well as from exfoliated single nanosheets such as smectic clays and phosphoantimonate ($\text{H}_3\text{Sb}_3\text{P}_2\text{O}_{14}$) [1,2]. These findings show that above a critical concentration, such materials tend to form liquid crystalline phases (mesogens) in which tubes and nanosheets tend to orient themselves parallel to each other (nematic, smectic & hexagonal phases). This is shown by studying by optical measurements as well as small angle X-Ray scattering. In the case of $\text{H}_3\text{Sb}_3\text{P}_2\text{O}_{14}$ an additional position order is found where the distance between the nanosheets can be controlled up to 250 nm leading to the first lamellar mesophase made of covalent sheets [3]. Usage of the mesogenic properties of these mineral liquid crystals [4] in various applications, such as nanocomposites [5] or NMR [6], will also be reported. [1] Solvent-induced Folding of the Mineral Chains $[\text{Nb}_2\text{PS}_{10}]_n$ into Nanotubes. F. Camerel, J.-C. P. Gabriel, P. Davidson, M. Schmutz, T. Gulik-Krzywicki, B. Lemaire, C. Bourgaux, P. Batail, Nano Letters, 2(4) 403-407, 2002. [2] a) Observation of Nematic Liquid-Crystal Textures in Aqueous Gels of Smectite Clays. J.-C.P. Gabriel, C. Sanchez, P. Davidson. J. Phys. Chem. 100(26) 11139-11143, 1996; b) The measurement by SAXS of the nematic order parameter of laponite gels B. J. Lemaire, P. Panine, J.-C. P. Gabriel and P. Davidson, Europhysic Letters, 59(1), 55-61. 2002. [3] Swollen Liquid-Crystalline Lamellar Phase Based on Extended Solid-Like Sheets. J.-C. P. Gabriel, F. Camerel, B. J. Lemaire, H. Desvaux, P. Davidson, P. Batail, Nature 413, 504-508, 2001. [4] Mineral Liquid Crystals from Self-assembly of Anisotropic Nanosystems. J.-C. P. Gabriel, P. Davidson Topics in Current Chemistry 226, 119-172, 2003. [5] Synthesis of a mesoporous composite material prepared by the self-assembly of mineral liquid crystals. F. Camerel, J.-C. P. Gabriel, P. Batail, J. Chem. Soc., Chem. Commun. 2002(17) 1926-1927, 2002. [6] a) The First Use of a Mineral Liquid Crystal to Induce Residual Dipolar Couplings in a NMR Study of a Non-Labeled Biomolecule. H. Desvaux, J.-C. P. Gabriel, P. Berthault, F. Camerel, Angew. Chem. Int. Ed. 40(2) 373-376, 2001; b) Dilute liquid crystals used to enhance residual dipolar couplings may alter conformational equilibrium in oligosaccharides. P. Berthault, D. Jeannerat, Y. Camerel, F. Alvarez-Salgado, Y. Boulard, J.-C. P. Gabriel, H. Desvaux, Carbohydrate Research 338, 1771-1785, 2003.

2:30 PM CC5.3

Mechanical Actuation of Carbon Nanotube-Elastomer Composites. Samit Ahir, Sebastien Courty, Judith Mine, Ali Tajbakhsh and Eugene Terentjev; Cavendish Laboratory, Cambridge University, Cambridge, United Kingdom.

Composites of carbon nanotubes in a variety of supporting media are

a subject of intense current investigation due to the new physical properties emerging from the combination of length scales and new interaction forces involved. We demonstrate, for the first time, the large electromechanical response in nematic liquid crystalline elastomers filled with a low concentration of carbon nanotubes (below percolation threshold), aligned along the nematic director at preparation of monodomain system. The nanotubes create a very large effective dielectric anisotropy of the composite. Their local field-induced torque is transmitted to the rubber-elastic network and is registered as the exerted uniaxial stress of order 1kPa in response to a field of order 1MV/m. We investigate the dependence of the effect on field strength, nanotube concentration and reproducibility under multiple field-on and -off cycles. The results indicate the potential of the nanotube-nematic elastomer composites as electrically driven actuators. We also report on a different actuation mechanism, driven by temperature changes across the nanotube composite and stimulated by IR radiation. The degree and the direction of actuation are sensitive functions of nanotube concentration. We use the isotropic PDMS rubber as supporting matrix, as well as the spontaneously nematic elastomer. The results tentatively suggest that nanotubes, when in a high concentration within the matrix (above percolation threshold), impart liquid crystal behavior into an otherwise non-mesogenic system. Thus, on irradiation, the highly loaded composites tend to contract along the alignment axis, while the composites with (aligned) nanotubes below percolation become longer on actuation. These intriguing findings merit full theoretical understanding.

2:45 PM CC5.4

Synthesis and Field-Driven Orientation of a New Class of Polymer Microrods. Rossitza Gueorguieva Alargova¹, Ketan H.

Bhatt¹, Devdutta S. Warhadpande¹, Vesselin N. Pounov² and Orlin D. Velev¹; ¹Department of Chemical Engineering, NC State University, Raleigh, North Carolina; ²Department of Chemistry, University of Hull, Hull, United Kingdom.

Rod-like microparticles align spontaneously in dispersed state forming phases similar to molecular liquid crystals and known as colloidal liquid crystals. Few studies of particle liquid crystals are available and no practical applications have been developed since there were no convenient and scalable processes for synthesis of such microrods. We report a novel process for formation of polymer rods with micrometer or sub-micrometer diameter and length that can be as large as tens of micrometers. The microrod synthesis is based on a liquid-liquid dispersion technique where a polymer solution is emulsified in an organic medium under shear stress. This method allows facile control of the particle sizes through a few experimental parameters and more importantly it is readily scalable to produce large amounts of microrods. The hydrophobicity and the charge of the polymer rods can be tailored by adding small amounts of amphiphilic additives. The microrods show interesting phase behavior suggesting formation of nematic liquid crystal-like phases since they align readily in one direction. Orientation of the rods in a desired direction can be achieved by applying electric or magnetic field. Such organized rod domains, which resemble the liquid crystals, can preserve their structure even after the external field is removed because the free energy of the rods is minimized when they interact laterally with each other. The rods align readily along the flow lines of fluids and may be used for visualizing microflows in small channels or systems with complex geometries. Hydrophobic rod suspensions also act as "superstabilizers" of foams and emulsions. Various nano- and microparticles can be embedded inside the polymer rods. Rod dispersions with embedded magnetic particles yield a new class of colloidal liquid crystals that respond to magnetic fields.

3:30 PM *CC5.5

Semiconductor Nanorods Can Form Liquid Crystal Phases.

A. Paul Alivisatos, Chemistry, University of California, Berkeley, Berkeley, California.

This talk will describe studies of the phase diagrams of these materials, as well as studies of switching in external fields. The possibility of novel phases in branched nanorod and tetrapod samples will also be discussed.

4:00 PM *CC5.6

Fluctuations of Semi-Flexible Polymers in a Nematic Solvent.

Zvonimir Dogic, Rowland Institute, Harvard University, Cambridge, Massachusetts.

We directly visualize single polymers with persistence lengths ranging from 0.05 to 16 microns, dissolved in the nematic phase of rod-like fd virus. Polymers with sufficiently large persistence length undergo a coil-rod transition at the isotropic-nematic transition of the background solvent. We quantitatively analyze the transverse fluctuations of semi-flexible polymers and show that at long wavelengths they are driven by the fluctuating nematic background.

We extract both the Odijk deflection length and the elastic constant of the background nematic phase from the data. Z.Dogic et. al. Phys. Rev. Lett. 92, 125503 (2004).

4:30 PM *CC5.7

Phase behavior of layered silicate dispersions: Characterization of and implications to polymer nanocomposites. Hilmar Koerner¹ and Richard A. Vaia²;

¹Nonmetallic Materials Division, Univ of Dayton Research Institute, Dayton, Ohio; ²MLBP, Air Force Research Laboratories, Wright Patterson Air Force Base, Ohio.

Polymer nanocomposites will soon become common in applications that require unique value-added properties not normally possible with traditional fillers, such as reduced permeability, tailored biodegradability, optical clarity, self-passivation, and flammability, oxidation and ablation resistance. The lower loadings (1-5 vol%) facilitate processing and reduce component weight compared to traditional fillers (15-40 vol%). A key element to improved properties is the presence of highly anisotropic inorganic elements, such as layered silicates (LS) or carbon nanotubes, embedded in a filler/matrix interface dominant environment. The challenge to forward the area of nanocomposites is the characterization of the distribution and the spatial/directional control of inorganic nanoelements. Fundamentally, conceptual similarities can be established with the phase behavior of nematic and discotic liquid crystals (LCs), articulated by Flory and De Gennes. Using this framework, the 'phase' structure and morphology of LS both quiescent and under external stimuli, such as shear and electromagnetic fields will be discussed. In-situ synchrotron experiments of orientation and relaxation behavior reveal many parallels to liquid crystals. Furthermore, dielectrophoresis and magnetic field alignment enable control of LS orientation, providing a means to not only examine local particle dynamics but also tailor properties, such as modulus and thermal expansion, of LS nanocomposites by 'dialing-in' of morphology. Recent studies on nanocomposites and suspensions show that many nanofillers are reminiscent of LCs and afford novel opportunities for the LC community.

SESSION CC6: Liquid Crystal Materials and Technology

Chairs: Harry Coles and S.T. Wu
Wednesday Morning, December 1, 2004
Room 313 (Hynes)

8:00 AM *CC6.1

Liquid Crystal-Based Adaptive Fiber Optic Coupling in an NxN Optical Switch. Dong-Feng Gu, Bruce Winker, Don Taber and Milind Mahajan; Rockwell Scientific Company, Thousand Oaks, California.

A novel adaptive fiber optic coupling device containing dual frequency liquid crystal was developed and demonstrated. This device was developed for an NxN fiber coupled optical crossbar switch and optimizes the fiber alignment each time an input port is switched to a different output port. This device also can be used to dynamically balance the output amplitude of each channel. The experimental data measured from a 4x4 switch indicates the device relaxes alignment tolerances for single mode fiber coupling by an order of magnitude, resulting in reduction of the assembly and packaging costs. Issues discussed include form and fit to a full duplex NxN liquid crystal optical switch, insertion loss reduction, and optimized drive waveforms.

8:30 AM *CC6.2

Electrically Tunable Microlens Arrays using Optical Patterning Technique. Hongwen Ren, Yun-Hsing Fan, Yi-Hsin Lin and Shin-Tson Wu; College of Optics & Photonics, University of Central Florida, Orlando, Florida.

We demonstrate two-dimensional planar microlens arrays based on the polymer/liquid crystal (LC) composite using patterned method. Each microlens of the arrays is composed of a plano-concave polymer lens and a plano-convex LC lens. To fabricate this kind of microlens arrays, we first coated prepolymer onto an indium-tin-oxide (ITO) glass substrate. Then we use a glass-based plano-convex microlens arrays, called stamper, to laminate the coated prepolymer. The laminated prepolymer is exposed under UV light and the stamper is peeled off. At this stage, the solid polymer presents concave microlens patterns on the substrate. After that the cavities of polymer layer is filled with LC materials. The LC materials are sealed with a top ITO glass substrate. Lenses with such a structure can be obtained with ideal spherical shape. To improve the optical properties of the microlens, we introduce LC based microlens arrays using polymer network liquid crystal (PNLC), as well as nanoscale polymer dispersed

liquid crystals (PDLC) instead of pure LC materials.

(1)**PNLC based microlens array** The formed structure of the PNLC based microlens was studied. The imaging property of the lens was evaluated. The focal length of the PNLC based microlens can be tuned with a large range and the operating voltage is not too high. For example, a lens with diameter 450 μ m and the cell gap $d = 45\mu$ m, the saturation voltage for the PNLC microlens is $60V_{rms}$. Due to the homogeneous LC alignment, this kind of lens is polarization dependent. The PNLC based microlens can reach 100% light efficiency for a linearly polarized light. The response time is 30 ms. (2)**Nanoscale PDLC microlens array** If we use nanoscale PDLC to fill the cavities of the polymer lens, then the nano-PDLC microlens array is polarization independent and the response time is 200 μ s during focus change. Another advantage of the nano-PDLC microlens is small aberration because the birefringence of the nano-PDLC is independent of the incident angle. Consequently, the optical efficiency and imaging quality are highly improved. The major shortcoming of such a 2D microlens array is the increased operating voltage (>200 Volts).

9:00 AM CC6.3

Fast-Response Dual Frequency Liquid Crystal Gels. Yun-Hsing Fan, Hongwen Ren, Xiao Liang, Yi-Hsin Lin and Shin-Tson Wu; College of Optics and Photonics, University of Central Florida, Orlando, Florida.

Liquid crystal (LC) gel (also known as polymer-stabilized LC) which normally consists of 3-8 wt% polymer in a nematic host exhibits an anisotropic light scattering behavior and has been used as switchable polarizer, light shutter, and reflective display. We demonstrate fast response time and high contrast ratio gels using a dual frequency liquid crystal (DFLC). The LC gels were fabricated by photopolymerizing the DFCLC/monomer mixture. The DFLC we formulated has following physical properties: cross-over frequency f_c 5 kHz, birefringence Δn 0.277 (at $\lambda = 633$ nm and $T = 22^\circ$ C), and dielectric anisotropy $\Delta\epsilon = 6.6$ at $f = 1$ kHz and $\Delta\epsilon = -4.14$ at 50 kHz. Two samples with 5 and 7 wt% monomer concentration were prepared. The photocurable monomer used in this study is bisphenol A dimethacrylate. The LC/monomer mixture was filled in the cells with gap $d = 8\mu$ m. In our experiment, two types of LC cells were studied: one has homogeneous alignment and the other has no polyimide alignment layer. The one using a homogeneous cell shows anisotropic scattering behavior while the other prepared using a cell without polyimide alignment layers exhibits isotropic scattering properties. For the homogeneous cell, the inner surfaces of the indium-tin-oxide (ITO) glass substrates were overcoated with a thin polyimide layer and buffed in anti-parallel directions. In both cells, the LC/monomer mixture was irradiated by a UV light (λ 365 nm) under the application of a bias voltage ($V_b = 15 V_{rms}$) across the cell so that the LC and monomer molecules were oriented at nearly perpendicular to the substrates. As a result, the formed chain-like polymer networks are along the electric field direction. Both DFCLC gels are highly transparent in the voltage-off state. Light scattering occurs when a high frequency voltage is applied. The isotropic gel exhibits a high contrast ratio and sub-millisecond response time (0.8 ms). The DFCLC gels are broad band devices. The spectral bandwidth covers the whole visible region. Potential applications of these gels for switchable polarizer, telecom optical switch, and reflective displays are emphasized.

9:15 AM CC6.4

Hybrid-Aligned Nematic Liquid Crystal with Dual Frequency Driving. Yanqing Lu, Xiao Liang, Yung-Hsun Wu, Fang Du and Shin-Tson Wu; College of Optics and Photonics/CREOL, University of Central Florida, Orlando, Florida.

Hybrid-aligned nematic (HAN) liquid crystal (LC) cell has been proposed for display and phase modulation applications. A shortcoming of the HAN cell is that it only has about a half phase change as compared with other LC alignments, e.g., the parallel alignment (PA) and vertical alignment (VA). This disadvantage limits the useful applications of the HAN cells for photonics applications in the infrared band. In this work, we studied the dual frequency liquid crystal (DFLC) in a HAN cell. We derived the equations of HAN LC director deformation under an external field with different frequencies. We demonstrated that the dual frequency fields can actively drive the LC molecules to either parallel or perpendicular to the substrates, so that the total obtainable phase change is thus doubled. To verify the theoretical predictions, the phase retardations of an 8.5 μ m DFCLC HAN cell were measured at 1.55 μ m wavelength under different driving frequencies. Both voltage and frequency can be used to tune the cell to a desired retardation state, which makes the active driving between two arbitrary states possible. When operating the cell between two frequencies that are far from the cross-over frequency of the employed DFCLC, the maximum phase tuning range is obtained which is equivalent to that of a PA cell with the same thickness. For example, to obtain π phase change, the HAN cell can be switched from a $-\pi/2$

phase state with a low frequency electric field to the $+\pi/2$ phase state through a high frequency field. The voltages for $\pi/2$ phase change thus may be used to obtain a π phase change. Comparing with a PA cell with the same thickness, the π phase change voltage is thus decreased. This merit not only greatly decreases the power consumption but also makes the device more stable. Based on the 8.5 μm DFLC HAN cell, a variable optical attenuator (VOA) around 1.55 μm wavelength was demonstrated. A compensation film was employed to add a fixed phase so that the VOA is "default-ON". When a 5.8 Vrms 1 kHz voltage was applied to the cell, the LC changed $-\pi$ phase and this VOA was switched to "OFF" state. The optical decay time from the "OFF" to "ON" state is about 90 ms. However, by using the dual frequency tuning, this decay time is shortened to 18 ms, which is 5X faster. A novel feature of the abovementioned VOA is that it has two stable "OFF" states corresponding to $-\pi$ and $+\pi$ phase change, respectively. Although it has binary amplitude states, it has ternary discrete phase states. The DFLC HAN cell thus supplies a simple ternary system under field-off, low frequency and high frequency states. Some related applications, e.g., the ternary phase modulator, ternary logic device, and positive and negative tunable LC lens, are expected.

10:00 AM *CC6.5

Telecommunications and novel display applications of liquid crystals. Tim Wilkinson, Engineering, University of Cambridge, Cambridge, United Kingdom.

Over the last few years, the applications of liquid crystal (LC) materials has gone beyond the mainstream application of flat panel displays into areas such as telecommunications, image processing, novel display systems and adaptive optics. These new applications use LC materials to modulate the phase of the light instead of its intensity, hence they have thrown up a whole range of new materials requirements and challenges. These applications have been further enhanced by the combination of LC phase modulation with silicon VLSI electronic backplanes in liquid crystal over silicon (LCOS) devices. The simplest phase modulators have been based on ferroelectric LCs, however these devices have been limited to binary phase modulation. Recently new devices based on nematic LCs have demonstrated multi-level phase modulation and even been made polarisation insensitive. This has allowed a new perspective on the potential applications of these devices. In this paper we intend to highlight two main applications which will greatly benefit from multilevel phase modulation. The first is reconfigurable optical interconnects using phase only holograms to steer beams of light. By going to multiple phase levels, we can increase the efficiency of computer generated holograms in telecommunications switches as well as improve the crosstalk by manipulating the noise field. A more futuristic and ambitious application of multi-level phase holograms is in two dimensional image projection. The benefits of far field diffraction generated images can be seen in terms of both efficiency, device robustness and resolution. Finally we will look into other possible liquid crystal electro-optical effects which may deliver multiple level phase modulation at faster rates than those demonstrated so far with nematic LCs

10:30 AM *CC6.6

Electrically Commanded Surfaces for Liquid Crystal Displays. Lachezar Komitov, School of Physics&Engineering Physics, Gothenburg University, Gothenburg, Sweden.

Conventional liquid crystal displays are operating on the basis of the electro-optic effects in liquid crystals, arising from the re-orientation of the liquid crystal by an applied electric field. This reorientation is possible due to the coupling between the electric field and the dielectric anisotropy and/or spontaneous or induced polarization of the liquid crystal. Hence this coupling is playing an active role in the switching process of the liquid crystal. In the conventional liquid crystal displays, an electric field applied across the cell reorients to a large extent only the bulk liquid crystal molecules turning them along the field or perpendicular to it for positive and for negative dielectric anisotropy, respectively. The position of the liquid crystal molecules at the confining surfaces, however, remains almost unchanged. Hence, the surfaces are acting as a brake, i.e. they are playing a passive role in the switching process determining only the field-free alignment of the liquid crystal. Several examples that demonstrate the active role of the surface in mediating switching of liquid crystals will be given in this talk. A special attention will be drawn to the electrically-induced surface mediated switching of the liquid crystal, the Electrically Commanded Surfaces (ECS) [1]. ECS is a new liquid crystal display concept according to which an electric field applied across the cell does not switch directly the liquid crystal bulk material. It does, however, switch the molecules of the alignment layer, which is further transferred to the liquid crystal bulk via elastic forces. The detected electro-optic response, due to the mediated switching of the liquid crystal by ECS, reveals that the switching of the sample optic axis takes place in the plane of the sample (in-plane switching) and,

moreover, that the switching is linear with the field. The ECS concept seems to open a broad field for further research on surface mediated switching processes that seems to have a large application potential. Developing further the concept of ECS, a new generation of polymeric materials for High Performance Alignment Layers (HiPAL), facilitating the switching of the liquid crystal by an applied electric field, is designed, synthesised and studied. These materials can be employed in liquid crystal displays and devices which operation requires homeotropic (VA) or planar (PA) alignment. The short response times, the high image contrast and high VHR are the most important characteristics of HiPAL for the vertical alignment (VA) mode that make this material very attractive for applications such as large area LC TV screens, PC monitors, LCoS, etc. HiPAL designed for the planar alignment (PA) mode exhibits the same features and seems to be attractive for display as well as for non-display applications such as photonic devices, light shutters and light protective devices (welding masks, for instance). [1]. L.Komitov, Journal of SID, 11, pp.437-441 (2003).

11:00 AM *CC6.7

Control of Liquid Crystalline Ordering at Interfaces for Optical Device Applications. Chang-Jae Yu and Sin-Doo Lee; School of Electrical Engineering, Seoul National University, Seoul, South Korea.

Liquid crystals (LCs) have been widely used in the field of information displays because of their low power consumption, light weight, high resolution, and high contrast ratio. Recently, there has been intensive research achievement effort to utilize the LCs in telecommunication applications such as optical switches and variable optical attenuators. For practical device applications of the LCs, it is extremely important to control molecular ordering of the LCs at various interfaces such as a glass-LC and an organic flexible substrate-LC interfaces. In this work, we report on two types of periodic molecular ordering phenomena at interfaces and demonstrate two binary grating devices, one of which is a phase grating and the other a polarization grating. LCs are very useful for constructing a variety of diffraction gratings due to pure phase grating characteristics and large anisotropic optical properties. Moreover, the phase profiles of the LC are electrically and geometrically controlled in a simple way. Most works have been focused on high efficiency of a binary phase grating with insensitive polarization. However, little has been studied on the effect of the polymer/LC interface or dual-domain boundary on the performances of the LC grating devices so far. First, we describe an LC polarization beamsplitter structure with binary phase grating to achieve the polarization-separating phase modulation and diffraction together with the wavelength tunability as a function of an applied voltage. In an alternating homeotropic and hybrid aligned LC geometry, the polarization of an input beam becomes well separated into two orthogonal components of the diffracted beam in a wide range of the wavelength under an applied voltage. It should be noted that in contrast to the previous LC grating, the anisotropic binary nature of our LC grating structure naturally gives the polarization-separation effect which depends on the input wavelength. Second, we demonstrate a LC polarization grating in an oppositely twisted configuration using a single-masking process of the photo-alignment technique. In order to achieve the oppositely twisted nature, the photosensitive polymer, repeatedly altering the direction of the LC alignment on the substrate, was used for aligning the LC molecules homogeneously. The basic structure of the LC polarization grating is such that the LC molecules are twisted periodically in an alternating oppositely twisted configuration in which the polarization modulation appears. The diffraction properties of the LC polarization grating were insensitive to the polarization of the input beam and the phase retardation of the LC layer. Moreover, the zeroth and first order diffraction beams were linearly polarized and perpendicular to each other. In conclusion, the two binary LC grating devices described above are expected to have a significant impact on various optical systems for optical signal processes and a switchable 2D/3D display system.

11:30 AM CC6.8

Ordering of Liquid Crystals on Films with Periodically Modulated In-Plane Anchoring Conditions. Ji-Woong Park^{1,2} and Edwin L. Thomas¹; ¹Materials Science and Engineering, MIT, Cambridge, Massachusetts; ²Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, South Korea.

We study the ordering of nematic liquid crystals on the surface of a self-assembled rod-coil block copolymer film with a periodic Neel wall-like domain pattern. In-plane orientation of the rod block on the copolymer surface is periodically modulated from 0 to 180 degrees across the domain walls with a periodicity in the range of 0.5-20 microns. When nematic LCs are sandwiched between the copolymer film and a glass cover slip, their ordering is frustrated because of two competing free energy terms, the surface anchoring energy and the bulk elastic energy. These energies vary with the wall periodicity at

the copolymer surface and the thickness of the LC cell. Depending on these parameters, the LCs can exhibit one of the three different director patterns: the periodic domain walls replicating the surface orientation pattern, arrays of disclination lines, and a uniform director pattern. When the nematic LC employed has a smectic-A range, the nematic-to-smectic A transition is significantly suppressed by the surface pattern to well below the bulk phase transition temperature. The growth of the smectic A phase occurs concomitant with the planar-to-homeotropic anchoring transition, most likely because the large in-plane bend deformation required by the surface pattern is forbidden in the smectic phase.

11:45 AM CC6.9

The Orientation of Nematic Liquid Crystals in Contact with Surfaces Presenting Well-Defined Gradients of Chemical Functionality. Brian Harlan Clare^{1,2}, Jan Genzer³ and Nicholas L. Abbott²; ¹Chemical & Biological Engineering, University of Wisconsin, Madison, Wisconsin; ²Chemistry, University of Wisconsin, Madison, Wisconsin; ³Chemical Engineering, North Carolina State University, Raleigh, North Carolina.

Surfaces which present gradients of chemical functionality are emerging as useful tools in a variety of disciplines, ranging from cellular biology to endeavors in materials research such as guided nano-particle assembly. As early as 1911, researchers have investigated the orientations of liquid crystals in contact with surfaces. The chemical and topographical features of a surface can give rise to a preferred orientation of mesogens at that interface. This orientation is propagated through the bulk phase as liquid crystals organize over long length-scales (100 μm). This so-called anchoring of liquid crystals by surfaces has found widespread use in the displays industry, and more recently as the basis for a variety of chemical and biochemical sensors. Here, we discuss an investigation of nematic liquid crystals in contact with silicon surfaces possessing well-defined gradients in chemical functionality. These surfaces were characterized by NEXAFS before put in contact with the liquid crystal. The results presented here suggest that 1) liquid crystals may be an alternative method for the spatial mapping of molecular gradients, and that 2) gradient surfaces could potentially be used to prepare thin LC films having desired gradients in optical properties.

SESSION CC7: Novel Materials and Characterization
Chairs: Edward Samulski and Robert Twieg
Wednesday Afternoon, December 1, 2004
Room 313 (Hynes)

1:30 PM *CC7.1

Innovative Design and Elegant Syntheses in Liquid Crystals. Mike Hird, Department of Chemistry, University of Hull, Hull, United Kingdom.

The discovery that cholesteryl benzoate exhibits a liquid crystal phase marked the beginning of a remarkable period for the design, synthesis and evaluation of liquid crystals. Progress was remarkable considering the limited availability of known synthetic methods and a lack of analytical techniques. It was soon established that rod-like molecules were essential for the generation of liquid crystal phases. The basic structures of the nematic, smectic and cholesteric (chiral nematic) phases were established, and as more rod-like molecules were synthesised structure-property relationships were developed. Hence it eventually became possible to predict the types of phases that would be exhibited by a particular molecular structure, and even to design materials with specific physical properties. The realisation in the 1960s that liquid crystals could be used in flat-panel, light-weight displays of low power consumption brought a surge of activity in the design, synthesis and evaluation of liquid crystals. The material requirements for suitable displays are demanding. Materials need to be stable, exhibit the nematic phase over a wide temperature range with low melting points, and in addition possess the correct combination of physical properties such as dielectric anisotropy, birefringence, elastic constants and viscosity. Clearly, a knowledge of structure-property relationships, innovative design and an appreciation of known synthetic methods would be essential to achieve all of these requirements. Liquid crystal displays have increased rapidly in complexity as miniaturized high technology devices have been developed, from simple watch and calculator displays, to more complex diary and mobile telephone displays, to larger, color lap-top computer displays, and very recently to the 50 inch flat-panel color television displays. Accordingly, the demands on the liquid crystal materials used in such devices have increased, and necessarily the molecular structures have to be much more complex, thus testing the design and synthesis skills of chemists in collaboration with physicists, theoreticians and device engineers. This invited talk will discuss the innovative designs of liquid crystal materials and the elegant methods through which they are synthesized, in terms of (i) enhanced

fundamental understanding of liquid crystals, their melting points, mesophase morphologies, and their physical properties, and (ii) the demanding requirements of liquid crystals in the various display technologies and how these requirements have been satisfied.

2:00 PM *CC7.2

Biaxial Thermotropic Nematic Liquid Crystals. Louis A. Madsen, Theo J. Dingemans, Michi Nakata and Edward T. Samulski; Chemistry, University of North Carolina, Chapel Hill, North Carolina.

Biaxial nematics (Nb) were predicted by Freiser in 1970[1]. Despite vigorous theoretical work, and many experimental efforts to observe them, the existence of Nb phases has never been confirmed in low-molar-mass thermotropic LCs. We have synthesized LCs based on an oxadiazole biphenyl (ODBP) "boomerang-shaped" core that exhibit atypical calamitic phases in the 100-220 deg C range. X-ray studies[2] have strongly indicated biaxiality in these ODBP mesogens, and NMR evidence provides unequivocal confirmation[3]. Relative to conventional biaxial-shaped calamitic mesogens, ODBP boomerangs have the added possibility of strong inter-molecular associations originating from the large electric dipole moment ($\sim 4\text{ D}$) of the oxadiazole ring. Such associations may help stabilize the Nb phase. These results and the general status of biaxial nematics will be covered in the lecture. 1. M. J. Freiser, Phys. Rev. Lett. 24, 1041 (1970). 2. B. R. Acharya, A. Primak, T. J. Dingemans, et al., Pramana J. Phys. 61, 231 (2003); reprinted in Phys. Rev. Lett. 92, 145506-1 (2004). 3. L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski, Phys. Rev. Lett., 92, 145505-1 (2004)

2:30 PM CC7.3

Wavelength and temperature effects on liquid crystal refractive indices. Jun Li and Shin-Tson Wu; College of Optics & Photonics, University of Central Florida, Orlando, Florida.

The temperature and wavelength dependent refractive indices are important to full-color direct-view and projection displays. In this paper, we derive the three- and two-coefficient Cauchy equations based on the three-band model for describing the wavelength dependent refractive indices of anisotropic liquid crystals. Four types of liquid crystal materials (5CB and three low birefringence TFT mixtures, MLC-9200-000, MLC-9200-100 and MLC-6608 ($\Delta n < 0$)) are measured. For high birefringence ($\Delta n \geq 0.2$) liquid crystals, the three-coefficient Cauchy model fits experimental results more accurately than the two-coefficient model. For low birefringence ($\Delta n \leq 0.12$) liquid crystal mixtures, the two-coefficient Cauchy model works equally well as the three-coefficient model in the off-resonance spectral region. The temperature dependent refractive indices are particularly important for elevated temperature operation of liquid crystal devices. Based on Vuks equations, we derive a four-parameter model describing the temperature effect on liquid crystal refractive indices. The four-parameter model fit the refractive indices of both low birefringence and high birefringence liquid crystals very well.

2:45 PM CC7.4

Super high birefringence isothiocyanato biphenyl-bistolane liquid crystals. Sebastian Gauza¹, Chien-Hui Wen¹, Shin-Tson Wu¹, Narayanasamy Janarthanan² and Chain-Shu Hsu²; ¹College of Optics & Photonics, University of Central Florida, Orlando, Florida; ²Applied Chemistry Department, National Chiao Tung University, Hsin-Chu, Taiwan.

High birefringence (Δn) liquid crystals (LCs) support a wide field of different applications such as flat panel display, telecommunication, and tunable-focus lens. For these devices, high Δn improves response time through cell gap (d) reduction. This advantage is especially important for laser beam steering and variable optical attenuator as these devices are normally operated in the near infrared region ($\lambda = 1.55\ \mu\text{m}$). In the long wavelength region, the LC Δn should increase in order to achieve the required phase change, which depends on the specific LC alignment. High birefringence helps to reduce the cell gap so that the fast response time can still be maintained. To achieve high birefringence, linearly conjugated molecules are the preferred candidates. Several high birefringence molecular structures, such as diphenyl-diacetylene, bistolane, naphthalene tolanes, and thiophenyl-diacetylene have been studied. The birefringence of these compounds is in the 0.4-0.6 range. The diacetylene compounds do not have adequate UV and thermal stabilities so that their application is limited. In this paper, we present some isothiocyanato biphenyl-bistolane compounds with extrapolated birefringence 0.7-0.8 at $\lambda = 633\ \text{nm}$ and $T = 23\ ^\circ\text{C}$. We call these compounds as super high birefringence (SHB) materials. To lower melting temperature, we tried different lateral substitutions, such as alkyl and fluoro groups. The smectic phases which normally appear in the NCS-based biphenyl tolanes or tolanes are completely suppressed. Such an unusual behavior is believed due to the laterally substituted ethyl chain(s) and/or the single fluorine atom. The lateral substitutions increase the molecular separation and break the molecular symmetry so that the

smectic phase is difficult to form. Although lateral substitutions lower the melting temperature, they also decrease the birefringence and increase the viscosity. Based on these compounds and some NCS tolanes, we formulated a eutectic mixture, designated as UCF-SHB with melting point at -28 °C and clearing point at 186 °C. The birefringence was measured at several discrete wavelengths at T 23 °C. At $\lambda=532$ nm, the birefringence of UCF-SHB reaches $\Delta n=0.65$. The mixture has a lower Δn than that of the individual SHB compound we employed because the mixture contains some NCS tolanes which have a lower birefringence (Δn 0.5). The visco-elastic coefficient (γ_1/K_{11}) of UCF-SHB was measured to be 260 ms/ μm^2 at T 23 °C. This high viscosity results from the long molecular size, large moment of inertia, and lateral alkyl substitutions. As the temperature increases, γ_1/K_{11} decreases rapidly. The visco-elastic coefficient is reduced by 8X and 13X, respectively, at T=40 °C and 70 °C. Within this temperature range, birefringence only decreases slightly because of the high clearing temperature. The UV stability of such high birefringence compounds and mixtures is a concern. Thus, they are more suitable for infrared applications.

3:15 PM CC7.5

NMR Studies on an Ideal Rodlike Nematic Liquid Crystal: Rewriting the Theory of Nematic Order? Louis A. Madsen, Theo J. Dingemans and Edward T. Samulski; Chemistry, University of North Carolina, Chapel Hill, North Carolina.

Order in calamitic nematic liquid crystals has been intensely studied by NMR and myriad other analytical methods. We have made deuterium (D) NMR observations on the labeled para-quinquephenyl liquid crystal, which very closely approximates a rigid rod. To investigate this high-melting nematic (range from 390 - 427 deg. C), we have fabricated a high-efficiency oven on an NMR probehead using fumed silica tiles from the Space Shuttle and utilizing only ambient air cooling. This system allows prolonged measurements at 450 deg. C or higher with excellent temperature stability and homogeneity. Our observations on p-quinquephenyl clearly and drastically deviate from the Maier-Saupe theory and all other relevant theories of nematics, thus indicating the necessity for more a complete theory (e.g., including microscopic director fluctuations) to describe nematic order. We will present a fully defined order tensor of this LC using combinations of quadrupole and dipolar NMR coupling constants and different D label positions. We will also discuss progress on refinements to nematic order theory and to the relation of NMR measurements to nematic order.

3:30 PM CC7.6

Dielectric Relaxation in Liquid Crystal Confined to Narrow Pores. Fouad M. Aliev and Manuel Rivera Bengochea; Physics, University of Puerto Rico, San Juan, Puerto Rico.

Dielectric spectroscopy was used to investigate the influence of confinement of the liquid crystals on phase transitions and the dynamics of molecular reorientations via rotation of molecules around their short axis. The pore size was varied from 200 nm then the system shows behavior close to the behavior of three-dimensional (3D) bulk liquid crystal - to extreme narrow confinement that may be considered a quasi-one-dimensional (1D) system. We did not observe either the N-I or nematic-solid crystal phase transition under quasi-1D-confinement: in contrast, in pores of larger pore sizes, these transitions are observed with a shift and broadening of the phase transition as compared to bulk LC. We observed that, instead of undergoing the N-I phase transition in the quasi-1D-system, liquid crystal inside the narrow pores solidifies. Relaxation of molecular origin freezes out upon cooling the sample from the isotropic phase. Molecular reorientations were dielectrically active at temperatures much above the bulk N-I transition temperature but with the relaxation rate much slower and dielectric spectrum much broader than in the bulk. The relaxation due to cooperative dynamics of fluctuations of director orientations (investigated in complementary dynamic light scattering experiments) was not observed in quasi-1D-system. We suggest that the slowing down of the mode, which is molecular in the bulk material, is may be due to enhancement of the effective viscosity liquid crystal under such narrow confinement and resulting glass-like dynamics.

3:45 PM *CC7.7

A Role for Liquid Crystals as Organic Semiconductors?

Robert J. Twieg¹, Yulia Getmanenko¹, Na Liu¹, Alexander Semyonov¹, Brett Ellman², Chandra Pokhrel² and Naresh Shakya²; ¹Chemistry, Kent State University, Kent, Ohio; ²Physics, Kent State University, Kent, Ohio.

Organic semiconductors are under investigation for a variety of applications that do not require the level of performance of crystalline silicon but rather performance more characteristic of amorphous silicon. Some applications proposed for organic semiconductors include light emission (in displays, for general lighting and even

lasing), energy conversion (solar cells) and in a basic transistor function (as in an RFID card). Many of these applications will exploit the potential for enhanced processability of organic semiconductors to create devices on unusual substrates (plastic, fabric) and configurations (flexible and non-planar) by low cost printing or inkjet techniques. Liquid crystal display technology that relies on a variety of conventional electro-optic mechanisms is already well established for large area planar devices and more recently on flexible substrates as well. The hope is to take advantage of the processability of liquid crystals and the propensity of liquid crystals to provide spontaneous organization that should enhance electronic properties such as charge mobility. We will describe our recent studies of organic materials designed for charge transport activity that encompasses a range from amorphous glasses to single crystals but with special emphasis on both calamitic and discotic liquid crystals.

4:15 PM CC7.8

Modular Mesogens and Designer Columnar Phases.

Vance Williams, Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada.

Columnar liquid crystal phases have received considerable attention for their potential as components in light emitting devices, chemical sensors and field effect transistors. Designing columnar phases with desirable macroscopic properties requires both a detailed knowledge of their structure-property relationships and a flexible synthetic strategy. We have therefore developed a highly modular synthetic approach that allows us to construct mesogens with variable shape, size and functionality. Using substituted phenanthrene quinone precursors, we have been able to construct large numbers of mesogens by condensation with 1,2-diamines. Many of these derivatives exhibit a variety of liquid crystal phases, including rectangular and hexagonal columnar phases and nematic phases. The nature of the functional groups present on these molecules is of paramount importance in determining the stability of these phases. These results can be rationalized on the basis of the specific interactions between mesogens. This has provided key insights into the role of noncovalent interactions in determining the formation of columnar phases. We will report our latest efforts at controlling this self-assembly process using symmetry effects, π -stacking, hydrogen bonding and metal coordination.

4:30 PM CC7.9

Fluoroalkylated Triphenylene Discotic Liquid Crystals: Effect of the Fluoroalkylation on the Spontaneous Alignment

Behavior. Yo Shimizu¹, Naohiro Terasawa¹, Hirosato Monobe¹, Kenji Kiyohara² and Nobutaka Tanigaki³; ¹Research Institute for Ubiquitous Energy Devices, Natl. Inst. Adv. Ind. Sci. Tech., Ikeda, Osaka, Japan; ²Research Institute for Cell Engineering, Natl. Inst. Adv. Ind. Sci. Tech., Ikeda, Osaka, Japan; ³Research Institute for Photonics, Natl. Inst. Adv. Ind. Sci. Tech., Ikeda, Osaka, Japan.

A series of hexasubstituted triphenylenes having perfluoroalkyl-terminated tails were synthesized and their mesomorphism was revealed that the fluoroalkylation of the peripheral tails contribute to the thermal stability of hexagonal columnar mesophase. In this work, the spontaneous alignment behavior of these mesogens in the columnar phase was investigated for a variety of substrates. The results indicate that the introduction of perfluoroalkyl groups in the peripheral tails surely changes the alignment behavior, probably due to the low surface tension. It was indicated the balance of molecular-level forces working between the substrate surface and perfluoro moieties of mesogens should be important for the property. This molecular design concept might be able to provide a novel design technique of mesogens of which spontaneous alignment property is involved in the device applications.

4:45 PM CC7.10

Electron Microscopy and Diffraction Analysis of Uniaxial Nanostructures Containing Discotic Liquid Crystalline

Material. Andreas Karl Schaper¹, Tetsuya Ogawa², Masaki Tsuji², Martin Steinhart³, Ulrich Goesele³, Christoph Weder⁴, Sven Zimmermann⁵ and Joachim H. Wendorff⁵; ¹Material Sciences Center, Philipps University of Marburg, Marburg, Germany; ²Institute for Chemical Research, Kyoto University, Uji, Japan; ³Max Planck Institute of Microstructure Physics, Halle, Germany; ⁴Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio; ⁵Institute of Physical Chemistry, Philipps University of Marburg, Marburg, Germany.

In recent times, the preparation of materials on a nanometer scale and the control of their internal structural organization, their size, geometry, and macroscopic ordered arrangement, are exciting challenges facing material sciences. Nanotubes and nanowires are of considerable interest in view of their potential practical importance. In particular, they can serve as one-dimensional confinements for various kinds of materials aiming at special functionality systems. Discotic liquid crystal (LC) compounds of the type

2-adamantanoyl-pentabutoxy-triphenylene (Ada-PBT) show the tendency to self-assemble into columnar hexagonal structures with high charge carrier and exciton mobilities along the director of the molecular stacks. If the LC phase is dispersed in another molecular or polymeric material, the properties of the resulting systems are controlled by the distribution of the liquid crystalline material within the second phase, and by its molecular orientation and ordering [1]. Tube- and wire-like nanostructures in the diameter range 25 to 400 nm were prepared by wetting nanoporous alumina templates from solution or melt, followed by selective removal of the template [2]. Besides integral x-ray diffraction analysis, local electron microscope-based diffraction and imaging are required to elucidate the distribution and alignment of the LC phase. Because of the extremely high irradiation sensitivity of the organic material, ultra-cryo work at liquid He temperature and the use of highly sensitive image plates for image recording were indispensable preconditions for these studies. Using LC/polymer mixtures, depending on the wetting conditions and the template pore size, the LC phase gets segregated either into a thin layer covering the inner polymer tube wall or forming a wire-like core. Nanotubes were also obtained of the pure LC phase and of LC/electron donor complexes. Electron diffraction due to the 0.35 nm intracolumnar disk spacing revealed high molecular alignment of the LC phase parallel to the long axis of the tubes. In addition, diffraction in the small angle region was detected arising from three-dimensional intermolecular ordering of the discotic columns (typical spacing 1.6 nm). Regions of the LC phase showing exceptional high order, particularly after annealing, could be identified analytically using energy filter microscopy. On the other hand, a general tendency has been observed of a gradual depression of the mesophase formation towards small pore diameters. [1] A. Bayer, J. Kopitzke, F. Noll, A. Seifert, J.H. Wendorff, *Macromolecules* 34 (2001) 3600. [2] M. Steinhart, Z. Jia, A.K. Schaper, R.B. Wehrspohn, U. Gosele, J.H. Wendorff, *Adv. Mater.* 15 (2003) 706.

SESSION CC8: Chiral/Ferroelectric LC Materials
Chairs: Robert Lemieux and Dave Walba
Thursday Morning, December 2, 2004
Room 313 (Hynes)

8:30 AM *CC8.1

Liquid Crystal Development in the Quest for Commercial Ferroelectric Liquid Crystal Displays. Michael David Wand, Kundalika M. More and William N. Thurmes; Displaytech, Inc., Longmont, Colorado.

Commercialization of FLC-based displays has been a goal for many companies throughout the past two decades. Advances in FLC materials and cell design have led to breakthroughs in FLC operating and storage temperature range as well as LC alignment quality. Novel FLCs incorporating silicon and fluorine into their structure have been designed and synthesized. They have been shown to effectively lower melting point while still retaining, or increasing the SmC* upper temperature range. The automation of LC measurement and evaluation has proved to be a key step in dramatically enhancing the speed of LC compound and mixture development. We will briefly touch on the instrumentation used. We also will describe a new class of FLC materials that do not show the typical shrinking effect upon cooling, leading to defect minimization. X-ray data will be presented that demonstrates near bookshelf behavior. The high quality alignment afforded by these mixtures will be demonstrated in an SXGA LCOS panel. In addition, the fast switching speed that these new FLC mixtures afford allows operation in the field sequential color mode with no blurring or other color artifacts.

9:00 AM *CC8.2

Orthoconic Antiferroelectric Liquid Crystalline Materials. Roman Dabrowski, Faculty of Engineering, Chemistry & Applied Physics, Military University of Technology, WARSAW, Poland.

Surface stabilized antiferroelectric liquid crystals (SSAFLCs) enable to build fast response electrooptic devices and displays[1]. Pretransitional effects and misalignment caused by the existence of microscopic defects on cells surface involve the bad extinction in the off state in displays and hamper their applications. Recently we synthesized chain fluorinated anticlinic smectics achieving 45 tilt in the smectic layers[2,3] called orthoconic antiferroelectrics. Their use leads to the more perspective and simple method in solving bad contrast of SSAFLCs because they show extremely small pretransitional effect and they are optically uniaxial negative liquid crystals with optic axis perpendicular to the cell glass plates at normal incidence of light. Therefore, when they are placed between crossed polarizers behave as an isotropic medium and surface defects are not seen, what generates the excellent true dark state[4]. The syntheses, phase transitions, smectic layer structure, optical tilt, spontaneous polarization, helical pitch and electrooptical properties of recently prepared high tilted antiferroelectric compounds of the

common formula:

$F_{2n+1}C_nX_{Cm}H_{2m}OPh(F,H)_{p1}COOPh(F,H)_{p2}COOC^*H(CH_3)C_6H_{13}$ (S) where X=COO, O or single bond; $p_1=2$ and $p_2=1$ or $p_1=1$ and $p_2=2$; the benzene rings are unsubstituted or substituted by a fluorine atom as well as their racemic (R,S) form and achiral analogues with $CH(CH_3)_2$ or $CH(C_3H_7)$ instead of $C^*H(CH_3)C_6H_{13}$ chain will be characterized. Differences in the stability of anticlinic order between the chiral and achiral compounds will be demonstrated. Correlation between the chemical structure of molecules and their tilt in the smectic layers and helical pitch will be discussed. The many prepared compounds exhibit antiferroelectric phase near the room temperature and without higher ordered phases below. They enable to prepare broad temperature (-20C to 100C) orthoconic antiferroelectric mixtures, having tilt independent upon temperature. The mixtures exhibiting excellent contrast and gray level scale will be presented. References: 1. S.T.Lagerwall, *Ferroelectric and antiferroelectric Liquid Crystals*, Wiley-VCH, (Weinheim and New York, 1999) 2. W.Drzewinski, R.Dabrowski, K.Czuprynski; *Orthoconic Antiferroelectrics. Synthesis and mesomorphic properties of optically active (S)-(+)-4-(1-methylheptyloxy carbonyl)phenyl 4-(fluoroalkanoxyalkoxy)biphenyl-4-carboxylates and 4-(alkanoxyloxyalkoxy)-biphenyl-4-carboxylates*, Polish J.Chem., 76, 273-284 (2002) 3. J.Gasowska, J.Dziaduszek, W.Drzewinski, M.Filipowicz, R.Dabrowski, J.Przedmojski, K.Kenig; *Influence of rigid core structure on layer tilt and mesomorphic properties in homologous series of three ring antiferroelectric esters*, SPIE (in press 2004) 4. S.T.Lagerwall, A.Dahlgren, P.Jagemal, P.Rudquist, K.Dhave, H.Pauwels, R.Dabrowski, W.Drzewinski; *Unique electro-optical properties of liquid crystals designed for molecular optics*, *Adv.Funct.Mater.*, 11 (2) 87-94 (2001)

9:30 AM *CC8.3

Dimeric Liquid Crystals with Wide Temperature Range Blue Phases. Mike N. Pivnenko and Harry J. Coles; Centre for Molecular Materials for Photonics and Electronics, University of Cambridge, Cambridge, United Kingdom.

Blue phase (BP*) liquid crystals show much promise in varied applications - for example, colour switching for displays or 3D bandgap lasing in photonics - but their temperature sensitivity has made their deployment problematic. The narrow temperature range, rarely more than one degree, over which the BP* exist is a characteristic feature of the phase, well established experimentally and theoretically and, at the same time, it has always been an insuperable limitation for the promising applications. In this paper we present a generic family of liquid crystal materials naturally exhibiting typically 40 degree wide BPI* phases. Eutectic mixtures of two symmetric liquid crystal dimers doped with a small percentage of a highly twisting chiral additive showed typically the following phase sequence on cooling (degrees C): Iso* 57.44 BPIII* 57.22 BPII* 56.99 BPI* 16.5 SmX* -28 Glass in a conventional 7 mkm thick liquid crystal cell with no aligning layers and also in a differential scanning calorimetry experiment. The observed texture of the BPI* - the platelet texture - was quite characteristic and easily recognisable. Taking into account a well known property of the BPI* to supercool with respect to the chiral nematic phase, particular attention was paid to check the stability of the BPI* at low temperature. The cell was maintained at 22-25 °C for 30 days and no visible changes were observed in the texture. The (110)-peak of the selective reflection showed a normal temperature dependence on cooling from 57.0 to 56.4°C; the wavelength increased from 490 to 565 nm respectively. On further cooling to 20°C the peak exhibited inverted temperature dependence; its wavelength dropped to 553 nm linearly with temperature. The latter effect was caused by a gradual decrease of the refractive index in the wide temperature interval while the BPI* lattice parameter remained constant. Under applied electric field the sample showed a reversible shift of the selective reflection peak from 533 to 515 nm. An electro-optic response with characteristic time from 1 to 10 ms depending on temperature was also detected. We will discuss the origins of the wide blue phase in the new materials and possible applications.

10:30 AM *CC8.4

Ferroelectric Liquid Crystals Induced by Dopants with Chiral Spiroindandione Cores: Controlling Conformational Equilibrium in the SmC Binding Site. Robert P. Lemieux, Jeremy Finden and Eaganie Yuh; Chemistry, Queen's University, Kingston, Ontario, Canada.

In previous studies, we have shown that dopants with atropisomeric biphenyl cores can induce very high spontaneous polarizations in SmC hosts with complementary core structures [1]. Intrinsically, the polarization power of any chiral dopant depends on the conformational bias of the polar chiral unit to orient in one direction along the polar axis of the SmC* phase. Molecular modeling suggests that, in the absence of chiral perturbations, the conformational bias of atropisomeric biphenyl dopants should be very small, on the order of

1 kcal/mol [2]. To develop new dopants with higher intrinsic polarization powers, we recently shifted our attention to molecules with chiral cores that should be conformationally more restricted in the binding site of a SmC host [3]. We synthesized a series of three dopants with a chiral spirobiindandione core in optically pure form and measured their polarization powers in four SmC hosts with different core structures. The results show that the polarization power depends strongly on the nature of the SmC host. In addition, the magnitude and sign of induced polarization in a given SmC host strongly depends on the position of the alkoxy side-chains. Conformational analysis suggests that, in the binding site of the SmC host, each dopant is in dynamic equilibrium between two conformations that induce polarizations of opposite sign, and that the host dependence of the polarization power can be rationalized based on a shift in this equilibrium. In order to test this model, the dopants have been modified by the introduction of a nitro group on the spirobiindandione core which should strongly favor one conformation over the other. Additionally, the use of ester side chains as well as the combination of nitration on the dopant core with ester side chains are being investigated. The effect of these changes on the sign and magnitude of the induced polarization will be discussed. (1) Lemieux, R.P. *Acc. Chem. Res.* (2001), 11, 845. (2) D. Vizitiu, C. Lazar, J.P. Radke, C.S. Hartley, M.A. Glaser and R.P. Lemieux *Chem. Mater.* (2001), 13, 1695. (3) Boulton, C.J.; Sutherland, J.J.; Lemieux, R.P. *J. Mater. Chem.* 2003, 13, 644-646.

11:00 AM *CC8.5

High Quality Alignment of FLC Glasses Processed from Main-Chain Polymer Fibers. David Walba^{1,3}, Lei Xiao^{1,3}, Patrick Keller^{4,5}, Eva Korblova^{1,3}, Michi Nakata^{2,3}, Darren Link⁵, Jon Fernsler^{2,3}, Renfan Shao^{2,3} and Noel Clark^{2,3}, ¹Dept of Chem and Biochem, University of Colorado, Boulder, Colorado; ²Department of Physics, University of Colorado, Boulder, Colorado; ³The Ferroelectric Liquid Crystal Materials Research Center, University of Colorado, Boulder, Colorado; ⁴Section De Recherche, Institut Curie, Paris, France; ⁵ESL, Harvard University, Cambridge, Massachusetts.

We have been working towards development of materials useful in second order nonlinear optics (NLO) applications based upon the FLC polar self-assembly. In order to obtain stable glasses from FLCs over a broad temperature range, oligomers or polymers with relatively high molecular weight are advantageous. Such materials are, however, difficult to align. Given that very high quality alignment is required in the most interesting NLO applications of polar organic glasses, approaches for achieving such alignment are under investigation. In this context, a class of main-chain polymers prepared by acyclic diene metathesis polymerization of NLO-active FLC mesogens have been reported. These polymers possess an isotropic-smectic C* phase transition at high temperatures, and freeze into apparently stable FLC glasses at temperatures well above room temperature. Furthermore, such polymers can be pulled into fibers with a very uniform layer structure, with the layers oriented normal to the fiber axis. In this presentation, the properties of thin films obtained by "squishing" such fibers between solid substrates while heated into the smectic C* phase will be described.

11:30 AM CC8.6

Structure and Electroclinic Response of Chiral Smectic A Liquid Crystals. Robin L. B. Selinger¹, Bryan Armentrout¹ and Jonathan V. Selinger², ¹Physics Dept., Catholic Univ., Washington, District of Columbia; ²Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington, District of Columbia.

Using mesoscale simulation techniques, we explore a range of possible microstructures of a chiral smectic liquid crystal and their electroclinic response in both two and three dimensions. We confirm the proposal of Meyer and Pelcovits [PRE 65, 061704 (2002)] that a smectic-C liquid crystal with modulations in the local tilt direction can have properties like those of a smectic-A, including a strong electroclinic response. However, as we vary elastic coefficients, we find a range of microstructures, most of which are quite different from those considered by Meyer and Pelcovits. In two dimensions, we find "stars and stripes" phase characterized by point defects decorated with branching stripes. This phase appears to have a stronger electroclinic response than a phase with point defects alone. In three dimensions, we find a novel phase with parallel threading line defects which branch and merge with one another randomly at intervals along their length.

11:45 AM CC8.7

Electro-Optical Devices from Surface-Stabilized Cholesteric ULH Structure with Dual Mode Switching. Sang Hwa Kim¹, Xiaoli Zhou¹, Liang-Chy Chien¹ and Lachezar Komitov², ¹Liquid Crystal Institute, Kent State University, Kent, Ohio; ²Physics and Engineering physics, Chalmers University of Technology and Gothenburg University, Goteborg, Sweden.

Uniformly lying helix (ULH) structure in short pitch cholesteric liquid crystals has a flexoelectro-optic effect and it can be operated with dielectric coupling after suitable stabilization of a ULH structure. Using polymer network formed in the liquid crystal medium, dual mode (in-plane and out-of-plane) switching made possible. We optimized layer structure of the polymer network with selective UV polymerization. For these studies, mono layer and double layer polymer network localized to the substrates formation studied. We will discuss monomer concentration effect and curing voltage dependence of the cell during UV polymerization with their morphological and electro-optical studies.

SESSION CC9: Novel Photonic Applications/Materials

Chairs: Shaw Chen and I.C. Khoo
Thursday Afternoon, December 2, 2004
Room 313 (Hynes)

1:30 PM *CC9.1

Abstract Withdrawn

1:45 PM *CC9.2

Direct Optical Holographic Fabrication of Tunable and Nonlinear 3-D Photonic Crystals in Polymeric Dispersed Liquid Crystals. Iam-Choon Khoo¹, Yana Zhang Williams² and Kan Chen³, ¹Electrical Engineering, Penn State University, University Park, Pennsylvania; ²Pennsylvania State University, University Park, Pennsylvania; ³Pennsylvania State University, University Park, Pennsylvania.

We have developed a compact 3-D optical holographic writing set up and fabricated 3-D photonic crystalline structures in polymer dispersed nematic liquid crystals. The resultant photonic crystals are typically about 10 micron thick, with grating spacing of about 0.5 microns, and they generally exhibit excellent Bragg diffraction properties and photonic bandgaps at various visible spectral region. Using methyl-red doped nematic liquid crystals, we have also made polymer dispersed liquid crystal films that possess usual characteristics such as low on-off state switching voltage, large contrast ratio, and capability for electronically tunable transient or permanent grating formation.

2:15 PM CC9.3

Infiltration of 2-D Photonic Crystals with Liquid Crystals. Julien Martz¹, Libero Zuppiroli¹, Frank Nuesch^{2,1}, B. Wild³, B. Lombardet³, A. Dunbar³, R. Ferrini³, R. Houdre³ and F. Robin⁴; ¹Laboratory of Optoelectronics of Molecular Materials, EPFL, Lausanne, Switzerland; ²Laboratory for Functional Polymers, EMPA, Duebendorf, Switzerland; ³Laboratoire de Physique des Dispositifs Semiconducteurs, EPFL, Lausanne, Switzerland; ⁴Communication Photonics Group - Electronics Laboratory, ETHZ, Zurich, Switzerland.

Filling the holes of 2-D GaAs Photonic Crystals (PhC) with a tunable refractive index material is of interest in changing or controlling the optical properties of the PhC, for example to select a chosen range of frequencies. The infiltrated material could also be used to compensate for fabrication imperfections and fluctuations of the PhC or to induce strong effects that might be used for optical switching. To guarantee a high refractive index contrast with the waveguide, the infiltrated materials should have a rather low refractive index. In this work, we focused on nematic Liquid Crystal materials (LC) and in particular LC-E7, which is a blend of cyanobiphenyl and cyanoterphenyl molecules, para-substituted with hydrophobic saturated chains. Infiltration experiments are achieved in a specially designed vacuum chamber. The technological process is developed in order to perform the infiltration of the 200 nm holes under vacuum and to chemically activate the GaAs surface. From optical transmission measurements, the shift of the Photonic Band Gap edge is measured and analyzed. This allows us to evaluate filling efficiency and determine the orientation of the liquid crystal molecules within the PhC holes. Different tuning methods of the PhC will also be discussed, such as LC-Temperature variation or the influence of an external electric field which changes the orientation of LC molecules thereby modulating the refractive index. In order to ameliorate the wettability of LC-E7 on the surface, the possibility of using surface adsorbed monolayers on oxidized GaAs semiconductor surfaces is investigated. A vapour growth method using vapour deposition of carboxylated derivatives on plasma activated surfaces is developed. Two types of molecular families are studied in this work: benzoic acids and fatty acids. Para-substituted benzoic acids with a wide range of electrical dipoles allow adsorption to be followed by measurement of the surface potential of the grafted substrates using Kelvin probe techniques. These model compounds yield important information on the grafting conditions and the stability of the monolayers. The quality of the

monolayer can be inferred from water static contact angle measurements and wettability studies using liquid crystals were also performed.

2:30 PM *CC9.4

Nonlinear Optical "Black Hole" in Dye-Doped Liquid Crystals.

Nelson Tabiryan, Manuel J. Mora and Svetlana V. Serak; Beam Engineering for Advanced Measurements Co., Winter Park, Florida.

We have encountered an extremely strong novel process of nonlinear absorption in liquid crystal (LC) materials doped by a dye at saturating level of concentration. It results in disappearance of the laser beam of as high power as over 20 mW in the material with no visible output. We report the details of the effect observed for a He-Ne laser beam ($\lambda = 633$ nm) focused on 30 mm-thick planar oriented nematic LC (NLC) 5CB containing up to 2 wt.% of the dye 1,8-dihydroxy,4,5-diamino,2,7-diisopentyl-anthraquinone. The effect can be observed also for a green laser beam ($\lambda = 532$ nm) in the same material. This "black hole" effect takes place for radiation of sufficiently high power at certain positions of the cell, symmetrically arranged with respect to the focus of a lens (20 mm focal length). Far from the focus, the transmission of the material is constant and is about 1% due to high concentration of the dye. As the cell is brought closer to the focus, the nonlinear optical process exhibits itself first as formation of a dark circle on a screen at the output of the cell. Moving the cell closer to the focus results in increasing of the diameter of the dark circle and fainting of the pattern up to its complete disappearance at a certain point. The transmission of the cell increases explosively (over 50 times with respect to the initial transmission) when the cell reaches the focus. The laser beam at that point looks more like a flashlight due to its enormous divergence, which changes from about 1.8 degree (half maximum at the level e^{-2} of intensity) just before the high transmission point to about 20 degrees. The preliminary studies of the mechanism of the "black hole" effect and accompanying processes indicate that it is related with substantial increase of the absorption coefficient of the material with increasing temperature. Formation of radiation-controlled associations of dye molecules in solutions is a plausible mechanism for such a nonlinear absorption. Choosing special dyes and solutions may reduce the operation power level and increase the initial transmission state of these material systems making them promising for a variety of applications.

3:30 PM *CC9.5

Multifunctional Glassy Liquid Crystals for Photonics.

Shaw H. Chen, ¹Chemical Engineering, University of Rochester, Rochester, New York; ²Laboratory for Laser Energetics, University of Rochester, Rochester, New York.

Liquid crystals are fluids characterized by various forms of long-range molecular order. They have found extensive uses in electro-optical devices, such as liquid crystal displays and spatial light modulators. For many photonic applications it is desirable to freeze liquid crystalline order into solid state without crystallization. This represents a unique class of advanced materials that we call glassy liquid crystals. Through prevention of molecular packing into a crystalline lattice, we have created a definitive set of morphologically stable glassy liquid crystals with elevated transition temperatures. Selected materials have served to demonstrate the concepts of large area nonabsorbing polarizers, optical notch filters and reflectors, strongly polarized fluorescent films, and nondestructive rewritable optical memory and photonic switching. The idea of mesomorphic glass has been generalized to the design of monodisperse conjugated oligomers capable of forming highly ordered glassy films potentially useful for electronics and photonics. In particular, strongly polarized and highly efficient organic light-emitting diodes have been accomplished. In this talk, we will focus on recent advances made in our laboratory.

4:00 PM *CC9.6

Tunable Laser Action in Nanostructured Liquid Crystal.

Masanori Ozaki and Katsumi Yoshino; Dept. of Electronic Eng., Osaka University, Suita, Osaka, Japan.

In a one-dimensional (1-D) periodic structure, the laser action has been expected at the photonic band edge where the photon group velocity approaches zero. Chiral liquid crystals such as cholesteric liquid crystal (CLC) and ferroelectric liquid crystal (FLC) have a helical structure and laser action in the 1-D helical structure has been demonstrated. Here, various types of tunable laser actions in dye-doped liquid crystals with 1-D periodic structure are presented. We have investigated lasing characteristics at the edge of the 1-D photonic band gap of dye-doped CLC under the field. The in-plane laser action has been detected from multi-cavities of the focal conic structure. In this configuration, the lasing wavelength can be tuned by the electric field. Lasing wavelength in dye-doped FLC can also be

tuned in a wide range upon applying an electric field. The dynamic response of the helix elongation of FLC has also been investigated and demonstrated the possibility of the microsecond modulation of the lasing wavelength. In-plane laser actions in waveguide configurations have been demonstrated in dye-doped CLC and FLC cells in which helix axes are parallel to the substrates. In this configuration, doped dye can be effectively excited by a pump beam illuminating perpendicularly the helical axis and the laser light emitted along the helical axis propagates in the waveguide. Twist defect mode (TDM) has been experimentally demonstrated in a transmission spectrum of the composite film consisting of two photopolymerized cholesteric liquid crystal (PCLC) layers. Self-organized helical structure of PCLC acts as 1-D photonic crystal, and the twist defect which is a discontinuity of the director rotation around the helix axis at an interface of two PCLC layers, induces the TDM. Optically pumped laser action based on the TDM has also been observed in a dye-doped double composite PCLC film. We have also demonstrated the possibility of the wavelength tuning of the defect modes in a chiral liquid crystal in the basis of the local deformation of the 1-D periodic helical structure. [1] M.Ozaki, M.Kasano, D.Ganzke, W.Haase, and K.Yoshino, *Adv.Mater.*, 14, 306 (2002) [2] T.Matsui, R.Ozaki, K.Funamoto, M.Ozaki and K.Yoshino, *Appl.Phys.Lett.*, 81, 3741 (2002) [3] M.Ozaki, R.Ozaki, T.Matsui and K.Yoshino, *Jpn.J.Appl.Phys.*, 42, L472 (2003) [4] K.Funamoto, M.Ozaki and K.Yoshino, *Jpn.J.Appl.Phys.*, 42, L1523 (2003) [5] M.Ozaki, M.Kasano, T.Kitasho, D.Ganzke, W.Haase, and K.Yoshino, *Adv.Mater.*, 15, 974 (2003) [6] M.Kasano, M.Ozaki, D.Ganzke, W.Haase, and K.Yoshino, *Appl.Phys.Lett.*, 82, 4026 (2003) [7] T.Matsui, M.Ozaki, and K.Yoshino, *Appl.Phys.Lett.*, 83, 422 (2003) [8] T.Matsui, M.Ozaki, and K.Yoshino, *Phys.Rev.E*, 69, 06171 (2004)

4:30 PM CC9.7

Electrically Tunable, Multimode 2-D Organic Photonic Crystal Lasers.

Rachel Jakubiak¹, Dean P. Brown¹, Vincent Tondiglia², Lalgudi Natarajan², Richard Sutherland², Timothy Bunning¹ and Richard A. Vaia¹; ¹Materials & Manufacturing Directorate, Air Force Research Laboratory, WPAFB, Ohio; ²SAIC, Dayton, Ohio.

Holographic polymerization of liquid crystal containing photopolymerizable resins enables one-step, rapid formation of multi-phase structures that exhibit partial photonic band gaps. These holographic polymer dispersed liquid crystals (H-PDLCs) provide a versatile platform for diffractive optical elements because the structures are not limited by multi-phase equilibrium but are controlled by the interference of multiple lasers at discrete angles. Incorporation of laser dyes into acrylate polymer and nematic liquid crystal H-PDLCs is demonstrated to create optically pumped distributed feedback lasers. While one-dimensional Bragg stacks afford single mode laser oscillation, multiple oscillations are derived from columnar 2-D lattices. Linewidths as narrow as 2 nm are observed with laser thresholds below 1 mJ/cm², compared to 9 nm and 25 mJ/cm² exhibited by 1-D H-PDLC Bragg stack lasers. In the 2-D lattices the energy of the laser action can be tuned within the gain spectrum of the lasing medium by an applied electric field or by judicious selection of pump fluence.

4:45 PM CC9.8

A Novel Optical Switch Based On Electrically Tunable Liquid Crystal Photonic Crystal Fiber.

Fang Du, Yan-Qing Lu and Shin-Tson Wu; College of Optics and Photonics, Orlando, Florida.

Photonic crystal fiber (PCF), microstructured waveguide which contains an array of air holes running down the length of fiber, provides an additional design freedom, compared with the traditional fiber designs, offering different light propagation properties by choosing air-hole periodic structure topology and structural parameters like pitch, core diameter and air holes filling. In general, PCFs guide light either by total internal reflection (TIR) or photonic band gap (PBG) effect, depending on the fiber structure. By introducing additional materials into the air holes the air-hole lattice structure not only provides more design freedom, but also broadens the potential applications of PCFs. Among the materials that can be used in this purpose, liquid crystal (LC) is of particular interest because its refractive index can be tuned by temperature or by electric field. A LC mixture was introduced into the air holes of a photonic bandgap type of PCF. In such a LC filled PCF system the LC has higher index of refraction than silica resulting in guiding due to total internal reflection (the so called index guiding). The light propagates through the LC filled fiber core. Therefore the guiding mechanism of the original air-core PCF switched from the original PBG effect to TIR guiding. By applying external electric field across the liquid crystal filled PCF, we demonstrated an electrically tunable optical switch. The LC molecules reorientation dramatically influenced the output beam which changed from a guided to a completely lossy output. A CCD camera and a detector, positioned after the fiber, were used in characterizing the output beam profile

and the total fiber throughput, respectively. The throughput drop followed the CCD camera behavior. In conclusion, by introducing LC mixture into an air-core bandgap PCF we achieved an index guiding PCF configuration. Furthermore, in this index guiding PCF we have demonstrated an electrically controllable optical switch. The disturbance resulting from the induced LC reorientation leads to a very dramatic and rapid vanishing of the fiber core guiding. Many useful applications in the fiber-optic systems are foreseeable.