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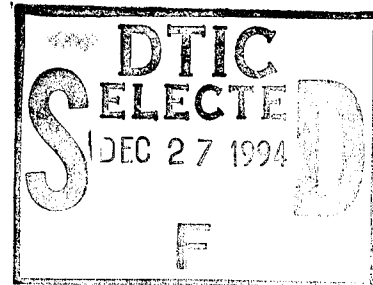
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Molecular Object Liquid Crystals:
An Approach to New Materials



by

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Submitted for presentation at the American Chemical Society meeting

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13. ABSTRACT (Maximum 200 words) The one aspect of the field of liquid crystals which remains largely undeveloped is the supermolecular dimension of self ordering oligomers and polymers. In our opinion it is here that many of the potential opportunities exist for truly novel materials. An example of super-molecular chemistry is the use of liquid crystallinity as a tool to form molecular object polymers of persistent shape. This will be illustrated through the bulk synthesis of two-dimensional (2D) polymers which may be described as nanometer-thick flat objects. One exciting observation has been the formation of "macroscopic" films from the layered assemblies with two completely different surfaces which reflect directly the chemical nature of opposite surfaces of the "molecular" assemblies. Other systems give rise to films with remarkably stable nonlinear optical properties and high thresholds for laser damage. A different example to be described by the lecture is that of discrete molecular aggregates of rodcoil polymers which form superlattices and melt into liquid crystalline phases. These systems should be of interest in the manufacturing of patterned surfaces for a wide variety of technologies.					
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Molecular Object Liquid Crystals: An Approach to New Materials

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The last two decades have seen the rapid development of the field of liquid crystal polymers (LCPs) and it is presently known that ordered polymeric fluids—nematic, smectic, and cholesteric—occur within a remarkably broad range of structural chemistry. Among their unusual properties is an enormous reorientational susceptibility under weak external forces which has no analogue among common polymers. A few examples from our own work involving surface, magnetic, and electric fields are cited here (1-3). Facile field orientation is clearly of importance in the area of polymer processing, however, many of the physical properties of LCPs in the solid state can be surprisingly similar to those of polymers which melt into isotropic media. The one aspect of the field which remains largely undeveloped is the supermolecular dimension of self ordering oligomers and polymers. In our opinion it is here that many of the potential opportunities exist for truly novel materials.

An example of supermolecular chemistry with liquid crystal polymers is to consider the formation of molecular object polymers, defined as macromolecules with well defined persistent shapes which survive solid-liquid state transformations. In pursuing this objective, we have used the liquid crystalline behavior of small reactive molecules as a tool to construct objects with limited conformational degrees of freedom. If the well defined shape of these molecular objects is anisometric we can expect to observe liquid crystalline behavior in the macromolecular objects themselves. Our first effort in this area has involved the bulk synthesis of two-dimensional (2D) polymers which can be regarded as molecular sheets of thicknesses on the order of a few nanometers (4). We have observed fluid smectic phases in 2D polymers developed in our laboratory and some of them exhibit unusual properties as solid materials. Some systems of 2D molecular architecture have been found to give rise to films with remarkably stable nonlinear optical properties and high thresholds for laser damage. Others have been found to form spontaneously "macroscopic" multilayer films by solvent casting with surface properties identical to those of analogous Langmuir-Blodgett monolayer films. This is interpreted as the result of macroscopic stacking of the planar assemblies and can therefore be considered materials with self organized surfaces.

A very exciting recent result along the lines of surface properties has been the spontaneous formation of "macroscopic" films with two completely different surfaces which reflect directly the chemical nature of opposite surfaces in the molecular assemblies themselves. The contact angles of water on opposite surfaces of these "macroscopic" films are 96° and 25° implying that hydrophobic and hydrophilic surfaces form spontaneously in this material. This observation has been made using the mesomorphic oligomer shown below. This oligomer contains a middle block containing unsaturated bonds which can crosslink to produce flat molecular objects,

Optical Microscopy of Phenolic Rodcoil

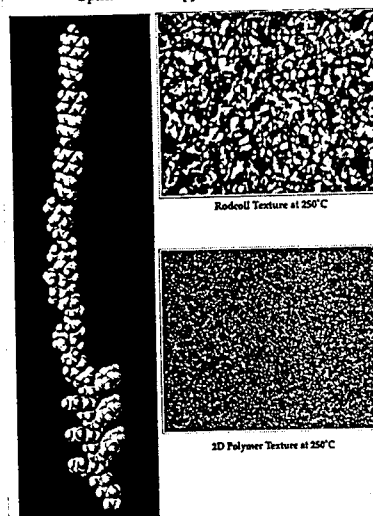
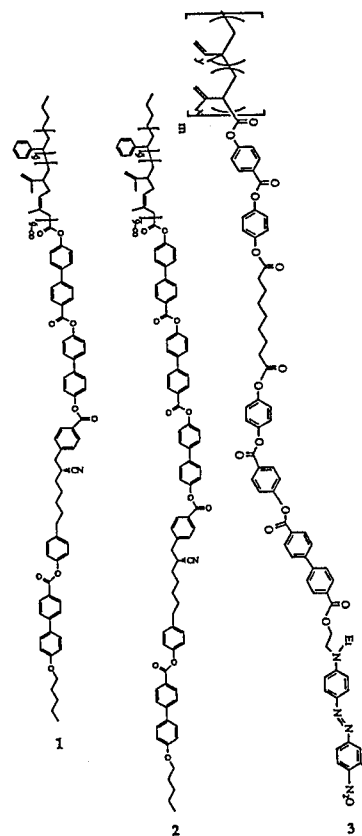


Figure 1

It is also possible to consider molecular object polymers other than those with 2D architecture. We have explored the route to such objects with higher molar mass rodcoil precursors. Three interesting structures synthesized in our laboratory are shown below,



The rod-like segment of 1, for example, exhibits a cholesteric phase of very high thermal stability (400°C). Attachment of the coil segment destroys this phase and opens the opportunity to create covalently-structured elongated objects (large diameter rods) which in principle should form nematic phases. This seems to be supported by our experiments. Rodcoil 3 with approximately 79 structural units in the coil segment and prepared by living polymerization (polydispersity 1.05) is an interesting example of polymeric mesogen aggregation leading to a supermolecular structure. These molecules have been discussed recently in two publications from our group (5,6). The transmission electron micrograph of figure 2 shows these longer rodcoils (relative to 1 and 2) aggregate to form a hexagonal superlattice of discs in which the light regions contain rod-like segments. The corresponding electron tomogram (middle) shows the aggregates are discs and not cylinders as observed in flexible block copolymers. The electron micrograph on the right hand side (top) shows a thicker section containing several layers of superlattice. The model at the bottom of the figure explains how these aggregates stack in three dimensions based on our electron microscopy and electron tomography studies.

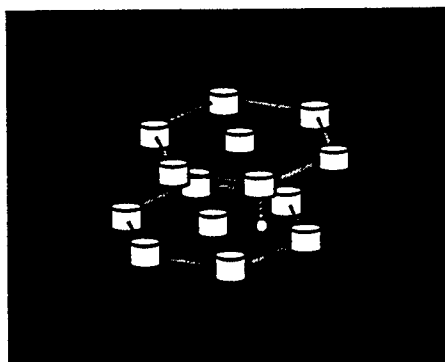
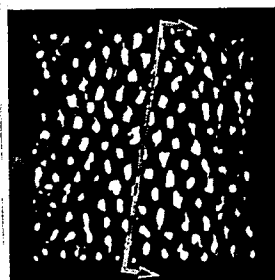
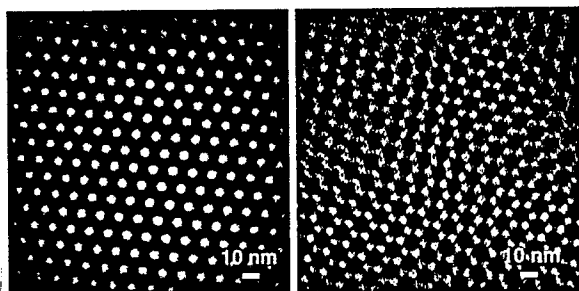


Figure 2

Most interestingly, the material organized in these superlattices melts into a liquid crystalline fluid at temperatures where the molecular aggregates are still stable and some long range order of the discs prevails. This is based on the fact that annealing at temperatures well above the solid to liquid transition is necessary to induce the observed organization after experimental samples are quenched to room temperature. These systems have great potential in the manufacturing of patterned surfaces for a wide variety of technologies, including nanolithography and self organization of sensors.

ACKNOWLEDGEMENTS

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- 7) L. H. Radzilowski and S. I. Stupp, to be submitted for publication.

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