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13. ABSTRACT A series of amphiphilic low molecular weight and polymeric compounds showing bulk ferroelectric liquid crystalline behavior was investigated as monolayers at the air/water interface and as thin films on solid substrates. The polymers investigated contained siloxane backbones and pendant liquid crystalline side chains. Investigations at the air/water interface used the Langmuir technique. The molecular packing, morphology, pressure relaxation, and thermodynamics of mixing were investigated. Investigations of thin films utilized Langmuir Blodgett techniques and layer-by-layer deposition to build defined multilayers. X-ray techniques were subsequently utilized by staff at NRL to quantify film thickness, molecular structure, and superlattice stability. Additional films were deposited on microelectrode arrays and switching studies were performed at NRL.			
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**"Structure and Physical Properties of Monolayers and Multilayers of Liquid
Crystals Showing Bulk Ferroelectric Properties"**

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A homologous series of side-chain liquid crystalline homopolymers, copolymers, and the corresponding low molecular weight side chains were investigated. All having the same mesogenic group (which generally led to ferroelectric liquid crystalline behavior in the bulk), the materials differed in the length of the alkyl spacer which decoupled the mesogen from the polymer backbone and the density of side chain substitution on the poly(siloxane) backbone. The molecular structure was such that most of the materials behaved as insoluble amphiphiles. The approach taken was to investigate the behavior of the compounds as monolayers at the air/water interface, and subsequently using Langmuir Blodgett transfer, to investigate well defined thin films and superlattices deposited on solid substrates.

By systematic studies with a Langmuir Trough coupled with complementary techniques such as Brewster Angle Microscopy, electronic spectroscopy and others, a description of the molecular ordering as a function of molecular concentration at a water surface was developed. With the low molecular weight side chains, the ultimate packing as well as onset of long range in-plane tilt orientational order was dominated by the mesogenic part of the molecule and was independent of the alkyl spacer length. Upon compression from gas-like 2-D densities, several phases were seen by microscopy. The observed polymorphism was strongly influenced by the subphase temperature, and transition temperatures were considerably depressed compared with the bulk, but following the trends seen with classical 3-D first order phase transitions. The polymers showed simpler polymorphism, and ultimate packing dominated by the siloxane part of the molecule. Due to their architecture, the homopolymers had inherent sufficiently high 1-D positional order (chemical substitution of mesogen-containing side chain every other atom along the polymer backbone) that the polymer chains aggregated, condensed, and solidified as the organic solvent evaporated from the interface, leaving monolayer-thick poorly formed 2-D crystals or anisotropic glasses at the water surface. In other words, local solvation forces were insufficient to break up cohesive interactions between the side chains at temperatures near ambient. As the side chain substitution density decreased, solvation and entropic effects were sufficient to lead to a 2-D fluid with no in-plane long-range tilt orientational order; however, with certain systems, applied lateral pressure sufficiently increased the mesogen packing density that pressure-induced birefringence indicative of a phase transition involving orientational order was observed. At high applied surface pressures, the copolymers also showed viscoelastic character, which was investigated. Finally, 2-D thermodynamic investigations of copolymers with their low molecular weight side chains were performed. Free energy calculations indicated miscibility over a wide range of compositions and applied pressures. Subsequent Brewster Angle Microscopy studies indicated that the miscibility was dominated by the steric fit of the low molecular weight species improving packing of the mesogens and likely partially dewetting the polymer backbone.

Defined thin films were prepared by the Langmuir Blodgett technique and investigated by X-ray diffraction and other complementary methods in collaboration with the group of Dr. Shashidhar at NRL. Quantitative transfer of copolymers to hydrophobic silicon over a range of applied pressures indicated that well-defined films could be formed, but may also be an indication of metastable character of the adsorbed polymer liquid crystals. X-ray reflectometry indicated that uniform, flat films were obtained, however further analysis indicated that interdigitation of mesogens between layers was likely. Further investigations of two component superlattice structures deposited with an alternate layer LB trough indicated that significant molecular mixing occurred quickly after the deposition process. Further analysis, largely at NRL, attempted to investigate the electron density profile normal to the substrate surface. Finally, the LB technique was used to deposit defined thin films of the copolymer on an interdigitated microelectrode array substrate. Subsequent investigations at NRL indicated that ferroelectric switching was observed. This switching was observed to occur at a faster rate and at lower potential than thicker films of the same material in a conventional liquid crystal switching cell.