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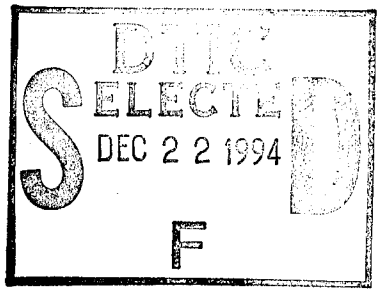


# Materials with Self Organized Surfaces: 2D Polymer Assemblies

by

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Submitted for presentation at the American Chemical Society meeting

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**13. ABSTRACT** *(Maximum 200 words)*

Our laboratory has developed the concept of "bulk" synthesized 2D polymers through self assembly of reactive oligomers into layered structures. The products from these supermolecular reaction schemes are high molar mass flat macromolecules which in fusible systems retain their shape during solid to liquid phase transitions. We describe here a new system based on nanophase separated rodcoils functionalized at one terminus with the objective of producing 2D polymers with two chemically different surfaces. One surface of the macromolecule contains closely packed methyl groups and it is therefore highly hydrophobic, whereas the other is hydrophilic being composed of phenolic or carboxyl functions. Interestingly, solvent cast "macroscopic" films of the layered assemblies develop spontaneously one hydrophobic surface and a very sticky one which is readily wet by water. This observation is possibly the first example of a bulk material with self organized surfaces, an important objective for the exploitation of self assembly in manufacturing. Such materials would open the door to concepts such as self organized interfaces for composite materials, self organized tapes and membranes with chemically defined surfaces, as well as tubes with chemically defined lumina.

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Materials with Self Organized Surfaces:
2D Polymer Assemblies

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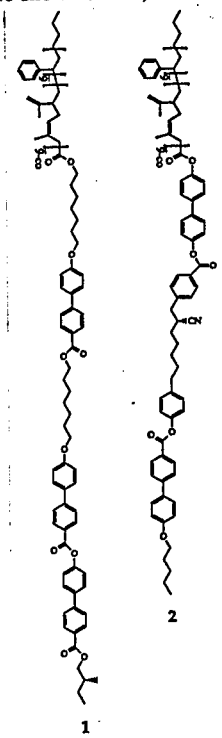
Over the past few years our laboratory has developed the concept of "bulk" synthesized 2D polymers which derive from the self assembly of reactive oligomers into layered structures (1,2). We have four distinct methodologies in place, molecular recognition among chiral oligomers, nanophase separation of rodcoil block structures, self assembly of molecules into layered hairpins, and the very recently developed approach involving hydrogen bonding among comb polymers. The products from these supermolecular reaction schemes are high molar mass flat macromolecules which in fusible systems retain their shape during solid to liquid phase transitions. In the first system developed (1), 2D polymers were formed which can stack at room temperature into single crystal assemblies and upon melting retain their flat molecular architecture as demonstrated by the smectic nature of their fluid state.

The second generation of precursors were rodcoil structures (2) which self assemble into layers containing three sub-layers, each a few nanometers in thickness. The general tendency of rodcoil structures to nanophase separate is clearly established in a recent publication from our group using molecules which are of much higher molecular weight than those used to synthesize 2D polymers (3). A typical construction contains a protecting sub-layer, a reactive sub-layer in which crosslinking occurs within a 2D space confined by the protecting sub-layer, and a third rigid sub-layer functions as the shape-granting skeleton of the molecular object. Typical rodcoil structures synthesized in our laboratory are shown below,



1



2

The work described here focuses on the surface properties of rodcoil-derived 2D polymers. We prepared solution cast films of 2D polymer from rodcoil precursor 1 and measured the contact angle of water on their surfaces. As a control we prepared Langmuir-Blodgett films using a similar rodcoil and also measured contact angles. We found that both the solution cast film and the LB film have identical contact angles in both value and uniformity. Furthermore we were able to change the stacking direction of 2D polymers on solution cast films depending on the substrate used. These results are summarized schematically in figure 1.

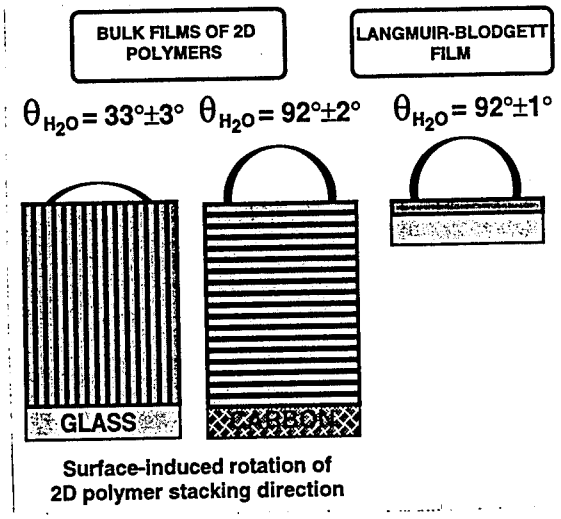
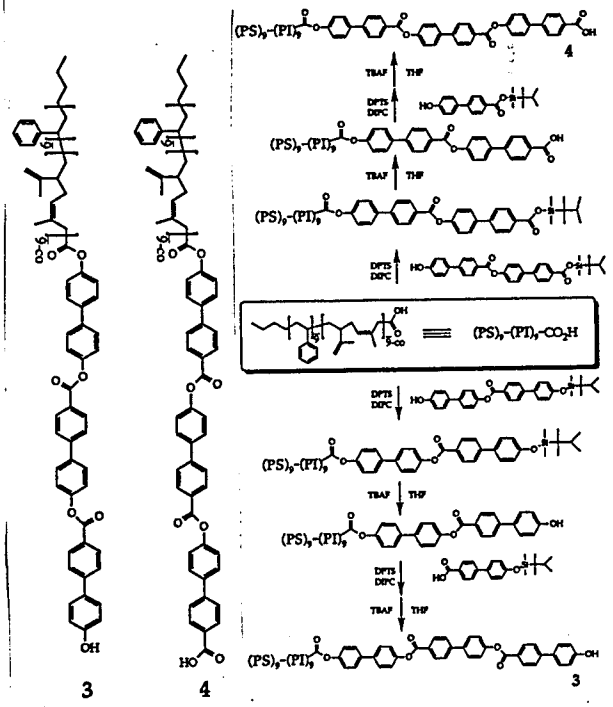



**Figure 1**

The results obtained on surface properties of solvent cast films suggest the concept of materials with self-organized surfaces. Macroscopic stacking of these 2D assemblies with a single stacking direction would generate films with surfaces having the same chemical structure present on the surfaces of the 2D molecular objects.

We introduce here rodcoil structures 3 and 4 functionalized at one terminus with the objective of producing 2D polymers with two chemically different surfaces. One surface of planar macromolecules prepared with these precursors would contain closely packed methyl groups and would therefore be highly hydrophobic, whereas the other one would be hydrophilic being composed of phenolic or carboxyl functions. These rodcoils are synthesized using the following scheme,




Both rodcoil molecules exhibit smectic phases and reveal exotherms in differential calorimetry scans fingerprinting the crosslinking reaction necessary to form 2D polymers. Most importantly, following the reaction the product obtained flows as a birefringent melt with extremely high thermal stability. This clearly indicates the product is not a crosslinked network but ensembles of planar molecular objects.

We have studied so far the surface properties of **5** and found that solvent cast "macroscopic" films of these molecules develop spontaneously one hydrophobic surface and a very sticky one which is readily wet by water. Shown below is a schematic representation of the film's ideal molecular structure and of the results obtained on its surface properties.

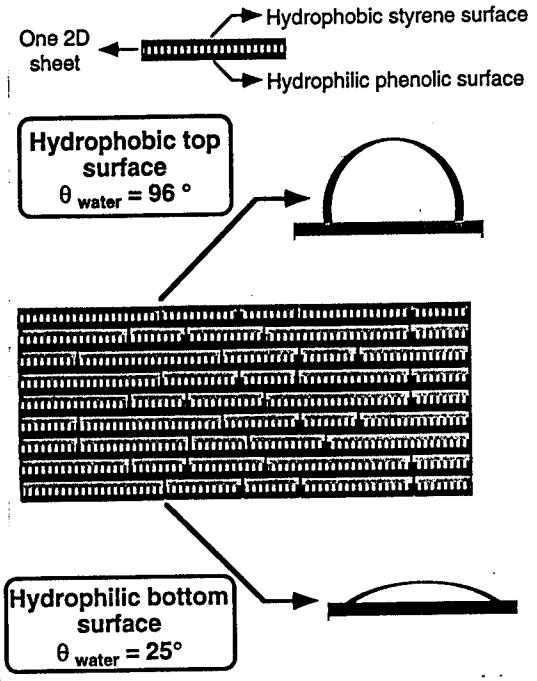



**Figure 2**

This observation is possibly the first example of a bulk material with self organized surfaces, an important objective for the exploitation of self assembly in manufacturing. Such materials would open the door to concepts such as self organized interfaces for composite materials, self organized tapes and membranes with chemically defined surfaces, as well as tubes with chemically defined lumina.

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