

SYMPOSIUM CC

Advances in Liquid Crystalline Materials and Technologies

November 26 – 29, 2001

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* Invited paper

SESSION CC1: SMECTIC AND CHIRAL L.C.

Chairs: David M. Walba and Noel A. Clark
Monday Morning, November 26, 2001
Commonwealth (Sheraton)

8:30 AM *CC1.1

ANALOG ELECTRO OPTICS USING CHIRAL SMECTIC LIQUID CRYSTALS. N.A. Clark, T. Bellini, R.F. Shao, D. Coleman, S. Bardon, D.R. Link, J.E. Maclennan, Department of Physics, University of Colorado, Boulder, CO; D.M. Walba, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO; X.H. Chen, M.D. Wand, Displaytech, Inc., Longmont, CO; P. Rudquist, and S.T. Lagerwall, Department of Physics, Chalmers University, Göteborg, SWEDEN.

I will report on recent progress in the development of analog electro-optics using chiral smectics having the molecules tilted with respect to the layers. Both smectic C and smectic A effects will be presented. The role of polarization conductivity, polarization charge stiffening of the molecular orientation field, cell architecture, and materials characteristics useful for obtaining analog electro-optic behavior will be discussed.

*Work carried out in collaboration with the members of the Ferroelectric Liquid Crystal Materials Research Center. Supported by NSF MRSEC Grant DMR 98-09555, NSF Grant DMR 0072989, and ARO Grant DAAG55-98-1-0446.

9:00 AM *CC1.2

FLEXOELECTRIC EFFECTS IN HIGHLY TWISTED NEMATIC BIMESOGENS. Harry Coles, Southampton Liquid Crystal Institute, Department of Physics & Astronomy, University of Southampton, Highfield, Southampton, UNITED KINGDOM.

We have recently shown that bimesogenic liquid crystals exhibiting a chiral nematic [1] (N^*) phase have macroscopic electro-optic flexoelectric properties that make them very interesting for both display and non display applications. Flexoelectricity in chiral nematics was shown [2] some years ago to have potential for fast 'in plane' electro-optic switching and linear response to the applied field. However, hitherto, typical fields, $\sim 80\text{-}100\text{V}/\mu\text{m}$, were required for very moderate switching angles ($\sim 5\text{-}10^\circ$) with response times of $\sim 100\mu\text{s}$. Through careful design of novel halogenated bimesogens we have produced [3] highly twisted chiral nematic phases with selectable switching angles of 45° or 90° at very moderate fields ($5\text{-}10\text{V}/\mu\text{m}$). Further the response times ($20\text{-}300\mu\text{s}$) and switching angles, at a given field, at room temperature are independent of temperature. The in plane switching is characteristic of this chiral nematic flexoelectric effect even though the applied field is applied conventionally in the viewing direction [4]. We have demonstrated a range of wide viewing angle birefringence, dye guest host (dichroic and fluorescent) and molecular mirror devices [5] and these will be discussed during the presentation. Finally we will discuss in depth the molecular design protocols for these fascinating new chiral nematic phases in terms of their ultimate use in devices. Such devices include displays, telecommunication switching, photonic transducers as well as nonlinear optical elements.

[1] B. Musgrave, P. Lehmann and H.J. Coles, *Liq. Cryst.*, 1999, 26(8), 1235-1249.

[2] J.S. Patel and R.B. Meyer, *Phys.Rev.Lett.*, 1987, 58, 1538-1540.

[3] H.J. Coles, M.J. Coles, S. Perkins, B. Musgrave and D. Coates, *Flexoelectric Bimesogens*. EP99119114.9 Filed 4th October 1999.

[4] B. Musgrave, M. Coles, S. Perkins, and H.J. Coles, *Mol.Cryst.Liq.Cryst.*, 2001, [In Press].

[5] M.J. Coles, B. Musgrave, S.P. Perkins and H.J. Coles, *Mol. Cryst. Liq. Cryst.*, 2001, [In Press].

9:30 AM CC1.3

CHIRALITY TRANSFER IN FERROELECTRIC LIQUID CRYSTALS. Carmen Lazar, Torsten Hegmann, Robert P. Lemieux, Department of Chemistry, Queen's University, Kingston, Ontario, CANADA; Matthew A. Glaser, Department of Physics and Ferroelectric Liquid Crystal Materials Research Center, University of Colorado, Boulder, CO.

Commercial SmC* mixtures suitable for SSFLC display applications are normally obtained by mixing a chiral dopant with high polarization power into an achiral SmC host formulation. Studies have shown that, unlike conventional dopants with chiral side-chains, the polarization power of dopants with chiral cores varies with the nature of the SmC liquid crystal host [1]. The origin of this host dependence is thought to arise from interactions between the chiral core of the dopant and the achiral cores of surrounding SmC host molecules. We have shown that the polarization power of chiral dopants with an atropisomeric biphenyl core depends strongly on the core structure of the SmC host, and obtained the highest polarization power values in a phenylpyrimidine host which provides the best structural match for chirality transfer via core-core interactions [2]. To account for these

results, we proposed that chirality transfer to surrounding host molecules causes a strong chiral distortion of the mean-field potential (binding site) which imposes orientational and translational ordering to the dopant molecule in the SmC host. As a feedback, this chiral distortion may affect the orientational distribution of the dopant transverse dipole with respect to the polar axis and/or the polar ordering of the dopant. Current efforts in this project are aimed at testing the Chirality Transfer Feedback model through the design of new dopants with helical bridged biaryl cores, and through a structural mix-and-match of atropisomeric dopants and SmC host molecules.

(1) H. Stegemeyer, R. Meister, U. Hoffmann, A. Sprick, A. Becker, J. Mater. Chem. (1995), 5, 2183.

(2) D. Vizitui, C. Lazar, B.J. Halden, R.P. Lemieux, *J. Am. Chem. Soc.* (1999), 121, 8229.

9:45 AM CC1.4

PLANAR ORIENTATION OF FERROELECTRIC LIQUID CRYSTALS BY SELF-ASSEMBLED BILAYER MOLECULAR ASSEMBLY. Sukhmal C. Jain, Vivechana Dixit, Vinod K. Tanwar, Polymeric & Soft Materials Div, National Physical Laboratory, New Delhi, INDIA.

UV-polymerized bilayer molecular assembly of amino propyl triethoxy silane (APTES) attached with cinnamoyl moieties have been shown to produce good uniform planar orientation of ferroelectric liquid crystalline materials. The highly ordered, densely packed bilayer molecular film has been grown on indium-tin-oxide coated glass and quartz substrates by self-assembly (SA) technique. The growth of the bilayer film has been monitored by (i) wetting studies, (ii) ATR-IR, (iii) XPS, (iv) UV-spectroscopy and (v) Atomic Force Microscope. The grown bilayer film was irradiated with a linearly polarized UV-light source to create an ordered anisotropic surface structure at the glass substrate. The ferroelectric liquid crystal cells prepared using the above glass substrates were characterized for their electro-optic properties. The cells showed a contrast ratio of $\sim 1:10$ and response times of $\sim 5\text{-}10\text{ms}$ on switching with appropriate dc field.

10:30 AM *CC1.5

MACROMOLECULAR AND SUPRAMOLECULAR APPROACHES TO HELICAL ORGANIZATIONS. Joaquin Barbera, Matthias Lehmann, Jose Luis Serrano, Teresa Sierra, Universidad de Zaragoza CSIC, Dept de Quimica Organica, Zaragoza, SPAIN.

Helicity in Liquid Crystals is responsible for some of the most interesting optical and electrooptical properties of these materials. In some cases, depending on the molecular arrangements within the mesophase, the presence of chirality in the molecule induces the formation of helical structures as occurs in the cholesteric or tilted smectic phases. As far as columnar phases are concerned, it is also possible to generate helical structures by means of the introduction of chirality in the molecule. In this communication we present three different approaches towards the achievement of helical superstructures using mesogenic or promesogenic units. Two of them correspond to supramolecular columnar arrangements of metallomesogens. In the first one, metal 1,3-diketone derivatives, chirality is introduced by means of stereogenic centers in the terminal chains. Depending on the number and length of these chains two different columnar phases have been detected: Hexagonal and rectangular. In this last case, electrooptical switching has been observed, thus confirming the ferroelectric behavior of the mesophase. The second approach, metal-oxazoline derivatives, is clearly different since chirality is introduced by means of stereogenic centers in the rigid part of the molecule. In this case, the steric hindrance of the chiral moiety makes difficult molecular stacking and it is necessary to introduce very long peripheral chains in order to increase the intermolecular interactions within the mesophase. The last approach, polyisocyanide derivatives, consists on the preparation of macromolecular helical structures using chiral promesogenic units. The main goal of this via is the application of the knowledge on molecular interactions in liquid crystal mesophases to the polymerization process.

11:00 AM CC1.6

MOLECULAR-SCALE SIMULATIONS OF BENT-CORE LIQUID CRYSTALS. Jianling Xu, Robin L.B. Selinger, Catholic Univ. Physics Dept., Washington, DC; Jonathan V. Selinger, R. Shashidhar, Naval Research Laboratory, Washington, DC.

We present Monte Carlo simulation studies of chiral symmetry-breaking in a system composed of achiral bent-core molecules. Each molecule is composed of seven interaction sites formed into a rigid V-shape, where the site-site interaction is the short-range repulsive Weeks-Chandler-Andersen potential. The angle between the molecule's two straight segments is 140 degrees. The simulation is carried out with 600 molecules in a box of fixed volume and flexible aspect ratio, with fixed particle density $\rho = 0.7$. We find chiral symmetry-breaking

in a crystalline phase. Each layer displays a finite tilt, but from one layer to the next, the tilt directions are neither aligned nor alternating in pattern. Upon increase of temperature, the system melts into an achiral Sm A phase. We speculate that some slight variation in the molecular shape or bend angle may allow us to find a tilted chiral smectic phase. This observation of chiral symmetry-breaking indicates that the phenomenon does not require internal degrees of freedom or chiral excited states. The "bumpy" nature of the molecular shape may play an important role in stabilizing the tilted phase, as it favors molecular packing with a slight offset between molecules.

11:15 AM CC1.7

IMPRINTING THE QUASI-BOOKSHELF TEXTURE OF A FERROELECTRIC LIQUID CRYSTAL INTO NANO-SCALED POLYMER FIBRILS. Sang Hwa Kim, S. Suresh, L.C. Chien, Kent State University, Kent, OH.

We report morphological and electro-optical studies of polymer-stabilized ferroelectric liquid crystals (PSFLCs). PSFLCs are made by photopolymerizing 3% reactive mesogenic monomer on the quasi bookshelf texture of a FLC. We observe the formation of nano-scaled polymer fibrils templated by the two dimensionally ordered host. The polymer fibrils capture the orientation of the host; locate between smectic layers with thinner branches of the polymer fibrils interweaving the smectic layers. The SEM study highlights the difference in morphology of the polymer fibrils depending on polymerization conditions; that is, polymerizing with or without the presence of electric field. The polymer fibrils provide the additional surfaces, which facilitate the switching and shorten the response time of the PSFLCs. We also demonstrate the V-shaped (threshold-less) switching of PSFLCs.

11:30 AM CC1.8

THERMO ASSISTED PHOTORECORDING IN CHIRAL SMECTIC AZODYE COPOLYMERS. Mikhail Kozlovsky, Wolfgang Haase, Inst. of Physical Chemistry, and Matthias Rehahn, Inst. of Macromolecular Chemistry, Darmstadt University of Technology, Darmstadt, GERMANY.

Photo-orientation of azodye copolymer films during the mesophase formation and photoaffected phase behaviour have been studied. Several series of copolymer methacrylates were used for the film preparation, those having the same chiral smectic matrix monomer but different azobenzene photochromic comonomers. Illumination of the films with polarized light at simultaneous cooling from above the phase transition to room temperature results in enhanced photoinduced birefringence, respectively diffraction efficiency of holographic gratings. For one of the copolymer series, a kinetically controlled phase transition has been observed for a certain range of compositions. In those materials, the photorecording during the mesophase formation was realized at constant temperature after a thermal shock. Influence of the illumination exposure and wavelength on the photoinduced birefringence and diffraction efficiency has been elucidated. The effect of main chain conformation on the photo-optical recoring is discussed. For some copolymers, the sequence of mesophases can be changed by light illumination, even with nonpolarized light of low intensity. Thus, illumination of such copolymer films through a mask during its cooling produces inhomogeneous films consisting of different mesophases in illuminated and dark areas. This allows for the photorecording of birefringence, absorption, and conductivity patterns of large area using standard light projection technique. Influence of the illumination exposure and wavelength on the light-controlled phase behaviour is studied, possible mechanisms of the effect are discussed.

11:45 AM CC1.9

LOW FREQUENCY DIELECTRIC BEHAVIOUR OF A NOVEL FERROELECTRIC LIQUID CRYSTAL AT ROOM TEMPERATURE. S. Lakshminarayana, P.A. Kumar and V.G.K.M. Pisipati, Centre for Liquid Crystal Research and Education (CLCRE), Faculty of Physical Sciences, Nagarjuna University, Nagarjuna Nagar, INDIA.

Spontaneous polarization, optical tilt angle, response times, viscosity and low frequency dielectric relaxation studies are carried out on a novel ferroelectric liquid crystal compound viz., (S)-1-[4'-octyloxy-carbonyl] phenyl]-4-[2-chloro-(4-benzamidoacetyl) phenylpropionato]-benzoate (OPCBPB), exhibiting nematic, cholesteric, Smectic-A and a room temperature smectic-C* phases. Temperature variation of spontaneous polarization, tilt angle in SC* phase agrees with Mean field prediction to infer long range transverse dipole interaction. Dielectric loss spectrum study in N, N* and SA phase reveal one relaxation while SC* phase exhibits a gold stone relaxation in addition to soft-mode. The effect of electric field on Gold-stone mode studied through Curie-Weiss law in SC* phase. Bias variation of Gold-stone mode relaxation is also reported.

SESSION CC2: LIQUID CRYSTAL GELS
Chairs: Rudolf Zentel and Heino Finkelmann
Monday Afternoon, November 26, 2001
Commonwealth (Sheraton)

1:45 PM *CC2.1

TUNABLE MIRRORLESS LASING IN CHOLESTERIC LIQUID CRYSTALLINE ELASTOMERS. H. Finkelmann, Albert-Ludwigs-Universität, Institut für Makromolekulare Chemie, Freiburg, GERMANY; S.-T. Kim, LG Cable Research Center, Optoelectronic Materials Dept., Kyungki-do, KOREA; A. Muñoz, Dept. of Physics, Universidad Autonoma Metropolitana, MEXICO; P. Palffy-Muhoray, B. Taheri, Liquid Crystal Institute, Kent State University, Kent, OH.

Due to their birefringence and helicoidal structure, cholesteric liquid crystals are 1-d photonic band gap materials. Light propagation is forbidden for one of the eigenmodes with wavelengths in the range $n_o p < \lambda_o < n_e p$, where n_o and n_e are the refractive indices of the liquid crystal, and p is the cholesteric pitch. If these materials are optically pumped, distributed cavity effects allow population inversion and mirrorless lasing[1]. Lasing occurs at the edges of the reflection band, where the density of states diverges and propagation is allowed. Liquid crystalline elastomers are novel materials, whose salient feature is the strong coupling between orientational order and mechanical strain. Cholesteric liquid crystalline elastomers have been synthesized recently[2]; in monodomain samples of these cholesteric liquid single crystal elastomers (LSCE), the cholesteric pitch p varies with strain. We have demonstrated mirrorless lasing in cholesteric LSCE samples doped with the dye DCM, and observed a change in the lasing wavelength as the samples were stretched[3]. We discuss the results of our recent studies of lasing in these materials, and consider potential applications.

1. A. Muñoz, P. Palffy-Muhoray and B. Taheri, *Optics Lett.* **26**, 804 (2001).
2. S.-T. Kim, H. Finkelmann, *Macromol. Rapid. Commun.* **22**, 429 (2001).
3. H. Finkelmann, S.-T. Kim, A. Muñoz, P. Palffy-Muhoray, B. Taheri, *Adv. Mat.* (in press).

2:15 PM *CC2.2

ELECTRO-OPTICS OF THIN LAYERS OF NEMATIC GELS. Robert B. Meyer, Physics Department, Brandeis University, Waltham, MA.

Thin layers of nematic gel are formed by polymerization of monomer and crosslinking material (total concentration about 10%) dissolved in a room temperature nematic liquid crystal, pentylcyanobiphenyl, in a parallel plate glass cell on the order of 10 micrometers thick, with ITO electrode surfaces and rubbed polyvinyl alcohol alignment coatings. An electric field is applied, and the response of the liquid crystal gel involves rotation of the nematic director, accompanied by shear strains of the gel. This produces a variety of textures, including uniform and periodic patterns. Experimental findings and theoretical analysis will be presented.

2:45 PM CC2.3

STRUCTURE AND MECHANICAL PROPERTIES OF FREE STANDING SMECTIC ELASTOMER FILMS. Jianjun Li¹, Ralf Stannarius¹, Ralf Köhler¹, Rudolf Zentel². ¹University of Leipzig, Faculty of Physics and Geosciences, Institute of Experimental Physics I, Leipzig, GERMANY. ²Institute of Organic Chemistry, University of Mainz, Mainz, GERMANY.

Liquid crystalline elastomers (LCEs)[1-3] are of widespread interest because of their special combination of polymer networks mechanics and LCs switching properties. They seem to be ideal systems to investigate the interactions of reorientation of polymer chains (induced by mechanical fields) and that of mesogenic groups (induced by electric field). Since these materials can show piezoelectricity and flexoelectricity, they have a remarkable application potential. For example, a high lateral electrostriction has been found recently in free standing ultrathin LCE films[4]. The mechanical properties are essential and lay the foundations of a physical understanding of the observed electromechanical phenomena, but until now many mechanisms are still far from being understood. We present a method to measure viscoelastic properties of smectic LCEs. Freely suspended photoreactive smectic polymer films are inflated to spherical balloons and crosslinked by UV irradiation[5]. After crosslinking, elastic moduli of the materials are determined from the relation between balloon radius (strain) and inner excess pressure (stress). X-ray measurements are performed to inspect the smectic structure and phase transitions in the free standing elastomer films. Two types of smectic LCE with different network topologies (inter-layer and intra-layer crosslinks) are studied. The influence of network topology and mesophases on the mechanical behaviour is discussed. Particular emphasis is concentrated upon mechanical properties at the

smectic-isotropic transition, hysteresis of the mechanical deformations and dynamic relaxation behavior.

- [1] M. Brehmer et al., *Macromol. Chem. Phys.* 195 1891 (1994); *Macromol. Chem. Rapid Commun.* 16 659 (1995); *Liq. Cryst.* 21 589 (1996).
- [2] I. Benne, K. Semmler, H. Finkelmann, *Macromolecules* 28 1854 (1995).
- [3] E. Gebhard, R. Zentel, *Macromol. Chem. Phys.* 201 902 (2000); *Macromol. Chem. Phys.* 201 911 (2000).
- [4] W. Lehmann, H. Skupin, C. Tolksdorf, E. Gebhard, R. Zentel, P. Krüger, M. Lösche, F. Kremer, *Nature*. 410 447 (2001).
- [5] H. Schüring, R. Stannarius, Ch. Tolksdorf, R. Zentel, *Macromolecules* (in press).

3:30 PM *CC2.4

STRUCTURE AND MOBILITY IN FERROELECTRIC LIQUID CRYSTALLINE ELASTOMERS AND GELS. Friedrich Kremer, Walter Lehmann, Holger Skupin, Jan Prigann, University of Leipzig, Faculty of Physics and Geosciences, Leipzig, GERMANY; Christian Tolksdorf, Elisabeth Gebhard, Rudolf Zentel, University of Mainz, Institute of Organic Chemistry, Mainz, GERMANY.

Ferroelectric Liquid Crystalline Elastomers (FLCE) from a novel class of materials with an extraordinary profile of features: They are ferroelectric and hence piezoelectric, they can be prepared as elastomeric "single crystals" on a macroscopic (\sim cm) scale and they can be obtained as self-supporting thin (\sim μ m and (ultra)-thin molecular layers. Furthermore their viscoelastic properties can be tailored by use of a photochemical crosslinking reaction. The structure and mobility of FLCE is studied by employing polarized, time-resolved Fourier-Transform IR-spectroscopy (1-3). This enables to analyze in detail the reorientation of the single molecular moieties in the supramolecular system (angle of reorientation, time constant, phase relationship) in response to an external electric field. To measure the (inverse) piezoelectric effect interferometric and x-ray methods are used (4,5). It is discovered that FLCE in a proper crosslinking density show the highest electrostrictive coefficients which were found up to now for organic materials. A microscopic interpretation of the observed macroscopic effects will be presented (5,6). FLCE offer a strong technological impact especially as materials for sensors and actuators in microsystem technology.

1. S.V. Shilov, E. Gebhard, H. Skupin, R. Zentel, F. Kremer *Macromolecules* 32: 1570 (1999).
2. H. Skupin, F. Kremer, S.V. Shilov, P. Stein, H. Finkelmann *Macromolecules* 32: 3746 (1999).
3. H. Skupin, F. Kremer, S.V. Shilov, W. Lehmann, H. Brodowsky, E. Gebhard, R. Zentel *J Macromol Sci-Phys B38*: 709 (1999).
4. W. Lehmann, L. Hartmann, F. Kremer, P. Stein, H. Finkelmann, H. Kruth, S. Diele, *J Appl Phys* 86: 1647 (1999).
5. F. Kremer, H. Skupin, W. Lehmann, L. Hartmann, P. Stein, H. Finkelmann, in press *Adv Chem Phys* (ed J Vij) (2000).
6. W. Lehmann, H. Skupin, H. Tolksdorf, E. Gebhard, R. Zentel, P. Krueger, M. Loesche, and F. Kremer, *Nature* 410: 447 (2001).
7. J. Prigann et al., submitted to *Macromolecules* (2001).

4:00 PM *CC2.5

LIQUID CRYSTALLINE PHYSICAL GELS: MICROPHASE-SEPARATED STRUCTURES AND SIGNIFICANT ELECTROOPTIC PROPERTIES. Takashi Kato, Norihiro Mizoshita, Univ of Tokyo, Dept of Chemistry and Biotechnology, Grad School of Engineering, Tokyo, JAPAN; Kenji Hanabusa, Shinshu Univ, Dept of Bioscience and Textile Technology, Grad School of Science and Technology, Ueda, JAPAN.

A new class of anisotropic gels, liquid crystalline physical gels, have been obtained by hydrogen-bonded self-aggregation of amino acid gelators in room temperature nematic liquid crystals. The liquid crystalline physical gels form microphase-separated structures of the liquid crystals and the fibrous solid aggregates of the hydrogen-bonded molecules. The thermal properties and phase transition behavior of the gels can be tuned by the choice of the components, liquid crystals and gelators. The nematic liquid crystalline physical gels show responses to electric fields. The electrooptic behavior of the liquid crystalline gels has been examined for twisted nematic (TN) mode. The TN alignment behavior and the response properties of the gels are greatly dependent on the microphase-separated structures of the liquid crystalline gels. Atomic force microscopy for the xerogels obtained from the liquid crystalline gels has shown that the morphology of microphase-separated structures formed in the liquid crystal cells depends on the combination of the components. A bola-form compound containing two valine moieties forms thick aggregates, while finely-dispersed network aggregates are formed for the gels based on mono-amino acid gelators. The electrooptic responses of such anisotropic gels with finely-dispersed network aggregates are faster than those of the neat liquid crystals. Liquid crystalline physical gels exhibiting faster responses, lower driving voltages, and high contrast can be obtained by the use of an efficient

gelator derived from lysine. These liquid crystalline gels have great potential for a new type of dynamically functional materials.

4:30 PM CC2.6

REVERSIBLE PHYSICAL NETWORK STABILIZED FERROELECTRIC LIQUID CRYSTALS. Christian Tolksdorf, Rudolf Zentel, University of Mainz, Institut of Organic Chemistry, Mainz, GERMANY.

A novel class of anisotropic gels has been obtained by the formation of self-associated molecular network in a ferroelectric liquid crystal. Anisotropic gels have great potential as functional materials such as active and passive optical devices and stimuli-responsive materials. In most cases nematic LC have been utilized. We present here a new route to self-organized ferroelectric gels. We have built up gel networks by adding trans-(1R,2R)-Bis-(dodecanoylamino)cyclohexane as gel forming agent to a low molar mass ferroelectric liquid crystal. Through this manufactured microphase separated network of the gelling agent a reversible stabilization of one polar state can be achieved. The addition of the gelling agent has no influence on the phase transition temperature. This is the first prove of the microphase separation. It can also be seen by electron microscopy. This signifies heating up the gel destroys the network and thereby the polar orientation. With cool down a new polar orientation can be rebuild analogous to a solvent-gel mixture where the gel can be destroyed when the solvent is heated up and vice versa. We investigated various gel mixtures (0% = pure FLC; 1% and 3%). These samples were placed on before salled E.H.C. cell and cooled down from the isotropic phase into the Sc-phase. During cooling down the gelification took place. If the sample was sheared under an applied DC-field (20V) the polar state was stabilized. The stabilization depend on the amount the amount of gelling agent. Afterwards the sample was heated up into the isotropic phase and cooled down, but now applying an AC-field (50Hz/20V)(Fig 2). In an AC-field continuous switching occurs and the mesogens dont prefer one orientation state. Now no stabilization of one switching state and no distinction in the switching times can be detected. So we can state that no polar orientation is stabilized. This procedure can be repeated many times. So these physical network stabilized ferroelectric liquid crystals present a system, which allows the reversible stabilization of different orientational and polar state.

4:45 PM CC2.7

Abstract Withdrawn.

SESSION CC3: PHOTOPOLYMERIZATION AND LIQUID CRYSTALS

Chairs: Martin Schadt and Bruce Winker
Tuesday Morning, November 27, 2001
Commonwealth (Sheraton)

8:30 AM *CC3.1

BIREFRINGENT POLYMER FILMS FROM REACTIVE LIQUID CRYSTALS. Bruce Winker, Dong-Feng Gu, Len Hale, Jane Hanamoto, Young Chung, Ellen Boehmer, John Flintoff, Rockwell Science Center, Thousand Oaks, CA; Zhiming Zhuang and Zili Li, Corporate Manufacturing Research Center, Motorola, Schaumburg.

This paper focuses on the processing of birefringent polymer thin films using UV polymerized acrylate liquid crystals. The chemistry and physics of polymerizable liquid crystals are discussed, as related to the processing of these materials into oriented, anisotropic polymer thin films. Examples of mono- and di-acrylate materials are given, along with a discussion of the mesophase and thermodynamic behavior relevant to thin film processing. Important process considerations are discussed. In particular, substrate cleaning, liquid crystal alignment, solvent casting, drying and UV polymerization process considerations are discussed in detail. Examples are given of defects that are unique to anisotropic polymer thin films. Several examples of anisotropic polymer thin films are described, including obliquely oriented retarders (i.e., A-plates and O-plates). The optical performance of such films used as retarders for compensating for liquid crystal displays is also briefly described.

9:00 AM *CC3.2

REACTIVE MESOGENS: SYNTHESIS AND APPLICATION IN OPTOELECTRONIC DEVICES. Peter Strohmriegl, Markus Jandke, Thomas Pfeuffer, Heiko Thiem, Bayreuth University, Macromolecular Chemistry I, Bayreuth, GERMANY.

Reactive mesogens possess polymerizable groups attached to a rigid, liquid crystalline core. From such molecules, densely crosslinked networks in which the liquid crystalline order is permanently fixed are formed by photopolymerization. Our major goal in the synthesis was the formation of glass forming reactive mesogens. Such compounds do not crystallize upon cooling but vitrify and form

supercooled LC-phases (LC-glasses). They exhibit broad LC-phases and enable us to carry out photopolymerization in a broad range of temperatures. We have systematically investigated how the topology of the reactive mesogens influences the stability of the resulting glasses. Comparing twin molecules with three- and four-armed stars we found that the supercooled LC-phase in the three-armed stars has a stability superior to both twin molecules and four-armed stars. In a three-armed star with suitable substituents the supercooled LC-phase is stable at room temperature for at least 9 months. Doped with suitable chiral molecules the glass forming nematics form cholesteric phases which were used for writing polarization holograms in a special geometry with s- and p-polarized writing beams. Furthermore we have extended our synthetic efforts to reactive mesogens with conjugated fluorene units as LC-core. After orientation, the mesogens were photocrosslinked and used as active layer in OLEDs that emit highly polarized blue light.

9:30 AM CC3.3

OPTO-MECHANICAL CHARACTERISTICS OF ORDERED REACTIVE MESOGEN FILMS. Michael J. Escuti, Jose Vedrine, Darran R. Cairns, Gregory P. Crawford, Brown University, Division of Engineering, Providence, RI.

Here we investigate the optical and mechanical characteristics of reactive mesogen films. In-situ transmission measurements of these ordered films under tensile strain were performed to examine the mechanical properties and birefringence under a variety of director and tensile configurations. The optical response with increasing strain was modeled and a dual wavelength technique for measuring birefringence was developed. Birefringence of the polymer reactive mesogen was also measured as functions of wavelength and cure-temperature. Transmission through the film is modeled using the normalized expression for a waveplate. Any change in the film's birefringence will appear as a variation in the period of oscillation and any change in the bulk nematic director will appear as a variation in amplitude. Varying amplitude is analogous to a change in transmission and monitoring this change in the reactive mesogen films with the use of dichroic dyes can provide a clearer understanding for the mechanical and optical properties of the director under varying tensile configurations. We dope the films with dichroic molecules to understand the molecular ordering under strain. This study will provide valuable information about the optical and mechanical response of pre-aligned reactive mesogen films.

9:45 AM CC3.4

Abstract Withdrawn.

10:30 AM *CC3.5

SPECIAL DIRECTOR PROFILES IN PHOTOPOLYMERIZED REACTIVE MESOGEN FILMS FOR LIQUID CRYSTAL DISPLAYS. J.A.M.M. van Haaren, D.J. Broer and P. van de Witte, Philips Research Laboratories Eindhoven, THE NETHERLANDS.

We used photopolymerization of reactive liquid crystals to make functional foils for liquid crystal displays (LCDs) with a wide viewing angle and a high brightness. Viewing angle artefacts in LCDs are related to the electrically tilted director profiles in the display. Such profiles modify the elliptical polarization of obliquely passing light. Reactive mesogen foils with a controlled splay help to correct these ellipticity effects. The foil's substrate promotes planar alignment of the mesogens. Reactive mesogen mixtures with planar alignment at the substrate and homeotropic alignment at the interface to air produce films with a high average tilt. Mixtures that favour planar alignment at both interfaces gave a low average tilt. Transmissive LCDs can be made brighter with polarizers that separate light by reflection and not by absorption. Such recycling polarizers may be made with cholesteric liquid crystals. The helical director profile reflects light with a circular polarization and with a wavelength that match the helix. Photo-induced diffusion and simultaneous polymerization was used to create a gradient in the cholesteric pitch over the film thickness. The reflection band of the resulting recycling polarizer extends over the entire visible spectrum. The transmitted circularly polarized light is converted to linearly polarized light by an additional quarterwave retardation foil. A rod-like dichroic photoinitiator in combination with polymerization in polarized light induces diffusion within the cholesteric pitch. This leads to a biased helical director profile. This bias has consequences for the optical properties of the film. Higher order reflection bands emerge and the transmitted polarization is no longer circular. This is a way to merge the quarterwave retarder and the cholesteric layer into a single-film. Special director patterns with splay, a gradient in the cholesteric pitch or a biased helix were frozen in by photopolymerization. Such foils improve the image quality of LCD-monitors.

11:00 AM *CC3.6

FUNCTIONAL LC-POLYMER THIN-FILMS: PHOTO-ALIGNMENT, SURFACE CORRUGATIONS AND LCD-APPLICATIONS. Martin Schadt, ROLIC Research Ltd., Allschwil, SWITZERLAND.

Our linear photo-polymerisation (LPP)-technology renders contact-free alignment of monomeric liquid crystal molecules (LCs) by optical means possible. Apart from photo-alignment and photo-patterning of liquid crystals sandwiched between two aligned substrates of a liquid crystal display (LCD), photo-alignment of polymeric liquid crystals (LCPs) on single substrates were shown enabling a plethora of novel birefringent functional optical thin-films and improved liquid crystal displays. Examples to be reviewed are multi-domain LCDs with broad field of view, stacks of LCP-molecular configurations with controllable spatial uniaxiality, non-absorbing interference color filters, positive and negative optical retarders, wide-view films for further improving the field of view of LCDs, photo-patterned dichroic polarizers and high-resolution phase retarders for optical security elements. Recently we presented the extension of our LPP/LCP photo-aligning and photo-patterning technology for polymeric liquid crystal thin-films with smooth surfaces towards novel optical polymer films with surface topologies. Nano- and micro-corrugated topologies on polymer thin-films were shown to result from optically-induced monomer phase-separation on surfaces. The new monomer-corrugation (MC)-technology enables high performance antireflection coatings for optical components of virtually any size, shape and material. It also enables a plethora of new functional polymer thin-films with isotropic as well as with anisotropic topologies, including photo-patterned topologies. MC-topologies enable diffuse thin-film reflectors with high gain for displays with paper-white performance. Beyond the display industry, photo-aligned and photo-patterned monomer and polymer LC-devices open up numerous new optically anisotropic thin-film applications; they are key for future complex plastic LCDs.

11:30 AM CC3.7

CHOLESTERIC COLOUR FILTERS FOR LCDS OBTAINED BY LIGHT-INDUCED COLOUR CHANGE. R.T. Wegh, C. Doornkamp, J. Lub and P. van de Witte, Philips Research Laboratories, Eindhoven, THE NETHERLANDS.

Cholesteric polymer films are of interest for application as passive optical components in LCDs. Here we present the use of such films as colour filter. One-step colour structuring of a cholesteric layer is obtained by making use of a photo-isomerisable chiral component. Upon UV irradiation the helical twisting power of the molecule and therefore the pitch length of the cholesteric film is changed. Hence, the reflection wavelength can be tuned to have any value from UV to IR by simply using the appropriate UV dose [1]. After patterning, the molecular ordering has to be stabilized. This is done by photo-polymerisation of liquid crystalline diacrylates present in the monomeric mixture [2]. Previously we prepared cholesteric colour filters by photo-isomerisation of cholesteric side-chain co-polymers [1]. However, in the new process the low viscosity of the starting monomers is advantageous for the ease of alignment of the cholesteric phase before and after photo-patterning. In addition, the formation of a polymeric network by photo-polymerisation results in better UV and thermal stability than for the side-chain polymer. Possible interference of the two irradiation steps is circumvented by careful choice of the materials and process conditions [3]. The number of process steps to make these cholesteric colour filters is highly reduced compared to that of pigmented colour filters. Moreover, the cholesteric colour filter has many optical properties integrated in one layer, i.e. colour filter, polariser, reflector, and diffuser. These advantages show the attractiveness of applying cholesteric colour filters in LCDs.

[1] P. Van de Witte, M. Brehmer, J. Lub, J. Mater. Chem. 1999, 9, 2087.

[2] R.A.M. Hikmet, J. Lub, Prog. Polym. Sci. 1996, 21, 1165.

[3] P. Van de Witte, J. Lub, EP 1053493, 2000.

11:45 AM CC3.8

SWITCHABLE PHOTONIC CRYSTALS FORMED USING HOLOGRAPHIC PHOTOPOLYMERIZATION AND LIQUID CRYSTALS. Timothy J. Bunning, Vincent P. Tondiglia, Lalguadi V. Natarajan, and Richard L. Sutherland, D. Tomlin, Air Force Research Laboratory, Materials and Manufacturing Directorate and Science Applications International Corporation, WPAFB, OH.

Using 4- and 6-beam holography, we have extended our work on 1-d switchable holographic polymer-dispersed liquid crystals (H-PDLCs) by fabricating an orthorhombic photonic crystal that diffracts light in the Bragg regime. The internal morphology of these structures is periodic in all 3-dimensions with small, nanoscale PDLC droplets periodically residing on a lattice commensurate with interference pattern dimensions. Periodicities of the two orthogonal transmission

gratings ranged from 500-1000 nm while the periodicity through the film (reflection grating) was between 150-200 nm. Like the 1-d case, we speculate that the LC droplets form in the regions of low intensity. The structures exhibit a very angular dependent opal effect due to diffraction of visible light. Most important, the first order diffraction spots or the notch due to the reflection grating can be modulated using an applied electric field. Diffraction efficiencies of >50% have been obtained. Upon switching, a dynamic range of >100 can be obtained.

SESSION CC4: NOVEL APPLICATIONS OF LIQUID CRYSTALS

Chairs: Dirk J. Broer and John Lawton West
Tuesday Afternoon, November 27, 2001
Commonwealth (Sheraton)

1:30 PM *CC4.1

FLEXIBLE PLASTIC LIQUID CRYSTAL DISPLAYS. John L. West, Greg R. Novotny, Michael R. Fisch and David J. Heineman, Liquid Crystal Institute, Kent State University, Kent, OH.

Flexible plastic liquid crystal displays (LCDs) offer a number of advantages. They weigh less than glass displays, they are unbreakable and they can be made using inexpensive roll-to-roll manufacturing techniques. In this paper we review the critical issues that must be addressed if flexible plastic LCD's are to reach their full potential. Most LCD's require polarizers to produce the electro-optic response. These displays therefore required non-birefringent substrates, severely restricting the types of plastic that can be used as substrates. Alternatively, LCD's not requiring polarizers, such as cholesteric, dichroic or light scattering displays, can utilize commercially available, birefringent substrates such as polyesters. The alignment layers must be compatible with the plastic substrates. This includes the solvents used to apply the alignment layers and the bake temperatures used to cure the alignment layers. Polymer networks and polymer walls can be used to increase the mechanical strength of flexible plastic LCDs. These polymer structures adhere the front and back substrates, maintaining uniform spacing even when the display is bent. The polymer structures may also increase the lifetime of the display and reduce the effects of gas diffusion. We report techniques to form these polymer structures. Finally, roll-to-roll processing of flexible plastic displays requires that the photolithographic techniques used to etch the electrodes on the current glass LCD's be replaced by printing techniques. We therefore report methods of etching the ITO electrodes on flexible plastic substrates using conventional wax transfer printing techniques. Finally we demonstrate a flexible plastic LCD fabricated using techniques compatible with roll-to-roll manufacturing.

2:00 PM *CC4.2

LIQUID CRYSTAL OPTICAL PHASE MODULATORS FOR BEAM STEERING. Jay Stockley, Xiaowei Xia, Teresa Ewing and Steve Serati, Boulder Nonlinear Systems Inc., Lafayette, CO.

Beam Steering using liquid crystals can be achieved with refractive or diffractive implementations. The common thread in these various structures is that the liquid crystal is employed as an optical phase modulator. Either nematic or smectic liquid crystal phases can be used to shift the phase of light and steer an optical beam. Various liquid crystal optical phase modulating schemes will be described. Examples include polarization independent and quasi-achromatic modulators. Model predictions and experimental results demonstrating the optical phase modulation and beam steering made possible using different liquid crystal based designs will be presented.

2:30 PM *CC4.3

FREQUENCY AGILE OPTICAL FILTERS USING NANOSCOPIC POLYMER DISPERSED LIQUID CRYSTALS. Keith Lewis, Gilbert Smith, Ian Mason and Katie Rochester, Defence Evaluation and Research Agency, Malvern, Worcestershire, UNITED KINGDOM.

The ability to realise frequency agile filters has always been a major goal of materials and device scientists. Polymer dispersed liquid crystal materials (PDLCs), in which the droplets are deliberately produced with dimensions smaller than the Rayleigh limit for optical scatter, provide a means of realising this goal. At visible wavelengths the material has the appearance of a phase-homogeneous medium both with and without applied electric field. The dimensional scales of the nanoscopic polymer composite ensure that optical scatter effects are minimal, even in the visible spectral regime. Refractive indices are an average of those of the liquid crystal and those of its host and can be described on the basis of effective medium approximations using orientationally averaged values for the randomly aligned LC material for the ambient state. On application of electric field, the individual liquid crystal molecules align with a resulting reduction in the effective index of the medium. In resonant cavity devices

incorporating the material, the extent of fringe shift as a function of applied voltage is a direct measure of the change in refractive index, and hence the electro-optic coefficient of the nanocomposite. Extensive studies of the variation of process parameters and their effect on the morphology of the composite have enabled field induced changes in refractive index in excess of 0.05 to be achieved without recourse to the use of polarisers and with little or no hysteresis effects. At wavelengths associated with WDM devices for telecommunication applications, the degree of scatter loss is negligible. Design trade-offs have been assessed for candidate tunable WDM filter structures.

3:30 PM *CC4.4

LIGHT-CONTROLLABLE CHIRAL PHOTOCROMIC MULTIFUNCTIONAL LIQUID CRYSTAL POLYMERS. Valery Shibaev, Chemistry Department, Moscow State University, Moscow, RUSSIA.

Among a variety of photosensitive materials used for the recording and storage of information the chiral photochromic liquid-crystalline (LC) copolymers with the helical supramolecular structure attract the significant interest as new smart materials with controllable supramolecular structure and optical properties. The principle of the creation of such light-controllable polymers is based on the synthesis of multifunctional LC side-chain acrylic polymers consisting of nematogenic monomer units (favourable to the nematic phase formation), chiral fragments (contributed to the nematic phase twisting and helical supramolecular structure formation) and photochromic groups provided the photosensitivity to such copolymers. In this paper three different types of acrylic LC polymers containing 'switchable' fragments (such as azobenzene, benzylidene-methanone, cinnamoyl, spiropyranes) are presented. The first type includes the binary copolymers containing mesogenic and chiral-photochromic monomer units. Irradiation of the copolymer films by the light with definite wavelength causes the photoisomerization of photochromic fragments that leads to the variation of their helical twisting power, pitch of the helix and optical properties. The second group consists of the ternary copolymers containing mesogenic and two different photochromic groups, one of which is chiral. The films of such copolymers display the dual photochromism depending on wavelength of irradiated light. This permits to manipulate effectively by their optical properties- to change the helix pitch and to stimulate the appearance of photoinduced birefringence. The principle of information storage for the third group of polymers is based on a realization of the reversible transition 'selective reflection - absorbance' in ternary copolymers containing nematogenic, chiral and photochromic side groups. It was shown that the chiral photosensitive LC copolymers can be considered as a novel family of promising materials for reversible and irreversible coloured data recording and optical data storage.

4:00 PM *CC4.5

NONLINEAR OPTICAL ABSORPTION AND RELATED PHENOMENA IN LIQUID CRYSTALS. N.V. Tabiryan, H. Margarian*, S.R. Nersisyan, Beam Engineering for Advanced Measurements Co. Winter Park, FL. *Presently with Yerevan State University, Yerevan, ARMENIA.

We will show that nonlinear optical absorption phenomena in nematic liquid crystals (NLC), doped by various dyes, accompany and have a strong influence on propagation of the laser beam as the processes of nonlinear refraction. The conventional mechanisms of laser beam influence on NLC that yield in nonlinear refraction, reorientation of the NLC and change in its order parameter, result also in nonlinear absorption. Thermal diffusion of the dye due to temperature gradients in the beam is an additional process that results in both nonlinear absorption and refraction. The strength and relative contribution of each mechanism of nonlinear absorption is determined by the experimental situation. These processes may find applications for laser beam measurement and control purposes. Particularly, we have demonstrated an optical fuse that drastically reduces the power of the laser beam at the output of the NLC-film when the incident power overcomes certain threshold.

4:30 PM *CC4.6

LIGHT INDUCED ORIENTATION OF DYES CONTAINING LC-POLYMERS. R. Rosenhauer, Th. Fischer, J. Stumpe, M. Pinol*, J.L. Serrano* Fraunhofer-Institute for Applied Polymer Research and *University of Zaragoza.

The defined preparation of anisotropic polymer films is a goal of great importance for various applications. The use of linearly polarized light offers a new approach to orient photochromic polymers perpendicular to the electric field vector of the incident light. In the case of copolymers the process causes a co-operative alignment of the non-photochromic side groups to the same direction and to a comparable degree of order [1-3]. In the presentation it will be shown that the cooperativity works in the case of multifunctional comb-like terpolymers containing

photochromic, mesogenic and dye side groups. The photo-induced order of the LCP films can be amplified significantly by annealing above the glass transition temperature in the liquid crystalline phase. So, a very high dichroism of all side groups is generated by the combination of photochemical treatment and thermotropic self-organization. This processing represents a new approach for the preparation of dichroic films.

- [1] J. Stumpe, L. Läscher, Th. Fischer, S. Kostromin, R. Ruhmann, *Thin Solid Films*, **284**, 252, 1996.
- [2] T. Fischer, L. Läscher, M. Rutloh, S. Czaplá, J. Stumpe, *Mol. Cryst. Liq. Cryst.*, **299**, 293, 1997.
- [3] J. Stumpe, Th. Fischer, M. Rutloh, R. Rosenhauer and J. G Meier, *Proc. SPIE* **3800**, 150, 1999.

SESSION CC5: POSTER SESSION
Chair: Timothy J. Bunning
Tuesday Evening, November 27, 2001
8:00 PM
Exhibition Hall D (Hynes)

CC5.1
ENHANCING MISCIBILITY IN BLENDS CONTAINING A LIQUID CRYSTALLINE POLYMER BY IMPROVING INTERMOLECULAR HYDROGEN BONDING. Sriram Viswanathan and Mark Dadmun, University of Tennessee, Dept of Chemistry, Knoxville, TN.

Our recent work has shown that a miscible blend containing a liquid crystalline polyurethane and an amorphous copolymer can be produced by optimizing the amount of intermolecular H-bonding between the two polymers, which is realized by controlling the space between the hydrogen bonding moieties on the amorphous copolymer. FT-IR was used to determine the extent of intermolecular H-bonding in the blend and DSC and optical microscopy were then used to correlate this information to the phase behavior of the blends. In our present work, we have also modified the liquid crystalline polyurethane to further improve the extent of intermolecular H-bonding in the blend. By eliminating hydrogen bonding among the liquid crystalline polyurethane chains, the results show that the increase in the extent of intermolecular H-bonding will continue to enhance the miscibility in such rod/coil polymer blends. The results demonstrate that the miscibility window of these true molecular composites can be tuned by slight modifications of the polymeric structure. This work, therefore, provides information that can be used to design and produce miscible blends containing a liquid crystalline polymer and an amorphous polymer.

CC5.2
Transferred to CC2.3

CC5.3
DISPLAY DEVICES BASED ON DEFORMED HELIX FERROELECTRIC LIQUID CRYSTAL MATERIAL. A.M. Biradar, D.K. Sharma, S.P. Singh and S.S. Bawa, National Physical Laboratory, New Delhi, INDIA.

The most widely studied liquid crystal displays based on ferroelectric liquid crystal material are the surface-stabilized ferroelectric liquid crystals (SSFLC) devices. In this configuration the helix of the material is suppressed by means of boundary conditions and all the liquid crystals molecules aligned parallel to the substrate and the smectic layer planes perpendicular to it. Bistability is the inherent in this configuration. The displays based on the deformed helix ferroelectric liquid crystals (DHFLC) material in many ways complementary to the surface-stabilized ferroelectric liquid crystal effect. It uses short-pitch FLC materials where the smectic planes are oriented perpendicular to the glass plates of the cell. It is a linear effect; i.e. it has no inherent bistability. As a consequence DHFLC exhibit no inherent optical threshold voltage. Another greatest advantage over the SSFLC is that the gray scales can be easily obtained by using DHFLC materials. In the present study we discuss the DHFLC devices by electro-optical and dielectric investigations. The latest result of electroclinic effect (Soft Mode) in the DHFLC material would be discussed in detail near the transition temperature of smectic C* - smectic A phases.

CC5.4
FIRST EXAMPLE OF A TRIPHENYLENE-BASED DISCOTIC SIDE GROUP LIQUID CRYSTAL POLYMER CONTAINING AZOBENZENE MOIETIES. Sidik Silong, Lutfur Rahman, Wan Yunus, Zaki Rahman, Mansor Ahmad, Jelas Haron, Department of Chemistry, Universiti Putra Malaysia, Serdang, Selangor, MALAYSIA.

The synthesis of a novel discotic side group liquid crystal polymer has been carried out based on acrylate backbone. The side group precursor was prepared from 4-aminobenzoic acid, which is diazotized and coupling with phenol to give 4-[(4-hydroxyphenyl)diazenyl]

benzoic acid. The flexible spacer of the liquid crystalline moiety was introduced by alkylation of this compound with 11-bromoundecanol to give corresponding 4-[(4-(11-hydroxyundecyloxy)phenyldiazenyl] benzoic acid and esterification of this compound with acryloyl chloride to yield the polymerizable monomer 4-[(4-(acryloyl-11-oxyundecyloxy)phenyldiazenyl]benzoic acid. The monomer was subsequent esterified with catechol to yield 1,2-dihexyloxy-[(4-[(4-(acryloyl-11-oxyundecyloxy)phenyldiazenyl]benzoyl)oxy]phenylene. A disk-like monomer 2,3,6,7,10,11-hexakis-[(4-[(4-(acryloyl-11-oxyundecyloxy)phenyldiazenyl]benzoyl)oxy]triphenylene was prepared by using a ferric chloride oxidation method. Finally the monomer was polymerized in tetrahydrofuran using azoisobutyronitrile as the initiator. Optical polarizing microscopy and DSC analysis shows that the monomer exhibited a wide nematic columnar mesophase. UV-vis spectra of azobenzene mesogens shows that a significant tailing, which would allow the use of laser in the visible range to photoinduce isomerization and reorientation.

CC5.5
INVESTIGATION OF PHOTOREFRACTIVE EFFECT IN HOMEOTROPIC LIQUID CRYSTAL CELL WITH PHOTOALIGNMENT LAYERS. Hyun-Wuk Kim, Jong-Duk Kim, Korea Advanced Institute of Science and Technology, Dept. of Chemical Engineering, Daejeon, KOREA.

Materials with photorefractive characteristics were widely interested as useful potentials for optical signal and data processing applications. Studies on photorefractive effects have been developed with various materials. Among them, the system with liquid crystals takes advantages of ease to prepare and switching possibility with several external voltages. Mechanism of photorefractive effects using liquid crystals is a little more complicated, different from that of other photorefractive materials, and attributed to refractive index change by reorientation of directors of liquid crystals from internal space charge field. Recent studies about photorefractive materials composed of liquid crystals include many types of polymer-dispersed liquid crystals (PDLCs) or layer structures which separate liquid crystal from photo-conducting polymer. The former is for the purpose of maintaining written data after removing external voltage and light source and the latter is for getting high gain coefficient and diffraction efficiency. But, these cases must suffer scattering due to switching disorder of liquid crystals under external voltages. So, it can be a pitfall to be applied for real device. In order to reduce the scattering, a junction of photoconducting polymer and alignment layer has been employed but it can induce high anchoring energy at interfaces between liquid crystals and alignment layers by rubbing process, orientation defects, and static electricity. So, we used photoalignment layers by UV-irradiation, especially, homeotropically photoaligned layers using dimerization. In this work, we used MLC-6610 (Merck) as liquid crystals with negative dielectric anisotropy oriented parallelly to alignment layers as applying external fields, buckminsterfullerene (C60) and 2,4,7-trinitro-9-fluorene (TNF) as photocharge generators, poly(9-vinylcarbazole) (PVK) as photoconducting polymer, and pendant cinnamoyl group with alkyl moiety as a vertical photoalignment layer. With this system, we could obtain a high photorefractive effects through general two-beam coupling experimental setup. This work was partially supported by the Brain Korea 21 Project and by Ministry of Science and Technology.

CC5.6
MULTIFUNCTIONAL CHIRAL NEMATIC MIXTURES: REVERSIBLE AND IRREVERSIBLE PHOTOREGULATION OF SUPRAMOLECULAR STRUCTURE AND OPTICAL PROPERTIES. Alexey Bobrovsky, Natalia Boiko, Valery Shibaev, Department of Chemistry, Moscow State University, Moscow, RUSSIA.

New photosensitive cholesteric mixtures containing two different chiral-photochromic fragments were prepared. Mixture I consists of phenylbenzoate nematogenic homopolymer and two low-molar-mass (LMM) chiral-photochromic dopants based on cinnamic acid and azobenzene. Mixture II consists of cholesteric copolymers with photosensitive azobenzene-containing side groups and LMM cinnamoyl-based dopant. Planarly-oriented films of mixtures selectively reflect light in visible and near infrared regions of the spectrum. UV and visible light irradiation leads to the changing of selective light reflection wavelength which associated with E/Z photoisomerization and decreasing of the helical twisting power of chiral-photochromic fragments during light action. It was shown that direction of the pitch of the helix changing can be easily controlled by incident light wavelength: in the case of mixture I UV irradiation leads to the long-wavelength shift of selective light reflection but visible light action leads to the short wavelength spectral shift. In the case of mixture II reverse behaviour was observed. The specific features of the kinetics of forward and back thermal processes were characterised. For such materials, their resistance with respect to the

repeated "recording-erasing" cycles was tested, and the fatigue resistance was shown to be rather high. As was demonstrated, these mixtures containing chiral groups sensitive to the light of different wavelengths may be used for reversible as well as irreversible recording of optical information.

CC5.7

COMPATIBILIZATION OF PP/TLCP BLENDS WITH POLY(ETHYLENE-ACRYLIC ACID) IONOMERS. Qi Wu, R.A. Weiss, Univ. of Conn., Polymer Program, Inst. of Material Science, Storrs, CT.

Due to the differences in polarity of PP and Thermotropic Liquid Crystalline Polymer (TLCP), they are immiscible and their blends show poor mechanical properties. The graft-copolymer formed in the reactive blending of TLCP and sodium salts of poly (ethylene-co-acrylic acid) ionomers by transesterification reaction can act as compatibilizer for the PP/TLCP blends. In this paper, the mechanical properties, melt rheology and morphology of the compatibilized blends have been studied. The effect of the graft-copolymer as compatibilizer is discussed.

CC5.8

Abstract Withdrawn.

CC5.9

EFFECT OF CONCENTRATED SODIUM HYALURONATE ON THE JOINT LUBRICATION. Seigen Mori, Masatoshi Naito, Fukuoka Univ., Dept of Orthopaedic Surgery, Fukuoka, JAPAN; Shigeaki Moriyama, Dept of Engineering, Fukuoka, JAPAN.

We investigated the role of articular cartilage and synovial fluid in the lubrication mechanism of natural synovial joints, and determined the effect of concentrated sodium hyaluronate (HA) on lubricating joints without the normal lubrication mechanism. We measured the coefficient of friction (CF) of fresh pig hip joints with cartilage (1) intact, (2) washed, scoured with (3) gauze and (4) sandpaper. We observed the cartilage using light microscopy and scanning electron microscopy. We used three formulations of HA which were 8×10^5 daltons, 1%; 20×10^5 daltons, 1%; 20×10^5 daltons, 1.5% (concentrated). Using scanning electron microscopy, the amorphous layer observed in the washed joint was disrupted after gauze scouring. Compared with intact cartilage, CF did not increase with washing; CF increased more in the joints scoured with sandpaper than that scoured with gauze. Each formulation of HA decreased CF of joints scoured with gauze, but only the 2 more viscous HA decreased the CF of sandpaper scoured joints. A negative correlation was found between the CF of the sandpaper scoured joints and the logHA viscosity ($r = -0.733$, $P = 0.0001$). This suggests the amorphous layer on the surface of the cartilage preserves intact lubrication. In joints damaged with sandpaper scouring, concentrated HA with higher viscosity was more effective at lubricating the joint.

CC5.10

SmC* HIGH-MOLECULAR-TILT MONOMERS AND POLYMERS. Giancarlo Galli, Emo Chiellini, Dept of Chemistry and Industrial Chemistry, University of Pisa, Pisa, ITALY; Lachezar Komitov, Gunnar Andersson, Dept of Microelectronics and Nanoscience, Chalmers University of Technology, Göteborg, SWEDEN.

SmC* high-molecular-tilt monomers and polymers Ferroelectric and antiferroelectric liquid crystals can have unique electro-optical properties when designed for molecular optics. In fact, ferroelectric liquid crystals with a molecular tilt of about 45° can exhibit a linear electro-optical response at low voltages, whilst at higher voltages a substantial change in the effective refractive index of the sample takes place. In the case of 45° antiferroelectric liquid crystals, the optically isotropic field-free state can be switched by an applied electric field to the birefringent state. We have prepared a series of new chiral LC monomers to be incorporated into LC polysiloxanes as side groups. The monomers formed a rich polymorphism, including the BP, N*, TGB, SmA*, and SmC* phases. The molecular tilt in the SmC* phase was relatively high with maximal values of up to 30° . In the corresponding polysiloxanes many of the chiral phases were suppressed, and only SmF* and SmC* phases were found. However, the molecular tilt angle was much greater in the polymers than in the corresponding monomers. This was attributed to a phase separation at the molecular level with the siloxane backbone being confined in the inter-layer region. The polymers were easily aligned in bookshelf geometry by applying a weak mechanical shear. The electro-optical response of a sandwich cell with uniformly aligned polymer was studied. It was found that the apparent tilt angle of the polymer in the SmC* phase was 45° resulting in a 90° switching. The characteristics of the electro-optical response of the polymers will be discussed. newline Acknowledgment. Work performed with financial support from the EU "ORCHIS" project.

CC5.11

CRYSTALLIZATION KINETIC STUDIES ON A NOVEL SERIES OF FERROELECTRIC LIQUID CRYSTAL MATERIALS DERIVED FROM L-TYROSINE. S. Lakshminarayana, P.A. Kumar and V.G.K.M. Pisipati, Centre for Liquid Crystal Research and Education (CLCRE), Faculty of Physical Sciences, Nagarjuna University, Nagarjuna Nagar, INDIA.

A systematic kinetic study leading to the crystallization from smectic-F* in a novel series of ferroelectric liquid crystals, 4-(*p*-butyloxy-2-chloro-tyrosinate)-2-hydroxy-benzylidene-4'-alkylanilines (BCTHBA) (where alkyl = pentyl-, heptyl-, nonyl-, dodecyl- and tetradecyl-) has been carried out using thermal microscopy (TM) and differential scanning calorimetry (DSC). The kinetics experiment is performed from the common kinetophase, smectic-F*, in all the compounds. The dimensionality in the smectic growth and the sporadic nucleation are estimated from the Avrami exponent, n . An unique mode of crystallization mechanism is predicted to operate for all the crystallization temperatures. The characteristic crystallization time (t^*) at each crystallization temperature is deduced from the individual plots of $\log t$ vs. ΔH . The impact of ferroelectric kinetophase (smectic-F*) on the rate of crystallization is also realized by a comparative study on various achiral smectogens possessing a common tilted phase.

CC5.12

MOLECULAR DYNAMICS SIMULATION STUDY ON THE PHASE BEHAVIOR OF THE GAY-BERNE MODEL WITH A TERMINAL DIPOLE AND A FLEXIBLE TAIL. Hiroo Fukunaga, Japan Chemical Innovation Institute, Research and Education Center, Nagoya Univ, Nagoya, JAPAN; Jun-ichi Takimoto, Yamagata Univ, Dept of Polymer Science and Engineering, Yonezawa, JAPAN; Masao Doi, Nagoya Univ, Dept of Computational Science and Engineering, Nagoya, JAPAN.

To study the effect of the alkyl tail and the terminal dipole on the liquid crystalline phase of 5CB (4-*n*-pentyl-4'-cyanobiphenyl), we have carried out molecular dynamics (MD) simulations with a coarse-grained model. In the model, a 5CB molecule was divided into a rigid part (4-methyl-4'-cyanobiphenyl moiety, hereafter referred to as CB), and a flexible part represented by a chain of united atoms (UAs). The generalized Gay-Berne (GB) potential and the Lennard-Jones (LJ) potential were used for the non-bonded potential between the CB-CB (or CB-UA) pair and between the UA-UA pair, respectively. In addition, a dipole moment was placed at the end of the GB ellipsoid opposite to the flexible tail. The interaction among the dipoles was truncated at some distance and corrected by the reaction field method.

Using the GB model with only the flexible tail, we examined the tail effect on the liquid crystalline phase. If the length of the rigid core is kept constant, the isotropic phase becomes favored with increasing the aspect ratio of the ellipsoid. If we include the terminal dipole, the transition temperature from the isotropic to the ordered phase falls and the density increases. Detailed comparison between the simulation results using the GB ellipsoid models (i) with the flexible tail, (ii) with the terminal dipole, and (iii) with both of the flexible tail and the terminal dipole will be presented.

This work is supported by the national project, which has been entrusted to the Japan Chemical Innovation Institute (JCII) by the New Energy and Industrial Technology Development Organization (NEDO) under METI's Program for the Scientific Technology Development for Industries that Creates New Industries.

CC5.13

A MOLECULAR DYNAMICS SIMULATION STUDY OF THE NONLINEAR OPTICAL RESPONSE OF A LIQUID CRYSTALLINE SYSTEM. Kenji Kiyohara, Koji Ohta, and Yo Shimizu, National Institute of Advanced Industrial Science and Technology-Kansai, Osaka, JAPAN.

We investigated the third-order nonlinear optical response of a Gay-Berne system at the isotropic, nematic, and smectic phases by molecular dynamics simulation. The components of the optical response were calculated for the three different axes with respect to the director of the system, separately. In the nematic phase, we observed that the response function did not vanish at long times. This means that the orientation of the director of the system is permanently changed by an instant irradiation of polarized light, as a result of third-order nonlinear optical response. Our results give a theoretical background at molecular level on the interpretation of the reported experimental observations of peculiar dynamics of nematic systems at irradiation of laser lights.

CC5.14

GLASSY NEMATICS WITH ELEVATED GLASS-TRANSITION AND CLEARING TEMPERATURES. Fred Y. Fan, Dimitris Katsis, Sean W. Culligan, John C. Mastrangelo, Shaw H. Chen, University of

Rochester, Dept of Chemical Engineering and Laboratory for Laser Energetics, Rochester, NY.

To furnish new insight into structure-property relationships governing glassy nematic liquid crystals, novel material systems were synthesized and characterized. Highly ordered, solid films were also prepared via spin-coating for the determination of optical birefringence. It was found that a linear nematogen, such as the cyanoterphenyl group, contributes to an elevated glass transition temperature and a wide nematic fluid temperature range with a mixed or an extended core structure. However, an angular nematogen, such as the cyanophenyl group, is more versatile in inducing glass formation with a broader range of core structures. Morphologically stable, glassy nematics with a glass transition temperature close to 130°C, a clearing point close to 350°C, a nematic fluid temperature range of 265°C, and an optical birefringence of 0.44 accomplished in this study represent significant improvements over existing materials. A stereochemical modification of the bicyclooctene ring from an exo,exo- to an endo, exo-configuration, fluorination of the cyanophenyl group, and a longer spacer to nematic pendants were found to depress clearing point to a much greater extent than glass transition temperature. An extension in the core structure accompanied by an increased number of nematic pendants per core was found to elevate glass transition temperature, but no consistent effect on clearing point was observed.

CC5.15
ELECTRO-OPTICS OF THIN LAYER OF NEMATIC GELS.
Guangnan Meng, Dmitri Kononov, Robert Meyer, Brandeis University, Department of Physics, Waltham, MA.

Unique stripe pattern was observed in thin layer of uniformly aligned nematic gel when electrical field was applied. The thickness dependence of stripes' periodicity and transition voltage was studied in wedge-shaped cells. A model with periodic director field and corresponding displacement field was proposed to approach the problem analytically. By using the elastic theory of both nematic elastomers and nematic liquid crystals, our experimental results were interpreted successfully. The coupling of rubbery elasticity of cross-linked polymer network and liquid crystalline degrees of freedom in liquid crystalline gels leads to the formation of this particular stripe pattern since the rotation of liquid crystalline molecules are constrained by the polymer matrix when electrical field was applied, under this circumstance, periodic texture of director field would be favored.

CC5.16
CAPILLARY INSTABILITIES IN THIN NEMATIC LIQUID CRYSTALLINE FIBERS. Ae-Gyeong Cheong, Alejandro D. Rey, McGill Univ, Dept of Chemical Engineering, Montreal, CANADA.

Bi-phasic polymer-liquid crystal blends are used as precursors in the fabrication of in-situ composites. A fundamental understanding of how liquid crystal fiber structure and morphology are affected by processing conditions is currently lacking but necessary for product property optimization. In this paper we model liquid crystal fiber stability processes relevant to the fabrication of polymer-liquid crystal in-situ composites. A complete identification and characterization of three distinct capillary instabilities in nematic liquid crystal fibers is presented. Linear stability analysis of capillary instabilities in thin nematic liquid crystalline cylindrical fibers is performed by formulating and solving the governing nemato-capillary equations. The surface disturbance is expressed in normal modes, which include the azimuthal wavenumber m to take into account non-axisymmetric modes of the disturbance. Capillary instabilities in nematic fibers reflect the anisotropic nature of liquid crystals, such as the orientation contribution to the surface elasticity and surface bending stresses. The exact nature (stabilizing and destabilizing) and magnitude of the elastic and capillary forces depend on the nematic orientation and the anisotropic contribution to the surface energy, and accordingly capillary instabilities may be axisymmetric or non-axisymmetric, with finite or unbounded wavelengths. Thus, the classical fiber-to-droplet transformation is one of several possible instability pathways while others include surface fibrillation.

CC5.17
AZODYE LIQUID CRYSTALLINE POLYMERS FOR HOLOGRAPHY APPLICATIONS. Fedor Podgornov, Mikhail Kozlovsky, Wolfgang Haase, Inst of Physical Chemistry, Darmstadt Univ of Technology, Darmstadt, GERMANY; Vladimir Lazarev, Inst of Crystallography, Moscow, RUSSIA.

Azo-dye polymers attract recently considerable attention due to possibilities of their practical utilization as optically controllable alignment layers and holographic medium. Among other polymer matrices, liquid crystalline polymers are of special interest for those applications because of high ordering degree and of the cooperative

reorientation of mesogenic monomer moieties. Here we report systematic holographic investigation of azo dye copolymer systems having the same matrix monomer inducing a chiral smectic phase but differing with type and concentration of azobenzene dye comonomer. It has been shown that illumination of the copolymers with a polarized light beam leads to the appearance of the photoinduced optical anisotropy. Furthermore, the copolymers have pronounced photo-optical response allowing for the holographic grating recording. Several processes are revealed responsible for the recording, namely thermal mechanisms, trans-cis-isomerization, and photoinduced birefringence. Dependencies of the temporal dynamics of the holographic recording on the concentration of azo dye, light intensity, wavelengths and polarization are investigated. Effect of the film thickness is also evaluated. The maximum diffraction efficiency achieves about 32%.

CC5.18
Abstract Withdrawn.

CC5.19
THERMAL AND LIQUID CRYSTALLINE PROPERTIES OF POLYMERS WITH AMPHIPHILIC-MESOGENIC SIDE-CHAINS. Seiji Ujiie, Shimane Univ, Dept of Material Science, Shimane, JAPAN; Yumi Yano, Akira Mori, Kyushu Univ, Fukuoka, JAPAN.

Liquid crystalline amphiphilic polymers, in which mesogenic groups are attached to a polymer backbone through water-soluble spacer chains, were synthesized. Polyethyleneimine and polyoxyethylene units were used as the water-soluble spacer. Their thermal and liquid crystalline properties were estimated. The liquid crystalline amphiphilic polymers showed thermotropic and lyotropic mesophases. In the thermotropic systems of the polymer (P5AzBu) having the polyethyleneimine spacer, the smectic A and C mesophases were formed on the heating and cooling processes. The thermotropic systems clearly showed the glass and smectic A-isotropic phase transitions. The X-ray diffraction pattern of the smectic A and C thermomesophases consisted of the sharp reflections at the small-angles and the broad reflection in the wide-angle region. The layer distance obtained from the X-ray diffraction measurements was 54Å in the smectic A phase and was changed to 49Å by cooling to the smectic C phase. In both the smectic A and C phases, a possible packing model is a bilayer structure. On the other hand, the lyotropic systems, consisting of the amphiphilic P5AzBu and water, exhibited a smectic C phase below 100 degrees centigrade. In the smectic C lyomesophase, schlieren and oilstreak textures was formed. The X-ray diffraction pattern of the lyotropic systems was similar to that of the thermotropic systems. The lyotropic systems also formed a bilayer structure. The smectic layer is composed of a sublayer produced by the anisotropic alignment of the mesogenic groups and a sublayer of water and hydrophilic spacer chains.

CC5.20
PHASE BEHAVIORS OF NEMATIC LIQUID CRYSTAL/STRUCTURAL (STAR AND HYPERBRANCHED) POLYMER SYSTEMS. Dong Kyu Yoon, Ho Jin Jung, Young Chan Bae.

Liquid crystal (LC) technology has a major effect on many areas of science and engineering as well as device technology. Recently, extensive progress has been made since LCs have widespread applications, such as LC displays, LC thermometers, and optical imaging, etc. Thermotropic transitions occur in most LCs, and they are defined by the fact that transitions to the LC state are induced thermally. In general, thermotropic mesophases occur due to anisotropic dispersion forces between the molecules and packing interactions. In this study, we investigate nematic-isotropic transition temperatures of LC/Structural (Star and Hyperbranched) Polymer systems comparing with those of LC/Linear-Polymer systems. Freed's lattice cluster model and Flory's lattice model are combined to describe phase behaviors of LC/structural polymer systems.

CC5.21
COMPUTATIONAL MODELING OF NEMATIC TEXTURE NETWORKS UNDER SHEAR FLOW. Tomohiro Tsuji, Shigeomi Chono, Kochi Univ. of Technology, Dept of Mechanical Engineering, Kochi, JAPAN; Alejandro D. Rey, McGill Univ., Dept of Chemical Engineering, Montreal, CANADA.

The molecular orientation field of nematic liquid crystalline flows has been computed using a second order tensor type theory. The nematic liquid crystalline material is quenched from isotropic temperature to nematic temperature, before rectilinear shear flow is applied. The nematic texture networks arise through the isotropic-nematic phase transition, and are reorganized during the defect coarsening stage. While the short-range order energy of the nematic molecular orientation field rapidly decreases, the long-range energy increases due to the nucleation of the nematic defect structures, at the phase transition stage. At the defect coarsening stage, both the short and

long range order energies decrease. Depending on the condition at bounding surfaces the nematic textures persist, forming the texture networks, and the free energies hold the higher values than those of the homogeneous orientation field. The nematic texture networks deform under the shear flow and thus have the strong effect on some rheological parameters. The discussion on the relation between the existence of the nematic texture networks and the viscosity of the nematic liquid crystalline polymers will also be discussed.

CC5.22

THE IMPROVEMENT OF LCD VIEWING-ANGLE PROPERTIES USING A FIBER-OPTIC FACEPLATE: OPTICAL MODELING.

Michael J. Escuti, Lara D. Oliver, and Gregory P. Crawford, Division of Engineering, Brown University, Providence, RI.

Here we explore the optical phenomena associated with Fiber-optic Faceplates (FOFPs) used for viewing-angle improvement in Liquid Crystal Displays (LCDs). In contrast to birefringent compensation films, this improvement occurs as a result of azimuthal-averaging through the fiber cores and is applicable to all LCD configurations, especially the Twisted-Nematic (TN). We will present the results of a thorough ray-tracing analysis and link geometric and material properties to desired optical effects. As the field-of-view is one of the most critical performance parameters of a high-information-content display, the poor off-axis contrast and grayscale inversions of most uncompensated LCD modes are unacceptable. As a result, tremendous effort has been put toward overcoming the leakage in the polarizers, the angular-dependence of the phase retardation in the LC layer, and anisotropic fields within pixels. Effective approaches include the development of birefringent retardation-films, multi-domain pixels, and novel nematic configurations. However, the transmission typically retains a polar and azimuthal dependence. Complementing or perhaps replacing several of these approaches, the viewing-angle improvement from an FOFP occurs due to the total-internal-reflection within the fiber cores. Adjacent light-rays with identical polar and azimuthal angles but slightly different spatial coordinates will spiral within the fiber cores along increasingly different trajectories and exit at the original polar angle but mutually-different azimuthal angles. When placed as the final layer of an LCD stack, this leads in an azimuthal-smoothing of the transmission irrespective of what display configuration is used. While thick (>2mm) glass-based FOFPs have experimentally verified the azimuthal-averaging effect, a coherent study of the geometry and materials in the LCD context is needed. Therefore, in this work we use ray-tracing models and theoretical considerations to explore the limits of core aspect ratios, the required core/cladding indices, and the effect of circular and non-circular fiber cores.

CC5.23

THEORY AND SIMULATION OF TEXTURE TRANSFORMATIONS IN CHIRAL SYSTEMS: APPLICATIONS TO BIOLOGICAL FIBROUS COMPOSITES. Gino De Luca,

Alejandro D. Rey, Dept of Chemical Engineering, McGill University, Montreal, CANADA.

Numerous studies have shown that the fibrillar structural components of biological skeletal systems, i.e., chitin, collagen and cellulose, tend to assemble in a three-dimensional way very close to that of chiral nematic liquid crystals. These strategic assemblies are vitally important because they give proper mechanical and optical functions but their mechanisms are not well understood. Noteworthy textures arising from these complex and accurate arrangements are observed in cross sections of biological systems such as crab cuticle, human bone, bird cornea, and plant cell wall. Using the Landau-Ginzburg-de Gennes theory, a macroscopic model of chiral nematic liquid crystals is established to mimic the texture transformation in chiral-biosystems. The dynamics of the tensor order parameter is obtained by setting the variational derivatives of the free energy density equal to the rotational torque. The model associated with a planar geometry and different type and degree of anchoring allows to reproduce the main textures found in biomaterials. Namely, the so-called planar, fingerprint, focal conic, homeotropic, and amorphous cholesteric texture. The pallet of texture reproduced is discussed in function of the different parameters involved, i.e., size of the pitch, type and degree of anchoring, ratio of long to short-range elasticity, and concentration. In addition, the tensorial approach of the problem provide the ability to capture the process of defects structure nucleation and coarsening when the system is quenched from the isotropic to the ordered state.

CC5.24

Abstract Withdrawn.

CC5.25

STRUCTURE AND DYNAMICS OF n-CYANOBIPHENYLS CONFINED IN POROUS SILICA MATRICES. C. Fehr, P.

Dieudonne, C. Goze-Bac, J.L. Sauvajol, E. Anglaret, GDCP, UMR

CNRS 5581, Universite Montpellier II, FRANCE; J. Primera, T. Woignier, LDV, UMR CNRS 5587, Universite Montpellier II, FRANCE.

We study the structure and dynamics of n-cyanobiphenyls (5CB and 8CB) confined in porous silica matrices with tailored pore size distributions. The structure of the compounds is investigated by neutron diffraction. The coherence length of the smectic A and crystalline phases depends both on pore size and cooling rate. Original structural organisations are observed in confinement which are not observed in the bulk. The vibrational signatures of these new phases are measured in Raman scattering and inelastic neutron scattering. Bulk and new (confined) phases coexist over a large range of temperatures. The volumic fractions essentially depend on pore size and surface area of the matrices. Finally, orientational order in the nematic phase is investigated by means of ¹³C NMR and polarized Raman experiments. Pore size dependence of the order parameter and nematic-isotropic phase transition temperature is measured and discussed.

CC5.26

SYNTHESIS OF NEW HOMOLOGOUS SERIES OF LIQUID CRYSTALLINE COMPOUNDS. J. Mahadeva^a,

K. Rajashekara Prasad^b, Nagappa^a and K.M. Lokanatha Rai^b, Department of Physics^a / Chemistry^b, University of Mysore Manasagangotri, Mysore, INDIA.

New liquid crystalline compounds of homologous series 2-(4'-pyridyl)-5-aryl-1,3,4-oxadiazoles, have been synthesized. The DSC and Optical microscopy studies reveals that these compounds exhibit nematic and smectic phases at different temperatures. The NMR, IR and Mass spectral studies have also been carried out to verify the purity of those compounds.

CC5.27

POROUS THIN FILM/LIQUID CRYSTAL COMPOSITE MATERIALS AND DEVICES. J.C. Sit, S.R. Kennedy, Electrical and Computer Engineering, University of Alberta, CANADA; D.J. Broer, Philips Research Laboratories, Eindhoven, THE NETHERLANDS; M.J. Brett, Electrical and Computer Engineering, University of Alberta, CANADA.

Using the glancing angle deposition (GLAD) technique, highly porous thin films can be fabricated with controlled columnar microstructure. One of the more interesting morphologies that can be generated using GLAD is the helical or chiral microstructure. Films with chiral morphology have been shown to possess unique optical response, including optical rotation and circular dichroism, similar to certain classes of chiral liquid crystals. When non-chiral nematic liquid crystals (LC) are introduced into the pores of GLAD films, the optical response of the film is found to be markedly enhanced, as the presence of the chiral film induces an orientation in the LCs similar to that seen in a chiral nematic phase. The pitch and handedness of the GLAD film, which can be easily controlled through the deposition process, control the wavelength at which peak optical activity is observed, allowing the spectral properties to be engineered. Results to date on GLAD/LC composite materials and devices include characterization of the optical response, influence of the underlying film microstructure, and electro-optic switching of the LC.

CC5.28

SIDE CHAIN LIQUID CRYSTALLINE POLYMER BRUSHES AS ALIGNMENT LAYERS LC DISPLAYS. Jürgen Rühle, IMTEK -

Institute for Microsystem Technology, University of Freiburg, GERMANY; Bin Peng, Diethelm Johannsmann, MPI for Polymer Research, Mainz, GERMANY.

In this contribution we report on the synthesis of side chain liquid crystal polymer (LCP) brushes attached to silicon oxide surfaces. The layers are prepared at the surface of the substrates by in situ polymerization from monolayers of radical chain initiators ('grafting from'). The mesogenic group of the LC-brushes consists of a phenylbenzoate moiety linked to the methacrylate main chain via a flexible spacer. The brush thickness and the graft density of the polymer chains is adjustable over range up to 200 nm by controlling polymerization parameters such as initiator conversion and monomer concentration. The LC behavior of the brushes was studied and compared to the properties of spin-cast films of the same polymer. The LCP brushes were subsequently used as alignment layers for LC displays. By adjusting the conditions used for sample preparation we were able to achieve the alignment of the low molecular weight mesogenes of the cell in macroscopic domains with tilt angles of the LC director different from homeotropic and planar orientation.

CC5.29

CARRIER TRANSPORT PROPERTIES IN CROSSLINKED POLYMER / LIQUID CRYSTALLINE SEMICONDUCTOR

COMPOSITES. Naoki Yoshimoto, Masahiro Funahashi and Jun-ichi Hanna, Imaging Science and Engineering Lab., Tokyo Institute of Technology, Yokohama, JAPAN.

Organic binary materials systems including a polymer exhibit a wide range of composites from solid solution to phase separated mixture. According to the composites, their electrical properties are governed by either hopping transport or percolation. Above all, the liquid-polymer composites is of interest because it exhibit different order of phase separation from "microscopic" to "macroscopic". In this study, we have investigated the carrier transport properties in a novel composite system containing a liquid crystalline semiconductor and a cross-linked polymer. It was found that this composite showed a wide range of phase separation as mentioned and that their carrier transport properties varied according to a concentration of including polymer: for example, the hole mobility did not degrade in comparison with that of a pure liquid crystalline semiconductor, e.g. 1.8×10^{-4} cm²/Vs in smectic A phase and 2.2×10^{-3} cm²/Vs in smectic B phase when the concentration of cross-linked polymer was less than 5 wt %, even though this system was comprised with polymer network. It was concluded that the cross-linked polymer/liquid crystalline semiconductor composite is a very unique materials system to realize high performance of carrier transport properties.

CC5.30

NUMERICAL SIMULATION OF A VOLTAGE-DEPENDENT SURFACE-INDUCED MOLECULAR REORIENTATION IN A CONFINED NEMATIC LIQUID CRYSTAL. J.J. Castro,

Departamento de Física, CINVESTAV México, D.F., MÉXICO; A. Calles, Departamento de Física, Facultad de Ciencias, UNAM, México, D.F., MÉXICO.

We present a computer simulation of the voltage-dependent orientational ordering of a nematic liquid crystal confined between two substrates with different anchoring for each surface. The system is studied through the lattice approximation. We particularly discussed the case for negative dielectric anisotropy that could have relevance for the voltage controlled twist effect. The simulation is carried through a numerical relaxation method for the total energy of the system.

CC5.31

PHOTOISOMERIZATION AND PHOTO-INDUCED ALIGNMENT OF ALL-AZOBENZENE FUNCTIONALIZED DENDRIMERS ON ULTRATHIN FILMS. Derek Patton, Mi-kyoung Park, Shuangxi Wang, and Rigoberto Advincula, Department of Chemistry, University of Alabama at Birmingham, Chemistry Building, Birmingham, AL.

Dendrimers are a new class of macromolecules characterized by their tree-like generational structure. Azobenzene dyes add photochromic behavior to these macromolecules allowing light induced structural and refractive index changes. This study focuses on the use of linear polarized photoisomerization (LPP) to control the shape anisotropy of the dendrimer at various concentrations within a polymer matrix. The materials were prepared as ultrathin films which should find applications in display materials, optical storage and phenomena. We are interested in the "globular" shape (or conformation) and functionality of the dendrimer and how the matrix material affects these properties. We have used evanescent waveguide techniques to characterize ultrathin films of these dendrimers in polymer matrices. In an ATR experiment, we are able to define the real and complex properties of the material three-dimensionally to correlate with the polarization of irradiated light. A comparative study is presented involving the azobenzene functionalized dendrimer, small molecule azo-dyes, and azobenzene side-chain polymers. We also describe investigations on the photo-induced alignment properties of ultrathin films as used in hybrid Liquid Crystal (LC) hybrid cells.

CC5.32

Abstract Withdrawn.

CC5.33

SYNTHESIS, CHARACTERISATION AND LIQUID-CRYSTALLINE PHASE TRANSITION STUDIES ON TWO HIGHER HOMOLOGUES OF 4O.M (M=14 AND 16) SERIES. C. Rama Chandra Prabh, V.G.K.M. Pisipati, R.V.R. & J.C. College of Engineering, INDIA.

The synthesis, characterization and phase transition studies of higher homologues of N(p-n-butoxybenzylidene)p-n-alkylanilines, Viz., 4O.m series (m=14 and 16) are carried out by thermal microscopy, differential scanning calorimetry, density, and refractive index studies. The compounds exhibit a phase variant of nematic and smectic-A. Density studies reveal a first order nature of IN transitions and a weak first order NA transitions. The refractive index anisotropies support a first order nature of IN transitions and a weak first order nature of NA transitions. Further the refractive index anisotropy in

both these compounds show an anomalous behaviour accompanied with a non-linear dip immediately after NA transition, in contrast to the reported nonlinear increase of optical anisotropy for the lower homologues reflecting the orientational disorder extended by increasing length of flexible end chain. An estimate of pressure dependence of the phase transition temperatures using the volume and enthalpy data are presented. A comparison of these results with other reported results in nO.m and other compounds are presented.

CC5.34

SYNTHESIS AND CHARACTERIZATION OF A NOVEL ANTIFERROELECTRIC LIQUID CRYSTAL COMPOUND DERIVED FROM L-TYROSINE. P.A. Kumar and V.G.K.M. Pisipati, P. Swathi, Nagarjuna University, INDIA.

A novel antiferroelectric liquid crystal, (S)-4-(2-chloro-3-phenyldodecyloxypropionato)-4-n-octyloxybiphenyldicarboxylate (CPDOBD), has been synthesized using L-tyrosine as a chiral ingredient. The thermal and phase behaviour of the compound is studied by thermal microscopy (TM) and differential scanning calorimetry (DSC). These studies reveal the existence of the phase variant, Iso-SmA-SmC*-SmC*A-SmF-Cryst. The ferroelectric characterization is carried in terms of spontaneous polarization (P_s), optical response times (τ) and viscosity (η). The identification of sub phases viz., C_α , C_γ ; in ferroelectric ordering is performed by the trend in the current profiles obtained during the spontaneous polarization study.

SESSION CC6: PHOTOPOLYMERIZATION AND LIQUID CRYSTALS

Chairs: C. Allan Guymon and Liang-Chy Chien
Wednesday Morning, November 28, 2001
Commonwealth (Sheraton)

8:30 AM *CC6.1

FORMATION OF ORDERED POLYMER MICROSTRUCTURES ON LIQUID CRYSTAL TEMPLATES. L.C. Chien, Kent State University, Kent, OH.

We describe a method of preparing periodic polymer microstructures using various pattern-forming states of liquid crystals as templates. These states are the result of complex combinations of dielectric, flexoelectric, and electrohydrodynamic torques induced by applying an electric field at specific amplitudes and frequencies as well as for specific ratios of the sample thickness to cholesteric pitch. In each case, key structural features of the patterned distortion in orientational order of the liquid crystal can be recorded into the morphology and optical anisotropy of an internal polymer network, which is formed via photopolymerization of a low concentration monomer additive. The observed morphologies include one-dimensional arrays of thin parallel or zig-zag walls, and multi-dimensional structures formed by twisting walls or square-lattice arrays. We also describe how the polymer network enhances the potential of complex pattern-forming states in liquid crystals for various electro-optical devices.

9:00 AM CC6.2

POLYMER NANOSTRUCTURE FORMATION IN POLYMER STABILIZED LIQUID CRYSTALS. Demetrius McCormick, Romana Chavers, C. Allan Guymon, University of Southern Mississippi, Dept. of Polymer Science, Hattiesburg, MS.

Liquid crystalline (LC) media offers a unique platform upon which to study the evolution of polymer nanostructure in organized media. The study of polymer nanostructure evolution in ordered media is important for a variety of reasons and has applications in a wide range of technologies. Recently, a considerable amount of research has been devoted to the understanding the kinetics associated with the polymerization of monomers in polymer stabilized liquid crystals, which has applications for flat panel displays. In addition, the polymerization of monomers in lyotropic liquid crystals (LLC) for the templating of LLC nanostructure for applications in separations media has been studied. This study focuses on the polymerization of aliphatic and perfluorinated monoacrylates and diacrylates in thermotropic liquid crystalline media. The monomer segregation behavior, orientation, and polymerization kinetics were investigated in detail. After polymerization, the polymer segregation behavior and orientation were characterized. For each of the monomer/LC systems substantial increases in the polymerization rate was exhibited as the order of the liquid crystalline solvent was increased, despite large decreases in the polymerization temperature. The monomers also displayed intriguing segregation behavior between the smectic layers of the liquid crystal. Interestingly, the linear perfluorinated polymers stay segregated between the smectic layers after polymerization, while the network and linear aliphatic polymer structures phase separate from the liquid crystal.

9:15 AM CC6.3

A NOVEL POLYMER PATTERNING METHOD BASED ON PATTERN FORMING STATES OF LIQUID CRYSTALS AS TEMPLATES. Shin Woong Kang, Liquid Crystal Institute and Chemical Physics Program, Kent State University, Kent, OH; Samuel Sprunt, Department of Physics, Kent State University, Kent, OH; Liang-Chy Chien, Liquid Crystal Institute and Chemical Physics Program, Kent State University, Kent, OH.

In recent years, polymer-liquid crystal composites have provided fertile ground for the development of various electro-optical devices, including displays, electrically-switchable diffraction gratings, and electrically-tunable microlens assemblies. We will describe a new polymer patterning technique that produces controllable morphological and optical anisotropy in a polymer network. This technique is based on the use of pattern-forming states of nematic and cholesteric liquid crystals as templates for forming ordered networks. One and two-dimensional patterns are induced by applying an electric field across a narrow gap of an electro-optical cell. These are then stabilized by UV photopolymerization of a typically 5 wt % reactive monomer, which, depending on specific conditions (e.g., mesogenic vs. nonmesogenic monomer), captures various degrees of the orientational order and spatial periodicity of the pattern-forming state. The fidelity of the templating effect is explored using polarizing optical microscopy and SEM. The mechanisms for the phase separation responsible for the basic network structure include gradients in the orientational order of the host and internal modulation of the UV intensity. We will discuss the relative importance of these effects. We also describe the effect of UV wavelength on the network morphology, and specifically show morphological control over the third dimension (normal to the cell substrates). Finally, we demonstrate the advantages of this control for practical applications in electro-optical devices.

9:30 AM CC6.4

REAL-TIME STUDY OF THE EVOLUTION OF ANISOTROPIC PHASE SEPARATION IN H-PDLCs. Lalgudi V. Natarajan, Vincent P. Tondiglia, Timothy J. Bunning, Richard L. Sutherland, Air Force Research Laboratory, Materials and Manufacturing Directorate/MLPJ, Wright-Patterson Air Force Base, OH.

We have investigated the dynamics of formation of a reflection hologram in a photosensitive formulation containing pre-polymer and liquid crystal. Kogelnik's two beam coupling theory of an isotropic material was expanded to account for variations in the x, y, and z directions. This theory predicts a different dependence of the p-polarized coupling coefficient, up, at different internal angles. At 45 degrees, a non-zero value for up implies a macroscopic anisotropy. A systematic series of investigations at internal angles of 45 and 90 degrees as a function of intensity, power dependence, and LC concentration has been performed. A broadband source was used as a probe to monitor the diffraction efficiencies (DE) during exposure for both s- and p-polarized light. The onset of a macroscopic ordering of the liquid crystal is observed when the DE of the p-polarized probe begins to grow. The real time experiments clearly establish the anisotropic nature of the gratings formed. Experimental data shows evidence of shrinkage, beam coupling and the dependence of the onset of anisotropy with laser intensity and liquid crystal concentration.

9:45 AM CC6.5

CAVITY MORPHOLOGY OF POLYMER DISPERSED SYSTEMS UTILIZING ATOMIC FORCE MICROSCOPY. Adam K. Fontecchio, Brown University, Dept of Physics, Providence, RI; Gregory P. Crawford, Brown University, Division of Engineering, Providence, RI; David Content, NASA Goddard Space Flight Center, Greenbelt, MD.

Atomic force microscopy (AFM) tapping techniques were employed to study the droplet cavity morphology of a Holographically-formed Polymer Dispersed Liquid Crystal (H-PDLC). Using a Coherent Verdi laser at 532 nm, we holographically formed a transmission grating structure within the H-PDLC. In these systems, the hologram is created by an interference pattern, with the polymer curing into planes in the bright fringes, and the liquid crystal (LC) separating into planes of droplets in the dark fringes of the hologram. Following the curing process, the H-PDLC film was removed from the glass supporting substrates, and the liquid crystal was dissolved from the film using organic solvents. The film was then examined using a Digital Instruments Nanoscope3A atomic force microscope. Utilizing the Tapping Mode method, we were able to image the structure inside the (now empty) droplet cavities. Inside the cavities, we discovered that the surface structure is not smooth, and that the structure strongly depends on the polymer used in the material set. As an example, multi-functional blended urethane acrylate resin, a common polymer used in H-PDLCs, has a structure with many hemispheres protruding from the cavity walls, all with similar radius of curvature. The result is a cavity that appears similar to the inside of a golf ball, with the patterning dependent upon the materials set. We report on

our investigations of the material sets, including AFM images, image analysis of the structures, pattern analysis, and the potential implications of such structures on liquid crystal anchoring within the droplet cavities. We will also discuss how this knowledge can be used to enhance H-PDLC performance.

10:30 AM CC6.6

MICROLENS ARRAYS VIA PATTERN-PHOTO-POLYMERIZATION-INDUCED PHASE SEPARATION OF LIQUID CRYSTAL/MONOMER MIXTURES USING MULTIPLE-WAVE MIXING. Thein Kyu, Scott Meng, Hatice Duran and Domasius Nwabunma, Institute of Polymer Engineering, The University of Akron, Akron, OH.

We introduced a novel method of fabricating electrically-focusable liquid crystal microlens through pattern-photopolymerization-induced phase separation in LC/monomer mixtures based on four-wave mixing, i.e. interference of two horizontal waves and two vertical waves. The microlens forming process has been simulated based on a pattern-photopolymerization technique in which the spatially modulated reaction rate was coupled with time-dependent Ginzburg-Landau (TDGL) Model C equations via incorporation of free energies pertaining to isotropic mixing, nematic ordering, and network elasticity. Our simulation revealed that the emerging LC microlens arrays are similar to compound eyes found in various insects such as flies, ants, and wasps. Supported by NSF-ALCOM through DMR 89-20147 and Ohio Board of Regents.

10:45 AM CC6.7

HOLOGRAPHIC POLYMER DISPERSED LIQUID CRYSTALS: EFFECT OF PARTIAL MATRIX FLUORINATION ON ELECTRO-OPTICAL AND MORPHOLOGICAL PROPERTIES. Michael D. Schulte, Stephen J. Clarson, University of Cincinnati, Dept of Materials Science and Engineering, Cincinnati, OH; Lalgudi V. Natarajan, Science Applications International Corporation, Dayton, OH; Timothy J. Bunning, Air Force Research Laboratory, Materials and Manufacturing Directorate, MLPJ, Wright-Patterson Air Force Base, OH.

Holographic Polymer dispersed liquid crystal (H-PDLC) films with partially fluorinated matrices were investigated. Electro-optical and morphological studies revealed that fluorinated composites were substantially different from non-fluorinated analogues. The addition of a fluorinated monofunctional acrylate monomer to a pentaacrylate-derived polymer matrix resulted in improved diffraction efficiency. These findings suggest that the partial fluorination of the host polymer decreases the compatibility between the matrix and liquid crystal phase. Morphological differences between fluorinated films and non-fluorinated control specimens were verified using scanning electron microscopy (SEM).

11:00 AM CC6.8

FAST OPTICAL RECORDING IN DYE-DOPED POLYMER-DISPERSED LIQUID CRYSTAL FILMS. Andy Y.-G. Fuh, C.-C. Liao, C.-Y. Tsai, C.-L. Lu, Department of Physics, National Cheng Kung University, Tainan, TAIWAN, ROC.

This letter describes a fast optical recording material based on a dye-doped polymer-dispersed liquid crystal (DDPDLC) film. A holographic grating is written in this film by using a single Q-switched Nd:YAG laser pulse having a duration of ~6ns. Such a grating is due to the reorientation effect of the liquid crystal molecules through the interaction with the photo-induced adsorption of the doped azo dyes. Experimental results indicate that the formed grating is permanent, but electrically switchable. Supported by the National Science Council of the Republic of China under Contract No. NSC 89-2112-M006-043.

11:15 AM CC6.9

MOLECULAR WEIGHT EFFECTS ON THE PHASE BEHAVIOR OF POLYMER AND LIQUID CRYSTAL MIXTURES: CORRELATION OF THEORY AND EXPERIMENT. Nathan Crawford, Mark D. Dadmun, Department of Chemistry, University of Tennessee, Knoxville, TN.

The production of polymer dispersed liquid crystals (PDLC) usually occurs via a mechanism where the liquid crystal forms droplets by phase separating from a matrix consisting of growing polymers. Essentially, liquid crystalline droplets are formed when the polymer chain becomes large enough to limit miscibility. There exists limited information in the literature, however, on the effect of polymer molecular weight on the phase behavior of such mixtures. In the studies that have been reported, the results have been correlated to traditional Flory-Huggins Theory. We will present results of recent experiments that have determined the phase behavior of 8CB and poly(methyl methacrylate) (PMMA) mixtures where the molecular

weight of PMMA is varied from 100,000 to 996,000 and attempt to fit this data to Flory-Huggins theory. Interestingly, Flory-Huggins theory can not adequately describe the results. Possible reasons for this discrepancy and implications of this result on the use of Flory-Huggins theory to design and produce PDLC will be discussed.

11:30 AM **CC6.10**

OPTIMIZATION OF THE PERFORMANCE OF POLYMER DISPERSED LIQUID CRYSTAL FILMS. Philip K. Chan, Kam-Wa Danny Lee, Tuyet L. Tran, Ryerson Univ, Dept of Chemistry, Biology and Chemical Engineering, Toronto, Ontario, CANADA.

The important performance criteria for polymer dispersed liquid crystal (PDLC) films are: (1) low switching field strength in the on-state, (2) good light contrast between the on- and off-states, and (3) fast relaxation time in the off-state. We present computer simulation results from a model that describes the magnetic-induced director reorientation dynamics within elongated nematic bipolar droplets. The model is composed of the Leslie-Ericksen and Frank theories for liquid crystals. The numerical results indicate that PDLC films should be formed with the bipolar droplet axis of symmetry normal to the film plane in order to minimize both the required switching field strength and relaxation time. On the other hand, the numerical results indicate that PDLC films should be formed with the bipolar droplet axis of symmetry oriented within the film plane in order to maximize the light contrast between the on- and off-states. The numerical results provide useful information for the proper design and control of PDLC films for optimal performance.

11:45 AM **CC6.11**

STUDY OF ANCHORING TRANSITIONS OF NEMATIC FLUIDS AT THE INTERFACE OF POLYMER DISPERSED LIQUID CRYSTALS (PDLC). Jian Zhou¹, David M. Collard², Jung Ok Park¹, Mohan Srinivasarao^{1,2}. ¹School of Textile and Fiber Engineering and ²School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA.

The direction of the preferred alignment of nematic liquid crystals (NLC) on a solid surface may be normal to the interface (homeotropic anchoring), parallel to the interface (planar anchoring), or tilted. The anchoring behavior depends on the molecular interactions between the surface and NLC, and on external fields. Transitions from one anchoring condition to another, i.e. normal-to-planar, occur under a variety of conditions. Here we focus on a study of the temperature-driven anchoring transition in a polymer/nematic fluid composite in which the transition temperature (T_t) can be far below the nematic-isotropic transition temperature (T_{NI}) of bulk NLC. In order to probe the subtle effects of the molecular structure of the polymer surface on anchoring behavior, a series of polyacrylates with methyl or ethyl branches along alkyl side chain are investigated. For example, a PDLC film made from TL₂₀₅/poly(2-methylheptyl acrylate) shows T_t of 76°C, which is identical to T_t of TL₂₀₅/poly(*n*-heptyl acrylate) system. However, use of poly(1-methylheptyl acrylate) as the polymer matrix results in a T_t below -14°C. A model is proposed to explain the observed effect of surface structure on anchoring transition temperatures of NLC.

SESSION CC7: EMERGING CONCEPTS IN LIQUID CRYSTALS

Chairs: Valery P. Shibaev and John W. Goodby
Wednesday Afternoon, November 28, 2001
Commonwealth (Sheraton)

1:30 PM ***CC7.1**

LIQUID CRYSTALS FOR USE IN MICRODISPLAYS AND PHOTONICS. J.W. Goodby, M. Hird, K.J. Toyne, R.A. Lewis, S.J. Cowling and A.S. Petrenko, Department of Chemistry, The University of Hull, Hull, UNITED KINGDOM.

Over the past three decades electronics has revolutionised communications, information management and entertainment, leading to the creation of the Internet, e-commerce and mobile communications. However, the exponential growth of the Internet is setting severe scientific and technological demands on materials and devices. The drive to smaller, mobile, low power and low cost devices, capable of dealing with the speed of transmission and complexity of information content will be revolutionised by the use of photonic and optical signal communication devices and speed of light materials. Of the materials used in light modulating devices liquid crystals have proved to be the most successful, as evidenced by the remarkable success of nematic liquid crystal displays (TNLCDs) with a current market capitalisation of 14B pa. This success has been so powerful that today LCDs dominate the market in the small (1 cm²) to medium (750 cm²) size regimes. However, the marketplace is changing rapidly with the development of information and communication

e-technologies and the invention of novel devices, particularly liquid crystal on silicon devices (LCOS), for use in applications such as head-up displays, 3-D holographic imaging systems, mobile communication devices, virtual reality systems, and optical network processing devices etc. Often these new applications do not require the archetypal nematic displays/light modulators currently commercially available, but rather new device concepts that have desirable operating properties. These required properties may include faster operating speeds, analogue and linear responses to electric fields, low power consumption, tuneable birefringence, grey scale, bistable operation, flexibility, portability, robustness etc. Such demands surpass those achievable from conventional nematics, and thus novel materials/phases are required to satisfy the constraints demanded by new device concepts, and to provide a foundation for their commercialisation. In this seminar the design, synthesis, development and commercialisation of nematic and ferroelectric materials for use in high definition microdisplays and telecommunication switches will be described. Novel developments in V-shaped switching modes in ferroelectric liquid crystals for grey-scale devices and high tilt antiferroelectric phases for use in light scattering devices will also be discussed.

2:00 PM ***CC7.2**

MOLECULAR DESIGN STRATEGIES FOR HIGH BIREFRINGENCE LIQUID CRYSTALS. Shin-Tson Wu, UCF School of Optics, FL.

High birefringence liquid crystals are attractive for displays and optical communications. However, their UV stability is a big concern for practical applications. We have systematically investigated the UV stability of some linearly conjugated liquid crystals. Results indicate that both molecular conjugation and structure play important roles for the observed material degradations. Guidelines for designing new liquid crystal structures with high birefringence and low viscosity will be described.

2:30 PM **CC7.3**

MULTIPODAL LIQUID-CRYSTALLINE MATERIALS BASED ON FERROCENE CORES. T. Meyer, R. Elsaesser, K.J. Sheperson, J.W. Goodby, G.H. Mehl, University of Hull, Dept of Chemistry, Hull, UNITED KINGDOM; D. Vos, P. Jutzki, University of Bielefeld, Department of Chemistry, Bielefeld, GERMANY; B. Donnio, D. Guillon, University Louis Pasteur, IPCMS, Strasbourg, FRANCE.

The synthesis of organic-inorganic hybrid materials, whether they are oligomeric, multipodal or dendritic in structure has been in the focus of research interest over the recent years and great advances have been made. Many of these microphase separating systems, consisting of materials of defined size and stereo-chemistry are based on scaffolds with silicon positioned in the centre of the molecules. Thus the extension to other metal containing centres is an attractive area of research. In this context the synthesis of materials containing centrally positioned ferrocene core structures is particularly interesting. Ferrocene based systems have been already used in the synthesis of dendritic systems and in the aromatic centres of liquid crystals and can be functionalised to be employed as central cores of liquid crystal multipodes. This presentation will focus on investigations concerned with the synthesis and the liquid-crystalline phase structures of a ranges of multipodes based on substituted ferrocene groups as central cores. These tetra and decafunctionalised cores are linked to a range of mesogenic groups at the periphery via hydrocarbon and siloxane spacer groups. The synthesis and the results of the investigations of the liquid-crystalline phase properties of these materials, determined by optical polarising microscopy and DSC studies will be presented and a model of the liquid-crystalline phase structures based on X-ray diffraction experiments will be suggested. The effects of a variety of mesogenic structures on the liquid-crystalline phase behaviour and stability range will be discussed and the results will be correlated with those of structurally related materials.

2:45 PM **CC7.4**

MESOMORPHIC CHARACTERIZATION OF NEW LIQUID CRYSTALLINE COMPOUND INVOLVING ESTER-AZO LINKAGES WITH TERMINAL HALOGENATED GROUPS. Chirag J. Vyas, Department of Chemistry, South Gujarat University, Surat, INDIA.

Three series having LC compound were synthesized having ester-azo linkages such as 3'-methyl-4'-(4''-n-alkoxybenzoyloxy)-4-x-azobenzene (where x = -cl, -br and n-alkoxy = 1to6,10,12-alkyl) and 3'-methyl-4'-(4''-n-alkoxybenzoyloxy)-4-x-azobenzene (where x = -f and n-alkoxy = 1to6,8,10,12,16-alkyl). All compounds were characterized by physical methods and to evaluated the effect of terminal and letaral substituted groups on phenyl ring system on mesomorphic properties. The thermal stabilities and mesomorphic properties of this series are compared with other structurally related series.

3:30 PM CC7.5

TRIPHENYLENE AND BEYOND: NEW SYNTHETIC APPROACHES TO DISCOTIC LIQUID CRYSTALS.

Vance Williams, Simon Fraser University, Dept of Chemistry, Burnaby, BC, CANADA.

Triphenylene derivatives have recently received considerable attention in the context of xerography and organic light emitting diodes. While the synthesis of symmetrical triphenylenes is relatively straightforward, derivatives with lower symmetry or with different aromatic cores are much more difficult to obtain. We are investigating new synthetic approaches that allow us to assemble polycyclic aromatic mesogens with a wide range of compositions. We will report on the synthesis of several such derivatives and discuss the liquid crystalline properties of these materials.

3:45 PM CC7.6

ALIGNMENT OF DISCOTIC LIQUID CRYSTALS ON SURFACES AND IN EXTERNAL FIELDS. S. Holger Eichhorn, Dept. of Chemistry & Biochemistry, University of Windsor, Windsor, ON, CANADA.

Since their first preparation in 1977, discotic liquid crystals have been investigated as potential organic photoconductors and semiconductors in technologies such as OLEDs, electrophotography, and catalysis. Other promising applications include liquid crystal displays in which discotic liquid crystals could function as optical compensation layer to improve the viewing angle of displays. All of those applications require the production of thin films of controlled supramolecular order and orientation. While the alignment of calamitic liquid crystals is well established, discotic liquid crystals have successfully opposed many conventional alignment techniques. The alignment of discotic liquid crystals will be reviewed by comparing the interaction of a range of discotic molecular structures with different types of surfaces and external fields. Finally, the alignment properties of unconventional low-molecular-weight and oligomeric discotic liquid crystals will be discussed. In particular, new discotic liquid crystals with hydrophilic and charged side-chains as well as star-oligomers will be presented along with their alignment techniques.

4:00 PM CC7.7

STRUCTURE-PROPERTIES RELATIONSHIPS OF DENDRITIC AND MULTIPODAL LIQUID CRYSTAL MATERIALS BASED ON SILSESQUIOXANE AND CARBOSILAZANE CORES. R. Elsaesser, J.W. Goodby, G.H. Mehl, Department of Chemistry, University of Hull, Hull, UNITED KINGDOM; D. Rodriguez-Martin, R.M. Richardson, H.H. Wills Physics Laboratory, University of Bristol, Bristol, UNITED KINGDOM; D.J. Photinos, Department of Physics, University of Patras, Patras, GREECE; M. Veith, Institute of Inorganic Chemistry, Universitaet des Saarlandes, Saarbruecken, GERMANY.

The research of liquid-crystalline dendrimers is a rapidly advancing field with a focus of research concentrating on the modulation of the phase behaviour by increasing the number of generations and the geometry of the dendritic core structures. [1,2] In this context the investigation of systems containing core structures which are both flexible and have a tendency to microphase separate from the hydrocarbon rich periphery are of interest. The presentation will focus on the investigations of the phase structures of a series of carbosilazane cores with a threefold symmetry decorated with a range of rod-shaped organic groups promoting liquid-crystalline phase behaviour and on materials based on silsesquioxane cores. [3] All of these monodisperse materials with structural features suitable for the formation of microphase separation exhibit the nematic phase as the highest stable liquid crystal phase. At lower temperatures the occurrence of smectic C and columnar phase behaviour could be detected. Of particular interest are the structural parameters and the structure-properties relationships of the low temperature smectic C and columnar phase of these materials for which the results of X-ray diffraction experiments will be presented. The features which determine the phase structure in the columnar phase and in the smectic C phase (eg tilt), which are the size, geometry, structure and flexibility of the inorganic core, the flexibility, branching and length of the spacer linking inorganic cores and the rod-shaped mesogenic groups will be discussed.

References:

- [1] R.M. Richardson, S.A. Ponomarenko, N.I. Boiko, V.P. Shibaev, *Liq. Cryst.* 26, 101, (1999).
- [2] V. Percec, W-D. Cho, G. Ungar, D.J.P. Yearley, *Angew. Chem. Int. Ed.* 39, 598 (2000), J. Barbera, M. Marcos, J.L. Serrano, *Chem. Eur. J.* 5, 1834 (1999).
- [3] R. Elsaesser, G.H. Mehl, J.W. Goodby, D.J. Photinos, *Chem. Commun.* 851, (2000), R. Elsaesser, G.H. Mehl, J.W. Goodby, M. Veith, *Angew. Chem. Int. Ed.* (in press) (2001).

4:15 PM CC7.8

LIQUID CRYSTALLINE NANO-SEGREGATED STRUCTURES IN HYDROGEN BONDED COMPLEXES OF FLUOROALKYL SUBSTITUTED BENZOIC ACIDS. Etsushi Nishikawa, Jun Yamamoto, Hiroshi Yokoyama, Japan Science and Technology Corporation, Yokoyama Nano-Structured Liquid Crystal Project, Tsukuba, Ibaraki, JAPAN.

Formation of supramolecular liquid crystalline structures due to non-covalent driving forces including amphiphilic effects like hydrophilic/hydrophobic effects, excluded volume effects, electrostatic interaction and hydrogen bonding interaction, is one of exciting research areas, where recently more and more researchers are coming together and finding new liquid crystalline structures. We have synthesized hydrogen bonded acid/base complexes between 4,4'-bipyridyl and new benzoic acid derivatives having fluorinated substituent and studied liquid crystalline phase behavior. These complexes are expected to form supramolecular structures owing to hydrogen bonding interaction and fluorophilic/fluorophobic effects resulting in high incompatibility between mesogenic cores and fluorinated moieties. We have found that one of such complex having a flexible long fluorinated moiety exhibits a liquid crystalline cubic phase with Ia3d symmetry, similar to the cubic phase of well-investigated 4'-alkoxy-3'-nitrophenyl-3-carboxylic acids, while complexes with a stiff fluorinated chain do not form cubic phases. Remarkably a complex with end-branched fluoroalkyl chain exhibits an interesting phase behavior e.g. a definite first order smectic A to smectic C phase transition. We will report syntheses and physical properties of the complexes in detail, which are investigated with Differential Scanning Calorimetry, Polarized Optical Microscopy and X-ray scattering technique.

4:30 PM CC7.9SUPRAMOLECULAR LIQUID CRYSTALLINE PHASES IN ORANGE II/ γ -CYCLODEXTRIN SOLUTIONS. David W. Jenkins¹, Mohan Srinivasarao^{1,2} and Jung O. Park¹. ¹School of Textile and Fiber Engineering, Georgia Institute of Technology, GA. ²School of Chemistry and Biochemistry, Georgia Institute of Technology, GA.

Orange II, a water-soluble azo dye, is known to aggregate and eventually form needle-like crystals at concentrations greater than 0.15 M. Upon visual observation, these solutions exhibit a seemingly homogenous, deep red color. However, when equimolar amounts of γ -cyclodextrin (γ -CD) are added to solutions containing Orange II at 0.03 M or higher, the solution's appearance rapidly changes in the sense that a striated pattern is present accompanied by a noticeable increase in viscosity. When viewed between crossed polarizers with an optical microscope, a highly birefringent, "tiger-striped" liquid crystalline texture is observed in the Orange II / γ -CD solution (approximately 0.05 M), which is absent in the solution with only Orange II at the same concentration. The nature of the Orange II (guest) / γ -CD (host) inclusion complex in solution was studied by fluorescence spectroscopy, microscopy, rheology and rheo-optics.

4:45 PM CC7.10

DESIGN, SYNTHESIS AND CHARACTERIZATION OF A NEW CLASS OF SUPRAMOLECULAR DISC-SHAPED MOLECULES BASED ON STRONG INTRAMOLECULAR HYDROGEN BONDING. Shu Wenmiao, Valiyaveetil Suresh, Department of Chemistry, National University of Singapore, SINGAPORE.

Hydrogen bonding is one of the many weak interactions explored recently to develop novel materials using self-assembly approach. We are interested in using hydrogen bonds to finetune the molecular conformation towards optimizing the structure-property relationship. During this talk, we will discuss our approaches to design a novel class of disc-shaped molecules and the full characterization of the liquid crystalline properties.

SESSION CC8: RHEOLOGY/THEORY

Chairs: Alejandro D. Rey and Patrick T. Mather

Thursday Morning, November 29, 2001

Commonwealth (Sheraton)

8:30 AM *CC8.1

MEASUREMENT OF A TUMBLING PARAMETER LESS THAN NEGATIVE ONE IN A CALAMITIC LIQUID CRYSTAL SOLUTION. Julia A. Kornfield, Michael D. Kempe, Maria L. Auad, Department of Chemical Engineering, California Institute of Technology, Pasadena, CA.

Liquid crystalline (LC) materials are commonly used in electro-optic devices that depend on controlling their orientation and optical uniformity. The effect of the polymer on the alignment and mechanical stability of a LC could be improved through the use of a

large molecular weight polymer that is homogeneously dissolved throughout the volume of the device creating a nematic gel. In this study, very large molecular weight side group liquid crystal polymers are dissolved in cyanobiphenyl based liquid crystal such as 5CB. The tumbling parameter for these solutions have been measured and found to have an unprecedented value less than negative one. When lower molecular weight side-group liquid crystal polymers are dissolved in small molecule nematic LCs a larger amount of polymer is necessary to achieve lower values for the tumbling parameter. Our studies on this type of solution have found a flow aligning condition to occur with greater than 7.5% polymer where the tumbling parameter is less than negative one and the steady state angle is close to the velocity gradient direction. The methods used in this study include conoscopic and rheological techniques. The results will be compared with a 2-D version of the Leslie Erickson theory and with theories by Brochard.

9:00 AM *CC8.2

X-RAY SCATTERING STUDIES OF MOLECULAR ORIENTATION IN NEMATIC POLYMERS AND SURFACTANTS IN TRANSIENT SHEAR FLOWS. Wesley Burghardt, Victor Ugaz, Franklin Caputo, Northwestern Univ., Department of Chemical Engineering, Evanston, IL; Weijun Zhou, Julia Kornfield, California Inst. Technology, Department of Chemical Engineering, Pasadena, CA.

Technological applications of liquid crystalline polymers are strongly impacted by changes in average molecular orientation induced by flow fields. We have developed in situ x-ray scattering methods to probe molecular orientation in main chain liquid crystalline polymers under shear. This talk will provide an overview of recent results, drawing upon three classes of materials: 1. Main-chain thermotropic liquid crystalline polymers with flexible spacers. Results will be presented on a polymer, DHMS-7,9, that is known to exhibit director alignment under shear, along with modeling of the polydomain rheology and orientation state using Ericksens Transversely Isotropic Fluid model. 2. Main-chain lyotropic LCP solutions. In contrast to the semiflexible thermotropes, lyotropic solutions of rodlike polymers exhibit director tumbling in shear. Data on molecular orientation in tumbling lyotropes collected in the 1-2 (flow-gradient) plane in a new x-ray shear cell will be presented. 3. Nematic surfactant solutions. Under appropriate conditions, surfactants self-assemble into rodlike micelles that can themselves organize into nematic phases. It has been shown that different surfactant systems form nematic phases that may either exhibit director tumbling or director alignment in shear. We will present data obtained in the 1-2 plane on two nematic surfactants that provide further insights into how molecular orientation evolves in transient flows of polydomain tumbling and aligning nematics.

9:30 AM CC8.3

SEMIFLUORINATED POLYMERIC LIQUID CRYSTALS AS A MECHANISTIC TOOL TO STUDY THE EFFECTS OF INTERFACIAL ENERGIES ON THE ORIENTATION OF LIQUID CRYSTALS. Rakchart Traiphol, Dennis W. Smith, Dvora Perahia, Clemson Univ, Dept of Chemistry and MS&E Program, Clemson, SC.

Spontaneous orientation and fast collective response of ultra thin liquid crystalline (LC) layers to external stimuli without memory effects, together with mechanically stable devices, are some of the major challenges to achieve the next generation of LC devices. The relationship between interfacial energies and structure and dynamics of support layers, which consist of a polymeric liquid crystal and their effects on surface orientation of liquid crystals are presented. We have been utilizing a new semi fluorinated polymeric liquid crystal (PLC), Poly perfluorocyclobutyl, α -methylstilbene, that can be further cross-linked to form oriented networks, as energy controlled surface to achieve different surface orientations and vary the response time to external stimuli. The structure and dynamics of the Polymeric LC itself and its capabilities as orienting media has been explored by X-ray scattering Polarized optical microscopy and neutron reflectivity. The PLC forms a layered mesophase, where the segregation between fluorinated and protonated segments has been a key factor in the formation of lamellar polymeric LCs. Polarized optical microscopy revealed that this polymeric LC exhibit homeotropic behavior at an interface with glass. When further cross-linked, the layered structure is maintained. The crosslinked network has then been utilized as orienting substrate. A well studied LC, 8-biphenyl cyanobenzene which exhibits nematic and smectic A phases, has been cast on top of the PLC. The nematic phase have been found to orient in a homogenous manner where homeotropic alignment has been observed for the smectic phase. Further studies, controlling the ratio of fluorine to hydrogen at the interface to control the interfacial energies and orientation properties and follow the orientational properties, are currently underway.

9:45 AM CC8.4

OPTICAL RHEOLOGY OF NEW LIQUID CRYSTALLINE THERMOSETS (LCTS): INFLUENCE OF SHEAR ON DISCLINATION TEXTURE. Haihu Qin and Patrick T. Mather,

University of Connecticut, Polymer Program and Chemical Engineering Dept., Storrs, CT.

Liquid crystalline thermosets (LCTs) have been under intensive study because of their outstanding mechanical performance and low viscosity during processing. We have successfully synthesized four kinds of nematic bismaleimide thermosets that differ in the nature of a pendant group substitution and that feature a thermally stable nematic phase. Importantly, the pendant groups were found to be efficient in depressing the melting point to a level that allows for flow and cure at reasonably low temperatures. By blending two particular monomers with monofunctional maleimide that we synthesized, N-(4-hydroxyphenyl) maleimide (HPMI), the melting point is depressed and the curing process is postponed to higher temperatures. Such a blend has a processing window amenable to much needed thermal and rheological characterization, particularly the evolution of disclination density during shear flow as cure progresses. While previous work on disclination density measurements during shear flow have revealed a particular scaling of dimensionless disclination density with dimensionless shear rate, the influence of shearing on the disclination density, flow patterns, and molecular orientation through gelation of thermosetting liquid crystals remains unexplored. In this presentation, we will follow a description of material synthesis with a report on the results of optical rheology experiments applied to the ternary blends containing HPMI and two bismaleimide monomers, detailing the influence of shear on disclination density through the gelation.

10:30 AM *CC8.5

THEORY AND SIMULATION OF FIBER TEXTURE FORMATION AND RHEOLOGY OF CARBONACEOUS MESOPHASES. Alejandro D. Rey, Department of Chemical Engineering McGill University, Montreal, Quebec, CANADA.

Carbonaceous mesophases are discotic nematic liquid crystals used as precursors in the manufacturing of high performance carbon fibers using the melt spinning process. To control and optimize the fibers property profile, a better fundamental understanding of fiber texture formation and rheology is required. This paper presents theory and simulation results of fiber texture formation and rheology of model discotic mesophases based on the Landau-de Gennes theory of liquid crystalline materials. The driving forces that control the formation of characteristic carbon fiber textures are discussed in terms temperature and fiber diameter. A simple geometric texture analysis explains the topology of the fibers. It is found that high temperatures favor the radial molecular orientation with a single disclination line along the fiber axis, while lower temperatures favor a bipolar textures with two off-the axis disclination line defects. The main predicted rheological material functions for shear flow, including apparent viscosity and first normal stress difference, are presented and validated with experimental data. The principles that govern rheological structure-property relations are summarized. It is found that at low shear rate, the rheology of carbonaceous mesophases is characterized by shear thinning and a negative first normal stress difference.

11:00 AM CC8.6

MONODOMAIN PRECURSORS AND MESOSTRUCTURE EVOLUTION IN LINEAR AND NEARLY LINEAR FLOWS OF RIGID, ELLIPSOIDAL MACROMOLECULES. M. Gregory Forest, Univ of North Carolina, Department of Mathematics, Chapel Hill, NC; Qi Wang, Florida State University, Department of Mathematics, Tallahassee, FL.

We focus first on bulk steady and time-dependent monodomains that form in the interior of shear and straining flows. We use mesoscopic tensor models derived from Doi kinetic theory to predict the dynamics of monodomains and their phase transitions. Many rich bifurcation phenomena arise from variations in flow rate and molecular aspect ratio, the latter indicating a direct correlation between molecular structure and collective response prior to structure development. We then turn to develop correlations between the various monodomain modes and the evolution of structure in monodisperse nematic polymers between shearing plates.

11:15 AM CC8.7

SHEAR RHEOLOGY FOR DISCOTIC NEMATIC LIQUID CRYSTALS. Dana Grecov and Alejandro D. Rey, McGill Univ., Dept. of Chemical Engineering, Montreal, Quebec, CANADA.

Mesophase pitches are multicomponent discotic nematic liquid crystals, whose characteristic molecular weight is intermediate to low molar mass and polymeric nematic liquid crystals. Mesophase fluids are anisotropic viscoelastic textured materials whose rheological material properties are a function of deformation rates and textural features. Flow modelling of these fluids is performed using a previously formulated mesoscopic viscoelastic rheological theory (Singh and Rey, 2000) that takes into account flow-induced texture

transformations. A complete extra stress tensor equation is developed from first principles for liquid crystal materials under non-homogeneous arbitrary flow. Predictions for simple shear flow, under non-homogeneous conditions for the apparent shear viscosity and first normal stress differences are presented. The predicted relations among rheological properties, shear-induced microstructure, processing conditions and material parameters of discotic mesophases are characterized and discussed. The rheological features are explained using macroscopic orientation effects, which predominate at low shear rate. A systematic investigation of different boundary and initial conditions was performed in order to characterize the relations between the boundary conditions and the rheological material functions for flow-aligning systems at low shear rates. The effect of change in nematical potential on rheological properties of discotic mesophases was also analysed. The model predicts normal stress differences and apparent shear viscosity in agreement with measured values.

11:30 AM CC8.8

FORCED WETTING OF NEMATIC FLUIDS ON CYLINDRICAL SUBSTRATES. Jung O. Park, Georgia Institute of Technology, School of Textile and Fiber Engineering, Atlanta, GA; Mohan Srinivasarao, Georgia Institute of Technology, School of Textile and Fiber Engineering, School of Chemistry and Biochemistry, Atlanta, GA; A.D. Rey, McGill University, Department of Chemical Engineering, Montreal, CANADA.

Liquid coating on a solid substrate is important in many industrial applications. This is usually accomplished by passing the solid object through the fluid of interest at various velocities. At zero velocity the film thickness is zero and at infinite velocity it will be zero as well, since the fluid does not have enough time to form a coating and air will be entrapped at the solid-liquid interface. Thus a maximum wetting speed naturally enters the problem of forced wetting. In this talk, we are interested in addressing the issue of forced wetting of complex fluids. We confine our attention to the special case of the solid substrate having a cylindrical geometry (fiber). In particular, we consider the case of a nematic liquid crystal fluid and polymer solutions being coated onto a monofilament polypropylene fiber. For nematic fluid and a polymer solution above the overlap concentration, the thickness of the initial fluid film coated on the fiber is found to be proportional to the capillary number, Ca , to the first power, where Ca is defined as the ratio of the viscous forces to the capillary force due to surface tension. We present a model to account for the observed thickness dependence on the capillary number.

11:45 AM CC8.9

FLOW BIREFRINGENCE APPLICATION FOR LIQUID CRYSTALLINE POLYMERS INVESTIGATION. Tatiana Filippova, Irina Shtennikova, Institute of Macromolecular Compounds of Russian Academy of Sciences, Saint-Petersburg, RUSSIA.

The term "liquid crystalline" for polymer molecules was introduced into physical chemistry of polymers after recent investigations of hydrodynamic, optical and conformational properties of new rigid-chain polymers served as a basis for the creation of high-strength thermally stable polymeric materials. This paper presents results of flow birefringence and intrinsic viscosity measurements in dilute solutions of some polyamides having a uniquely high equilibrium rigidity of the molecular chain. Study of these macromolecules allowed the general laws characteristic of all rigid chain polymers to be established and the nature of high strength and high thermal stability of polymeric fibers based on the rigid chain polymers to be explained. Subsequent investigations of these compounds showed their ability to form lyotropic LC which served for the development of technology of manufacturing fibres with superhigh modulus. The results of this work showed that uniquely high intramolecular order in the polymer chains can be realized by increasing the equilibrium rigidity of their backbone.

SESSION CC9: MAIN CHAIN/LYOTROPIC SYSTEMS

Chairs: Wesley R. Burghardt and Elliot P. Douglas
Thursday Afternoon, November 29, 2001
Commonwealth (Sheraton)

1:30 PM *CC9.1

STRUCTURE AND PROPERTIES OF LIQUID CRYSTALLINE EPOXIES. Seunghyun Cho, Jianxun Feng, Elizabeth J. Robinson, Elliot P. Douglas, University of Florida, Dept of Materials Science and Engineering, Gainesville, FL.

Liquid crystalline epoxies (LCE's) offer promise as new high performance matrices for advanced composites. LCE's combine the beneficial properties of liquid crystalline polymers with the processing advantages of conventional thermosets. Thus, LCE's have potential as

a new class of thermoset materials with improved chemical resistance, resistance to environmental changes, and enhanced mechanical properties. We have been investigating fundamental aspects of the cure behavior of these materials, as well as the properties that result from the liquid crystalline order. Rheological measurements of gelation show that gelation is independent of conversion as predicted by standard theories and is unaffected by the liquid crystalline phase present. In contrast, the phase changes that occur during cure are dependent on conversion, due to the change in isotropization temperature with molecular length as the cure reaction proceeds. Properties are enhanced due to the liquid crystallinity. For example, fracture toughness is enhanced and moisture permeability is decreased. However, in some cases there is a complicated interplay between the stoichiometry of the epoxy/hardener mixture and the liquid crystalline morphology which can affect the properties.

2:00 PM CC9.2

EFFECTS OF HEAT-TREATMENT AND MOLECULAR ARCHITECTURE ON THE SUB-MICRON MICROSTRUCTURE OF THERMOTROPIC LIQUID CRYSTALLINE POLYMERS. Jennifer Taylor, Stevens Institute of Technology, Dept. of Materials Engineering, Hoboken, NJ; Angel Romo-Uribe Ticona (Celanese AG), Summit, NJ; Matthew Libera, Stevens Institute of Technology, Dept. of Materials Engineering, Hoboken, NJ.

The microstructure of high performance liquid crystal polymer (LCP) fibers has been intensively studied over recent years because of its influence on ultimate mechanical properties. For the study of sub-micron microstructure, a transmission electron-optical technique was developed to spatially resolve the molecular alignment of LCP at length scales as small as 100 nm. Crystallite distribution with respect to the local degree of molecular alignment is examined by coupling the developed technique with dark-field imaging. Experiments are carried out within the limitation of a critical radiative dose beyond which the integrity of the original structure is questionable. The effects of heat-treatment and molecular architecture are studied in two types of fibers composed of 1) hydroxybenzoic acid (HBA) hydroxynaphthoic acid (HNA) and 2) HBA, HNA, terephthalic acid, biphenodiol (COTBP). Strikingly, a bimodal phase is seen in the as-spun HBA/HNA fibers suggesting that a micro-defect structure with length scales on the order of 100-200 nm is present. A highly oriented continuous phase is seen in the heat-treated fibers indicating that the annealing process eliminates the micro-defect structure. A structural gradient within a micron of the fiber surface is found in the heat-treated fibers despite the large shear rates imposed during processing and the tightening of the molecular packing that occurs upon annealing. In some fiber samples, dark-field imaging revealed a lack in observable crystallinity near the surface of the heat-treated HBA/HNA fibers. Comparison of diffraction data collected from heat-treated COTBP fiber, which has a straighter molecular architecture, shows a more tightly packed structure. Larger crystallites are observed in the heat-treated COTBP fibers compared to the heat-treated HBA/HNA fibers although the number of random moieties that compose the former is greater.

2:15 PM CC9.3

LIQUID CRYSTALLINE THERMOSETS FOR COMPOSITE AND ELECTRONIC APPLICATIONS. Theo Dingemans, Erik Weiser, Terry L. St. Clair, Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, VA.

One of the major challenges for NASA's next generation reusable launch vehicles (RLVs) is the design of a cryogenic lightweight composite fuel tank. A potential resin system needs to exhibit a low coefficient of thermal expansion, good mechanical strength and excellent barrier properties at cryogenic temperatures under load. In addition the resin needs to be suitable for a variety of processing techniques, and includes resin transfer molding, resin film infusion and thermoforming. In order to meet these requirements we have designed a wholly aromatic liquid crystal resin, that can be processed between 250 - 300°C. The melt viscosity of the nematic phase can be as low as 10 poise, and after processing the temperature is raised to 350°C to obtain a nematic cross linked network, or thermoset material. In this presentation we will present the chemistry of these materials and discuss their mechanical properties as well as their processing characteristics. Although this material has been developed for cryogenic fuel tank applications, we believe that these high T_g liquid crystal thermoset materials can also be used in a multitude of electronic application such as connector parts, print boards and flex circuits.

2:30 PM CC9.4

PERIODIC DOMAIN WALLS IN ROD-COIL DIBLOCK COPOLYMER FILMS. Ji-Woong Park, Edwin L. Thomas, Massachusetts Inst of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

Two diblock copolymers comprised of polystyrene (PS) and 3-(triethoxysilyl)-propylisocyanate (PIC) were synthesized by anionic polymerization. The total molecular weights of the copolymers were 62K and 223K respectively with PIC rod of 23K for both. The volume fraction of the rods are 37 and 10% respectively. The films were prepared on glass or silicon substrates by casting from the 0.3 ~ 3% polymer solutions in toluene. The block copolymers microphase-separated into smectic layers with periods of about 50 and 120 nm where the rod domain spacing was about 25nm for both copolymers as estimated from AFM images. The domains were separated by a type of Neel reorientation wall where the layers undergo a reorientation of 180 ° across the wall. The walls usually appear along the direction of solvent evaporation. For example, if a ~5 mm droplet of polymer solution is evaporated slowly, parallel walls are formed in the radial direction. The average distance between domain walls varied between 1 ~ 10 microns with uniform over the areas of 50 X 50 μm². Ultra-thin films prepared for TEM also showed similar patterns employing RuO₄ to selectively stain the PS domains. The unidirectional wall formation may be induced by the differential solvent evaporation in the lyotropic smectic liquid crystalline state of the rod-coil diblock copolymer/toluene mixture.

3:15 PM *CC9.5

PHOTOPOLYMERIZATION OF LYOTROPIC LIQUID CRYSTALLINE SYSTEMS: A NEW ROUTE TO NANO-STRUCTURED MATERIALS. C. Allan Guymon, Christopher L. Lester, Univ of Southern Miss, Dept of Polymer Science, Hattiesburg, MS.

Lyotropic liquid crystalline (LLC) materials are ordered liquids consisting of an amphiphile (soaps, surfactants, etc) and a typically aqueous solvent. At sufficient amphiphile concentrations a variety of ordered phases are formed with well-defined nanoscopic pore sizes. Polymerizations of lyotropic liquid crystals (LLCs) and templated polymerizations in LLCs have been of particular interest due to the range of geometries produced by different mesogenic phases. Applications ranging from biomimetic materials to bioseparation and nanocomposite synthesis have been proposed and investigated. The primary reason that these materials have not been used more extensively is the difficulty in retaining and controlling the structure throughout polymerization. In this study the photopolymerization behavior and structural evolution of LLC systems will be detailed utilizing two particular routes to prepare material possessing the desired LLC morphology. One is the polymerization of amphiphiles that are, in and of themselves, polymerizable; whereas, the other utilizes the segregation of monomers in LLC phases of common low molecular mass surfactants. The polymerization behavior of polymerizable surfactants are heavily dependent on the type and degree of LLC structure. Lamellar aggregates polymerize faster than either cubic or isotropic morphologies due to diffusional limitations on the growing polymer chain. Similar trends are observed in the polymerization of polar nonamphiphilic monomers in the various mesophases of common surfactants. Once again the fastest polymerization rates are observed in the lamellar phase when compared to other morphologies. The opposite trend is observed with nonpolar monomers that segregate in the LLC phases. The fastest polymerization rates occur in micellar aggregates and the slowest in lamellar morphologies. Initial studies indicate that to a large extent the original LLC order of these systems is being retained upon photopolymerization. Additionally, polymeric gels synthesized in this fashion have exhibited vastly different and controllable physical properties that could be utilized for improved electrophoretic media, drug delivery applications, ophthalmic adhesives and contact lens materials.

3:45 PM CC9.6

INVESTIGATING THE NEMATIC PHASE OF ROD AND ROD POLYMER SYSTEMS AT AND ABOVE THE ISOTROPIC-NEMATIC COEXISTENCE. Kirstin Purdy, Zvonimir Dogic, Seth Fraden, Martin Fisher School of Physics, Brandeis University, Waltham, MA.

The semiflexible rod-like virus, fd, exhibits liquid crystalline phases when in solution. Small angle x-ray diffraction from a single-domain nematic state has been done and the orientational distribution function of this state has been deduced as a function of concentration and ionic strength. By genetic modification the length of the virus can be modified, and at the isotropic-nematic coexistence, the orientational distribution function of the nematic phase coexisting with the isotropic phase has been measured for mono and bi-disperse solutions of rods of different lengths. The effect of the addition of polymer to the rod solution at the isotropic-nematic coexistence has also been investigated and it was found that the addition of polymer widens the coexistence region significantly, opening the phase diagram for interesting new behavior.

4:00 PM CC9.7

MAGNETIC FIELD INDUCED INSTABILITIES IN NEMATIC SOLUTIONS OF POLYHEXYLISOCYANATES. Mohan Srinivasarao, Georgia Institute of Technology, School of Textile and Fiber Engineering, School of Chemistry and Biochemistry, Atlanta, GA; Jung O. Park, Georgia Institute of Technology, School of Textile and Fiber Engineering, Atlanta, GA.

Magnetic field induced Fredericksz transition in the twist geometry of an initially well aligned nematic solution of a rod-like polymer, polyhexylisocyanate (PHIC), is studied. For the angle between the magnetic field and the unperturbed director, one finds a homogeneous distortion if this angle is less than 45 degree. For angles greater than 45 degree, the reorientation is inhomogeneous, and is coupled to secondary flow, giving rise to spatially periodic structures. The director deformation involves an out-of-plane tilt at short times, which manifests itself as a phase-grating for transmitted polarized light. It is found that the wavelength of the instability is independent of the magnetic field strength in the experimental range, contrary to prior results for nematic solutions of polybenzylglutamate. We postulate that the insensitivity of the wavelength of the periodic structure is due to the nonflow-aligning character of PHIC solutions.

4:15 PM CC9.8

DIFFUSION IN ORIENTED SUSPENSIONS OF RODLIKE PARTICLES. Matthew A. Borthwick, Péter Falus, Adrian Rühm, Laurence B. Lurio, MIT, Center for Materials Science and Engineering and Department of Physics, Cambridge, MA; Simon G.J. Mochrie, Departments of Physics and Applied Physics, Yale University, New Haven, CT.

A close analogue to the model rigid, rodlike colloidal particle is available in needle-like boehmite particles. For rods in a colloidal suspension, the emerging technique of X-ray Photon Correlation Spectroscopy (XPCS) can in principle provide direct measurements of the rods' dynamic structure factor on length scales comparable to their dimensions, while conventional Small-angle X-ray Scattering and Polarized Light Microscopy techniques reveal the degree and direction of orientational ordering. We present the results of XPCS measurements of boehmite rod diffusion in semidilute and concentrated suspensions. The orientational dependence of the dynamic structure factor is used to characterize the diffusion parallel and perpendicular to the rods' axis.