Functional, Nanostructured Materials via the Polymerization of Liquid Crystal Assemblies

D. L. Gin,* Y. Xu, W. Gu, M. Zhou, T. J. Kidd and A. C. Sentman[1]

*University of Colorado, Boulder, Colorado (USA) 80309
Fax: 1-303-492-8595, e-mail: gin@spot.colorado.edu
[1]University of California, Berkeley, California (USA) 94720

New functional, nanostructured organic materials based on the cross-linking of lyotropic (i.e., amphiphilic) and thermotropic liquid crystal (LC) assemblies are presented. In particular, the inverted hexagonal LC phase will be presented as one example of our general approach in using polymerizable lyotropic LC assemblies as a materials synthesis platform. The use of cross-linked inverted hexagonal phases in two newly developed areas of application will be presented: (1) as heterogeneous solid acid catalysts with enhanced performance, and (2) as nanoporous membranes for size-selective molecular separations. Issues pertaining to the contribution of nanoscale architecture to the performance of these functional systems will be highlighted. In addition, our recent work in the design and synthesis of functional, thermotropic LC-based materials will also be presented. We recently designed and synthesized the first example of a polymerizable bent-core mesogen, as a novel approach to generating polar, noncentrosymmetric polymer networks. Bent-core mesogens have recently received a great deal of attention in the LC and organic materials communities; however, functional analogs of these mesogens are unprecedented. Our achiral bent-core LC monomer exhibits a switchable smectic phase and can be successfully aligned and cross-linked in phase to afford ordered, polar polymer networks with bulk pyroelectric properties.
Key words: nanostructure, liquid crystals, polymer, functional, materials

1. INTRODUCTION

There has recently been a great deal of interest in the use of polymerized lyotropic (amphiphilic) and thermotropic liquid crystal (LC) assemblies as functional, nanostructured polymer materials.[1,2] Through appropriate molecular design, LC monomers can be synthesized that present different functional properties into the resulting cross-linked assemblies to afford a variety of nanostructured organic materials with enhanced properties. For example, the inverted hexagonal (H_{II}) phase (Fig.1), which is a close-packed ensemble of inverted cylindrical micelles, has received considerable attention in the functional materials area because of the number of applications possible in the one-dimensional aqueous nanochannels.[1] These ordered, nanoporous assemblies have been used as templates for the synthesis of ordered organic–inorganic nanocomposites.[3-5] More recently, lyotropic LC monomers with Brønsted basic and Lewis acidic headgroups have been synthesized that allow the resulting networks to function as heterogeneous base and Lewis acid catalysts with enhanced reactivity and/or selectivity.[6,7] Cross-linked thermotropic LC phases, on the other hand, have generally been used as polarizers and alignment materials if achiral LC starting materials are employed. If chiral LC starting materials are employed, the resulting ordered, non-centrosymmetric polymer networks have been used as organic transducer materials.[2]

Herein, we present preliminary data on the design and use of cross-linked H_{II} lyotropic LC assemblies in two new application areas: (1) as heterogeneous strong Brønsted acid catalysts (i.e., catalytic organic analogues to zeolites and molecular sieves), and (2) as molecular size-selective nanofiltration membranes. The lyotropic LC monomers that allow us to do this are presented in Fig.2 below. In addition, we also present data on the design of a novel, polymerizable, thermotropic bent-core LC that generates noncentrosymmetric, polar polymer networks with electrical transducer properties that do not require the use of chiral starting materials (Fig.3). The design of the appropriate monomers and the properties of the resulting nanostructured materials are presented.
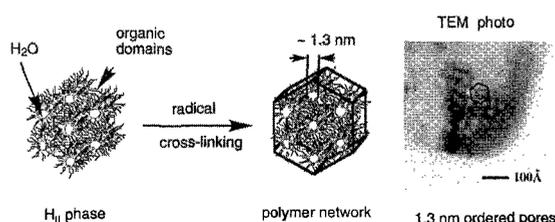

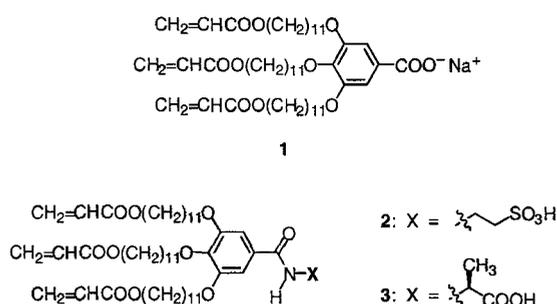Fig.1. Cross-linking of the lyotropic LC inverted hexagonal (H_{II}) phase.

Fig.2. Lyotropic LC monomers that form the H_{II} phase and be cross-linked with retention of LC phase microstructure.
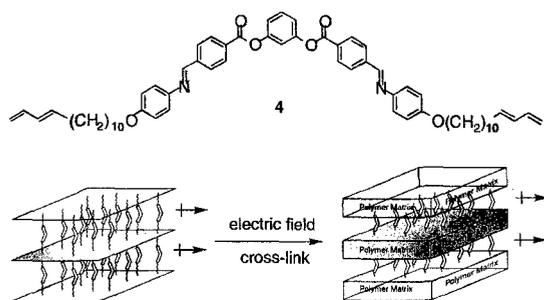

Fig.3. Alignment and cross-linking of polymerizable bent-core LCs to give ordered, polar, noncentrosymetric networks.

2. EXPERIMENTAL SECTION

2.1 Materials and general procedures

All solvents, reagents, and commercial polymers were purchased from Aldrich, Fisher Scientific, or Fluka. Lyotropic LC monomer 1 was synthesized as previously described.[3-5] Sulfonic acid monomer 2 was synthesized by reacting the acid chloride of 1 with 2-aminoethanesulfonic acid and then acidifying the resulting potassium salt on an ion-exchange resin.[8] Amino acid monomer 3 was synthesized by first converting parent monomer 1 to the corresponding acid chloride with $SOCl_2$ and then coupling it with L-alanine in aqueous K_2CO_3. Neutralization of the potassium salt of the resulting amide compound with aqueous HCl affords the desired amino acid derivative.[8] Thermotropic bent-core LC monomer 4 was prepared as described in a recent publication.[9] All syntheses were carried out under a dry argon atmosphere with dry solvents using Schlenk line techniques. ^1H and ^{13}C NMR spectra were acquired using Varian VXR300 and VXR400 spectrometers, respectively. FT-IR analysis was performed using a Perkin-Elmer 1616 series spectrometer. Optical textures were obtained using a Leica DMRXP microscope equipped with a programmable Linkam THMSE 600 hot stage. DSC traces were obtained using a Perkin-Elmer DSC-7. X-ray diffraction (XRD) profiles were obtained using an Inel CPS 120

diffraction system (CuK_α radiation) equipped with a programmable capillary oven. For ferroelectric and pyroelectricity measurements, samples were loaded into and analyzed in Displaytech ferroelectric test cells, consisting of two glass plates coated with ITO electrodes, a polyimide alignment layer, a cell gap of 4 µm, and an electrode area of 0.25 cm^2.

2.2 Photopolymerization of LC mixtures

The H_{II} mixtures were prepared as described previously,[1,8] with 1 wt % 2-hydroxy-2-methylpropiophenone added as a radical photo-initiator. The pasty lyotropic LC samples were then spread onto glass slides or Al sample pans for preparation of the bulk samples and irradiated with 365 nm UV light (ca. 1.8 mW/cm^2) overnight at ambient temperature under an inert atmosphere. For the thin films on polymer supports, a solution of 1 in MeOH was cast onto the polymer supports and photopolymerized in the same manner after allowing the solvent to evaporate. Retention of LC phase architecture in the cross-linked samples was confirmed by XRD before and after photopolymerization. The extent of acrylate conversion was determined by monitoring the loss of the acrylate IR band at 810 cm^{-1} (absorbance mode). Samples of 4 were thermally cross-linked by maintaining the samples in the tilted, layered smectic C (SmC) phase at 135 °C for 16 h. XRD analysis of the resulting material showed retention of the phase order even at temperatures well above the clearing point of the original monomer and down to room temperature. Similar results were observed for samples of 4 that were mixed with 2 wt % of a radical photoinitiator and irradiated with 365 nm UV light for 30 min.

3. RESULTS AND DISCUSSIONS

3.1 Design of strong Brønsted acidic lyotropic LC monomers.

One property that has been fairly elusive in surfactant and lyotropic LC design is Brønsted acidity, which would be very useful for certain catalytic applications. Only a small number of amphiphiles containing a Brønsted acidic headgroup (i.e., $-SO_3H$ and $-PO_3H_2$) are known to exist, and fewer still have been found to exhibit lyotropic LC behavior (typically planar lamellar (L) phases).[10-13] Usually, salts of long chain organic acids behave as surfactants or lyotropic LCs, not the parent acids themselves. Prior work in our group with derivatives sulfonic and phosphonic acid derivatives of H_{II} phase-forming lyotropic LC monomers 1 and 2 revealed these acidic lyotropic LC derivatives only form L or mixed lyotropic LC phases in the presence of water, rather than the desired high-curvature H_{II} phase.[8,12] In order to direct the 2-aminoethanesulfonic acid derivative of 1 (i.e., monomer 2) into a well-defined H_{II} phase, this monomer was blended and copolymerized with the L-alanine derivative of 1 (monomer 3).[8] Amino acid monomer 3 exhibits a strong tendency to form the H_{II} phase in the presence of

DMF, even though it possesses a poor hydrophilic headgroup (i.e., a weakly ionic COOH moiety). IR analysis of the resulting H_{II} phases of **3** revealed the presence of intermolecular amide H-bonding near the headgroup, which appears to help organize the system into an H_{II} phase even with a poor hydrophilic headgroup on the monomers. In the IR, these mixtures exhibit a strong v_{N-H} band at 3338 cm^{-1}, whereas the non-associated amide N–H stretching band is typically at 3440 cm^{-1}. By blending and subsequently photo-cross-linking amino acid monomer **3** with sulfonic acid monomer **2**, strongly acidic H_{II} assemblies can be formed.[8] Mixtures of **2** and **3** as high as 5:1 and as low as 1:5 (mol/mol) were found to form H_{II} assemblies in water.[8] A polymerized 5:1 (mol/mol) mixture of monomers **2:3** exhibits XRD peaks at 41.2, 24.1, 15.6, and 13.8 Å, which is consistent with the 1: 1√3 : 1√7 : 1√9 d-spacing ratio indicative of a H_{II} phase (with the 1√4 peak systematically absent).[1] FT-IR analysis also showed amide H-bonding in the polymerized mixtures (v_{N-H} = 3362 cm^{-1}).[8]

3.2 Preliminary heterogeneous acid catalysis studies

In order to study the reactivity of our nanostructured lyotropic LC acid resins, their performance was compared to commercial Amberlyst-15 and Nafion NR50 acid resins, which are also sulfonic acid-based polymers but amorphous in nature. Using the acid-catalyzed esterification of benzyl alcohol with *n*-hexanoic acid as a test platform (5 mol % solid acid catalyst), it was found that a cross-linked 5:1 mol/mol mixture of **2** and **3** in the H_{II} phase possesses overall reactivity comparable to Amberlyst-15 and Nafion NR50.[14] However, the lyotropic LC acid resin exhibits much higher selectivity for the desired ester product over dibenzyl ether side-product (Fig.4).[14]

A systematic series of control experiments was performed and showed that catalyst nanostructure is the primary factor responsible for the enhanced reactivity and selectivity in the lyotropic LC acid resin systems over the amorphous solid acid resins. It appears that the nanostructured LC acid resin presents a much more uniform local acid microenvironment for reaction compared to the amorphous solid acid resins.[14] Temperature-programmed desorption studies using aniline as a weak base also showed that the LC acid resin has approximately the same relative acidity as Amberlyst-15. Thus, the differences in observed selectivity cannot be attributed to differences in acidity between the resins. Studies are currently underway to explore the scope of reactions in which they demonstrate enhanced reactivity or selectivity over commercial solid acid resins.
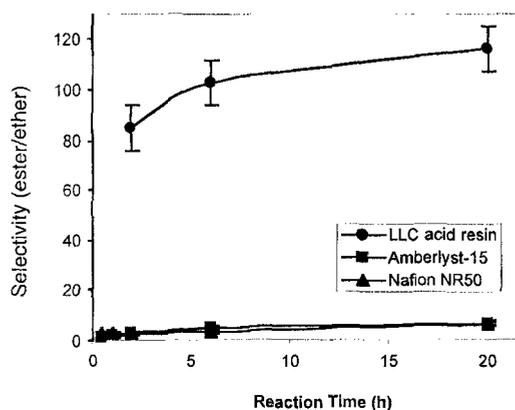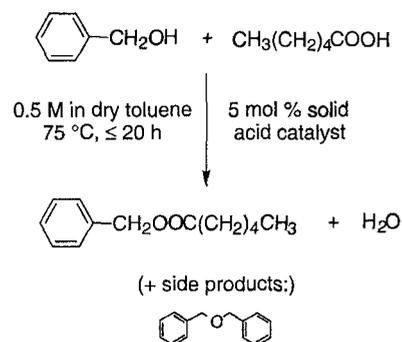

Fig.4. Ester/ether product selectivity for the reaction of benzyl alcohol with 1-hexanoic acid in dry toluene at 75 °C catalyzed by various solid acid resins (5 mol % H^+ loading).

3.3 Preliminary nanofiltration studies with the cross-linked H_{II} phase

Aside from their use as catalytic organic analogues to molecular sieves, an obvious potential application of the cross-linked H_{II} phase based on its microstructure is aqueous nanofiltration. The uniform, ordered aqueous nanochannels in these materials would be ideal for the removal and separation of dissolved molecules in water based on their diameters (ca. 1.3 nm monodisperse). In order to test the basic viability of this idea, thin films (0.3 μm thick) of monomer **1** were cast from solution on commercially available polymer supports (polyacrylonitrile (PAN) and polysulfone (PSf) ultraporous membranes) that exhibit good pure water permeability in the pristine state.[15] XRD analysis of the coated film samples showed that the characteristic low-angle XRD peaks for the H_{II} phase can be seen superimposed on top of the wide angle XRD peaks from the semi-ordered polymer supports.

Using this configuration, pure water fluxes on the order of 0.79 kg/m^2/h were observed through the composite membrane at 60 psi applied pressure. When an aqueous solution of a cationic rigid blue dye (Alcian Blue pyridine variant, 1.0 mg/mL) with a molecular diameter (~2.02 nm) slightly larger than the 1.3 nm nanopores is forced through the membrane, the blue dye is

completely filtered out. No trace of the blue dye is present in the filtrate, as confirmed by UV-vis spectroscopy. When a water solution of a red dye (Phenol Red, 1.0 mg/mL) with a diameter (0.96 nm) which is smaller than the nanopores is forced through the membrane, the red dye is able to pass through with only a small reduction in concentration. Finally, when a 1/1 (w/w) water mixture of Alcian Blue pyridine variant and the smaller Phenol Red dye (a green colored solution) is forced through the lyotropic LC-coated membrane, the resulting filtrate was found to only contain Phenol Red by UV-visible analysis, consistent with molecular size selectivity.[15] Current work is focused on control experiments and challenging these nanoporous membranes with rigid probe molecules of different charge character and size to confirm their molecular sieving properties.

3.4 Design of a polymerizable, ferroelectric, achiral bent-core LC

Bent-core (i.e., "banana"-shaped) LC) have recently emerged as one of the most significant discoveries in the area of ferroelectric LC.[16] These polar, chevron-shaped molecules have the ability to form switchable ferro- and antiferroelectric LC phases, even though the molecules are achiral.[16] There is currently a great deal of interest in bent-core mesogens because they offer certain advantages over traditional rod-like chiral SmC mesogens as switching materials in ferroelectric LC displays,[17] and as building blocks to ordered, noncentrosymmetric polar polymer materials (e.g., for nonlinear optical, piezoelectric, and pyroelectric applications)[18-20] because enantiomerically pure or enriched starting materials are not required. Polymerizable or cross-linkable bent-core LCs would afford the ability to stabilize/trap the switchable mesophases. However, it is very difficult to design and synthesize polymerizable derivatives of bent-core mesogens that retain the desired LC properties. For example, Ikeda and co-workers recently made a diacrylate derivative of a bent-core mesogen.[21] However, this compound was found to be completely non-mesogenic,[21] suggesting sensitivity or incompatibility of this bent-core platform to conventional polar, bulky polymerizable groups in the tails. In order to overcome this molecular design problem, we successfully prepared a polymerizable bent-core LC (4) with the same central core by using polymerizable alkyl 1,3-diene tails.[9] The modular alkyl 1,3-diene tail system was developed by our group for use on sensitive LC platforms.[22] This linear tail system closely resembles the shape and nonpolar character of normal *n*-alkyl tails prevalent on LCs, while retaining good radical polymerization activity.

Compound4 was found to exhibit well-defined enantiotropic LC behavior without premature diene polymerization.[9] Upon cooling from the isotropic melt at 5 °C/min, 4 initially enters a stable LC phase with a fan-type optical texture at 143 °C, which persists down to 128 °C. XRD

analysis of this mesophase revealed a single diffraction peak at 49.6 Å, consistent with a layered smectic phase with a layer spacing of that magnitude. Based on the calculated length of 4 of 54 Å, the observed layer spacing is consistent with a tilted SmC phase with a tilt angle of 23°, assuming little or no tail interdigitation. This LC phase was found to be ferroelectric in nature. The resulting current vs. applied voltage curve of 4 at 135 °C (Fig.5) exhibits a single peak during voltage ramp-up and ramp-down, with a maximum polarization of 210 ± 30 nC/cm^2 and a rise time of 190 μs.
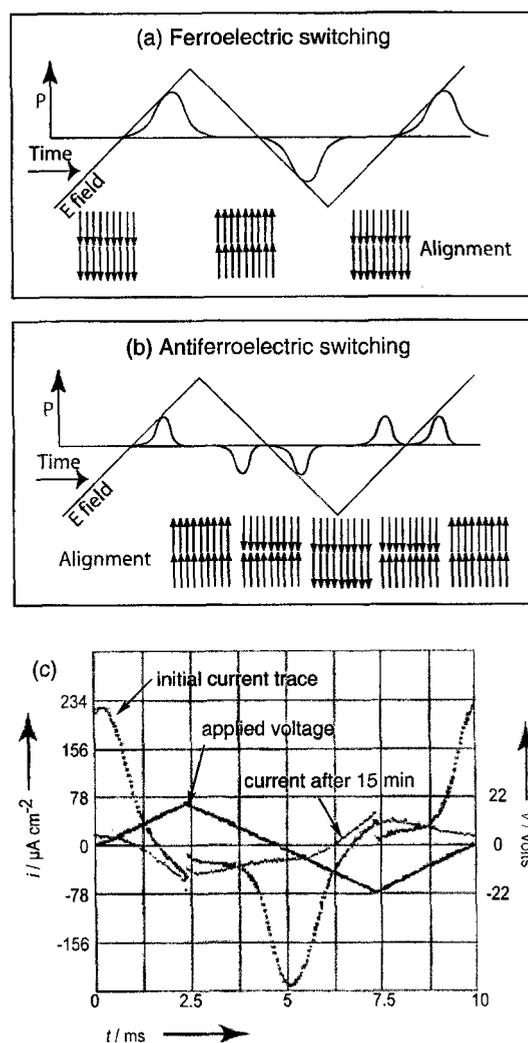

Fig.5. Figures showing (a) expected ferrolelectric switching behavior, (b) expected anti-ferroelectric switching behavior, and (c) observed electrical switching behavior of a sample of aligned and cross-linked 4 in the SmC phase.

This single-peak response is characteristic of ferroelectric behavior not anti-ferroelectric behavior.[23] Based on these structural and electrical switching data, 4 most likely adopts a ferroelectic SmC_SP_F or SmC_AP_F phase configuration.[23] Both of these LC phase configurations can be aligned by an applied

electric field. Unfortunately, the magnitude of the observed polarization and the switching behavior steadily decrease over several minutes due to accelerated thermal cross-linking under the oscillating electric field. Upon cooling below 128 °C, 4 forms an anisotropic phase with a blue fan-type texture that does not respond to applied pressure, consistent with the so-called solid B_4 phase.[16] Below 101 °C, 4 forms a crystalline phase.

3.5 Transducer properties of cross-linked, aligned samples of bent-core mesogen 4

In order to demonstrate that the bent-core monomer can be aligned and cross-linked to form an ordered, polar noncentrosymmetric network, a sample of 4 was placed in an 4 μm thick ITO cell and thermally cross-linked in the SmC phase for 3 h under a static 10 V electric field. Retention of order in the polymerized sample was confirmed by observation of the optical texture even down to room temperature. Pyroelectric measurements were performed on the sample to confirm the presence of a permanent net polarization. As can be seen in Fig.6, the polymer exhibits a well-defined electrical response with changes in temperature, indicative of an aligned material with a permanent net polarization.[24] In contrast, a sample of 4 cross-linked in the absence of an applied field yields no pyroelectric response.

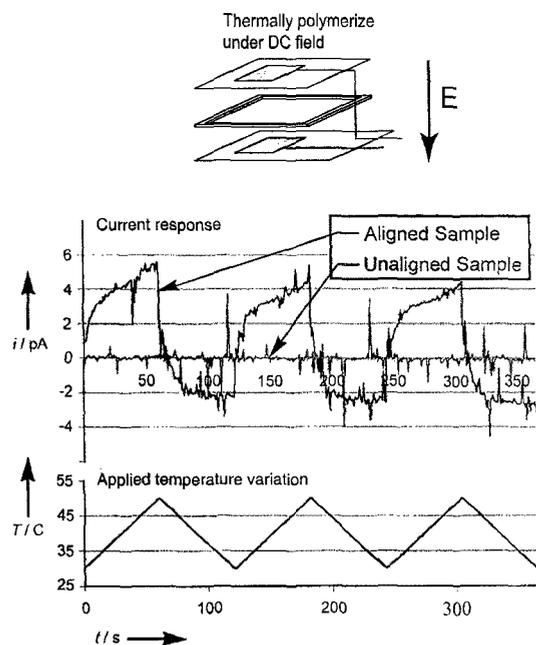Fig.6. Pyroelectric response of a partially aligned, cross-linked sample of bent-core mesogen 4 in the SmC phase.

The calculated pyroelectric coefficient for the material is 4.8 μC m^{-2} K^{-1},[9] which is on par with values observed for noncentrosymmetric Langmuir-Blodgett films (10–20 μC m^{-2} K^{-1}) and poled polymers (30–40 μC m^{-2} K^{-1}).[24,25] The optical texture of 4 aligned and cross-linked in the field shows that it is still a polydomain sample.[9] If methods can be developed for surface-

aligning bent-core mesogens, samples with more uniform alignment under applied field and better transducer properties should be possible.

4. SUMMARY

Cross-linked H_{II} assemblies can be used as heterogeneous strong Brønsted acid catalysts with enhanced selectivity via appropriate lyotropic LC monomer design and templating with an appropriate lyotropic LC structure-directing agent. Preliminary results also show that polymerized H_{II} phases can also be applied as coatings onto commercial polymer membranes to generate nanoporous composite polymer membranes that exhibit molecular sieving properties. We have also designed and synthesized the first example of a cross-linkable bent-core mesogen. This achiral mesogen adopts a SmC phase with switching behavior consistent with a ferroelectric phase. When aligned and cross-linked in the LC state under a static electric field, ordered polymer networks with a net polarization are generated that exhibit pyroelectric properties.

5. ACKNOWLEDGMENTS

6. REFERENCES

[1] D. L. Gin, W. Gu, B. A. Pindzola and W.-J. Zhou, *Acc. Chem. Res.*, **34**, 973 (2001).

[2] S. M. Kelly, *J. Mater. Chem.*, **5**, 2047 (1995).

[3] H. Deng, D. L. Gin, and R. C. Smith, *J. Am. Chem. Soc.* **1998**, *120*, 3522 (1998).

[4] D. H. Gray and D. L. Gin, *Chem. Mater.*, **10**, 1827 (1998).

[5] J. H. Ding and D. L. Gin, *Chem. Mater*, **12**, 22 (2000).

[6] S. A. Miller, E. Kim, D. H. Gray and D. L. Gin, *Angew. Chem. Int. Ed.*, **38**, 3021 (1999).

[7] W. Gu, W.-J. Zhou and D. L. Gin, *Chem. Mater,*, **13**, 1949 (2001).

[8] W.-J. Zhou, W. Gu, Y. Xu, C. S. Pecinovsky and D. L. Gin, *Langmuir*,**19**, 6346 (2003).

[9] A. C. Sentman and D. L. Gin, *Angew. Chem. Int. Ed.*, **42**, 1815 (2003).

[10] Krishnamurti and R. Somashekar, *Mol. Cryst. Liq. Cryst.*, **65**, 3 (1981).

[11] G. Klose, A. Petrov, F. Volke, H. Meyer, W. G. Foerester and W. Rettig, *Mol. Cryst. Liq. Cryst.*, **88**, 109 (1982).

[12] S. R. Hammond, W.-J. Zhou, D. L. Gin and J. K. Avlyanov, *Liq. Cryst.*, **29**, 1151 (2002).

[13] R. K. Paul, V. Vijayanathan and C. K. S.

Pillai, *Synth. Met.*, **104**, 189 (1999).

[14] Y. Xu, W. Gu and D. L. Gin, *J. Am. Chem. Soc*, submitted for publication.

[15] D. L. Gin, M. Zhou and R. D. Noble, "Liquid Crystal Nanofilter Membranes," Provisional U.S. Patent No. 60/416,077; USA; October 3, 2002.

[16] G. Pelzl, S. Diele and W. Weissflog, *Adv. Mater.*, **11**, 707, (1999) and references therein.

[17] A. W. Hall, J. Hollingshurst and J. W. Goodby "Handbook of Liquid Crystal Research", Ed. by P. J. Collings and J. S. Patel, Oxford University Press, New York (1997) pp. 17–70.

[18] R. A. M. Hikmet, *Macromolecules*, **25**, 5759 (1992).

[19] M. Trollsås, C. Orrenius, F. Sahlen, U. W. Gedde, T. Norin, A. Hult, D. Hermann, R. Rudquist, L. Komitov, S. T. Lagerwall and J. Lindström, *J. Am. Chem. Soc.*, **118**, 8542 (1996).

[20] J. Oertegren, G. Andersson, P. Busson, A. Hult, U. W. Gedde, A. Eriksson and M. Lindgren, *J. Phys. Chem. B*, **105**, 10223 (2001).

[21] C. Keum, A. Kanazawa and T. Ikeda, *Adv. Mater.*, **13**, 321 (2001).

[22] B. P. Hoag and D. L. Gin, *Macromolecules*, **33**, 8549 (2000).

[23] D. M. Walba, E. Körblova, R. Shao, J. E. Maclennan, D. E. Link, M. A. Glaser and N. A., "Anisotropic Organic Materials - Approaches to Polar Order", ACS Symposium Series 789, Ed. by R. Glaser and P. Kaszynski, American Chemical Society, Washington, DC (2001) pp. 286–281.

[24] T. Kamata, J. Umemura, T. Takenaka, N. Koizumi, K. Takehara, K. Isomura and H. Taniguchi, *Jpn. J. Appl. Phys.*, **33**, 1074 (1994).

[25] R. W. Whatmore and R. Watton, "Infrared Detectors and Emitters: Materials and Devices, Electronic Materials 8", Ed. by P. Capper and C. T. Elliott, Kluwer Academic, Boston (2001) p 118.