PREPARATION OF PROTON EXCHANGE MEMBRANES AND LITHIUM BATTERIES FROM MELAMINE-CONTAINING ORMISILS

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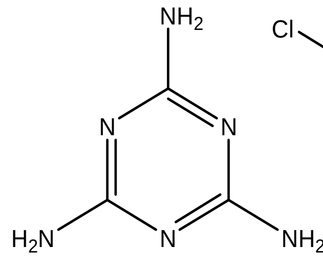
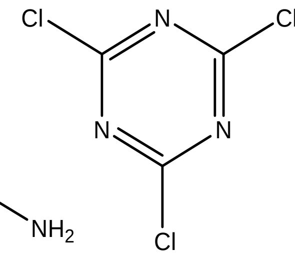
Our laboratory has recently reported a series of rod-coil polymers for lithium batteries that display dimensionally stable films with good ionic conductivity.[3] The rod segments consist of rigid linear and branched polyimides and the coil segments are polyethylene oxides (PEO). It has been proposed that good mechanical and transport properties are due to phase separation between the rod and coil segments. It was also observed that increased branching and molecular weight lead to increased conductivity.

The following study was undertaken to assess the effects of phase separation in polyalkylene oxides connected by melamine linkages. Melamine was chosen as the linking unit because it provides a branching site, cation binding sites to help ionic transport between polymer chains, and the opportunity for self assembly through hydrogen bonding. Polymers were made by the reaction of cyanuric chloride with a series of amine-terminated alkylene oxides (Jeffamines®, Huntsman).[4] A linear polymer was first made, followed by reaction of the third site on cyanuric chloride with varying ratios of monofunctional Jeffamine and (3-aminopropyl)triethoxysilane. The lithium trifluoromethane sulfonamide-doped polymers are then crosslinked through a sol-gel process to form freestanding films. A phase separation between the inorganic/aromatic network and the coil segment occurs by the nature of the crosslinking reaction. Conditions that were varied include the oxygen to lithium ratio, molecular weight of the PEO backbone (MW = 600, 2000), MW of the side chains (MW= 1000, 3000), and ratio of PEO to silane in the side chain. Initial results have shown mechanically strong films with lithium conductivities on the order of 2 x 10^{-5} S/cm at ambient temperature. Our best results have been observed by using a 2000 MW poly(ethylene oxide) in the polymer backbone and a 1:1 ratio of 1000 MW PEO:silane on the branching site. We found the optimum oxygen:lithium ratio to be 21:1.

In a separate study, organically modified silanes (Ormosils) that contain sulfonic acid derivatized melamines have been incorporated into proton exchange membranes. The membranes are made by reaction of the primary amine groups of various ratios of melamine derivative and difunctional Jeffamine (MW = 2000) with the epoxide group of (3-Glycidyloxypropyl)trimethoxysilane. The films were then cross-linked through a sol-gel process. Resulting sulfuric acid doped films are strong, flexible, and have proton conductivities on the order of 2 x 10^{-2} S/cm (120°C, 25% relative humidity). Our best results have been observed when films contain 60% PEO and 40% sulfonated melamine.

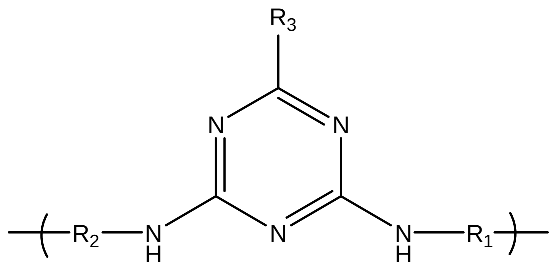


Melamine



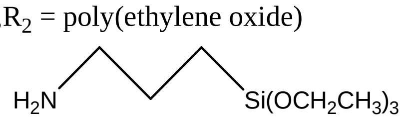
Cyanuric Chloride

Scheme 1. Lithium Battery Polymers

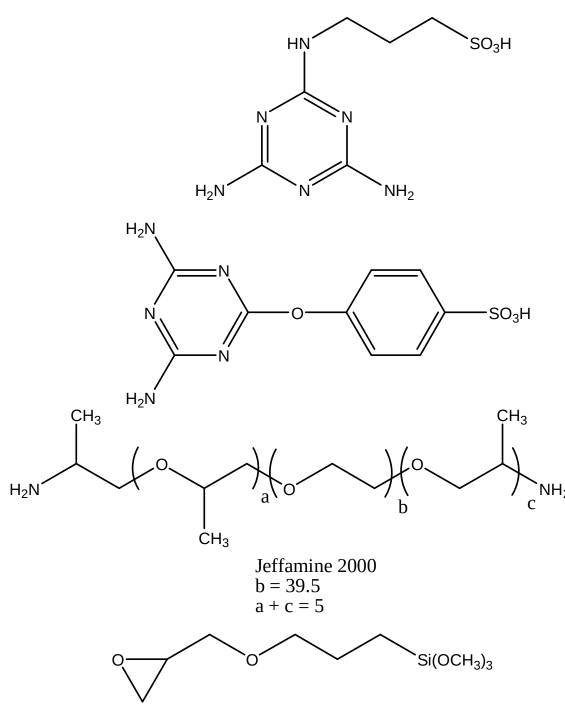


R_1,R_2 = poly(ethylene oxide)

R_3 = PEO,



Scheme 2. Fuel Cell Monomers



1. Employed by Ohio Aerospace Institute
2. Employed by QSS Group, Inc.

3. M. A. B. Meador, V. A. Cubon, D. A. Scheiman, W. R. Bennett; *Chem. Mater.*, **15**, 3018-3025 (2003).
4. J. Z. Jan, B. H. Huang, J.-J. Lin, *Polymer*, **44**, 1003-1011 (2003).