Supramolecular Rigid-Rod Polymers as Ionically
Conducting Membranes

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In the search for high performance polymer materials for polymer electrolyte fuel cells and batteries, effective ion transport is of key importance. The development of polymer electrolytes has mostly resulted from material evolution, rather than strategic material design. By tailoring the molecular architecture, it is possible to optimize the microstructure in order to promote ionic conductivity. The self-organization properties of liquid-crystalline polymers are one way of achieving such structures.

A family of liquid-crystalline polymers based on sulfonated forms of poly(p-phenyleneterephthalamide (PPTA) display supramolecular aggregation.¹⁻³ The properties, however, are sensitive to the placement of the sulfonic acid group. Sulfo-PPTA (Figure 1a) forms aggregates in water, with the nematic phase observed at concentrations around 10wt%. Hydrogen-bonding between the sulfonic acid and the amide group result in gel formation. Sulfo-invert-PPTA (Figure 1b) displays nematic behavior above 1wt%. Although supramolecular aggregation occurs, there is no gel formation due to the increased distance between the sulfonic acid and amide groups. Sulfo²-PPTA (Figure 1c), with twice the number of sulfonic acid groups, exhibits the smallest aggregates but is the most soluble in water. The liquid-crystalline properties are also both temperature and concentration dependent. In contrasting the behavior of these three polymers, supramolecular aggregates formation appears to be related to π - π interactions between the *un-substituted* aromatic rings.

Further alignment of liquid crystalline polymers can be achieved by applying an external force, either by mechanical shear or with the use of electric or magnetic fields. Viale et al.^{1,4} have demonstrated shear and magnetic alignment of Sulfo-PPTA and Sulfo-invert-PPTA respectively. Thus it is expected that such techniques can be implemented to manipulate the polymer microstructure to achieve optimum ion conduction.

The inherent water solubility of these polymers provides an advantage for proton conductivity, but at present, imposes limitations on the mechanical properties of the materials. To be viable for electrolytic devices, the materials must be mechanically stable under the operating conditions. Methods for stabilizing the materials are being investigated. The conductivities however, are comparable to that of Nafion under similar experimental conditions. In this presentation, the most recent findings will be discussed and the applicability of liquid-crystalline polymers for batteries and fuel cells addressed.

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References

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Figure 1. Sulfonated poly(p-phenyleneterephthalamides: a) Sulfo-PPTA, b) Sulfo-invert-PPTA, and c) Sulfo²-PPTA. The sulfonic acid protons can also be exchanged with lithium ions.