290u Nanoparticle-Induced Desilylation of Substituted Acetylene Polymers to Prepare Gas Separation Membranes with Exceptional Chemical Resistance

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Many membrane applications require separation of organic vapors from permanent gases.[1] Such separations include the purification of natural gas and hydrogen recovery in refineries. Potential membrane candidate materials include substituted polyacetylenes, which have permeation and selectivity properties that are desirable for organic vapor removal from permanent gases. For instance, the mixed gas n-butane/CH4 selectivity is 48 and the pure n-butane permeability is 80,000 barrer in poly(1-trimethylsilyl-1-propyne) (PTMSP).[2] Moreover, both n-butane/CH4 selectivity and n-butane permeability increase when surface treated fumed silica nanoparticles have been dispersed in the polymer.[2] The utility of substituted polyacetylenes for these applications is limited by poor membrane chemical stability towards organic liquids and vapors. PTMSP, poly[1-phenyl-2-[p-(trimethylsilyl)phenyl]acetylene] (PTMSDPA), poly(4-methyl-2-pentyne) and poly(methylacetylene) readily dissolve in industrially relevant organic components (toluene, hexane, etc.) that could be present in industrial feed streams to the membrane.[3-6] However, polyacetylenes such as poly(acetylene) and poly(diphenylacetylene) (PDPA) are insoluble in most organic solvents.[6,7] Currently, the only reported method for making PDPA is to desilylate PTMSDPA using trifluoroacetic acid, so these chemically stable materials cannot be prepared as membranes via conventional processing protocols. Although the resulting material is chemically stable, the permeability and n-butane/permanent gas selectivity decrease significantly.[8] We discovered a method for preparing partially desilylated polyacetylene nanocomposites. Basic nanoparticles (e.g., MgO), when dispersed in polymers such as PTMSDPA, remove trimethylsilyl groups from the polymer backbone. Small molecule compounds were also used to demonstrate the desilylation reaction. Then, the polyacetylenes were partially desilylated using nanoparticles. When possible, the products of the reaction were characterized using XPS, FTIR, and NMR. Gas transport properties were characterized. Interestingly, nanoparticle-desilylated polymers are insoluble in common hydrocarbon solvents, and they have higher gas permeability than the polymers before desilylation. This discovery permits the preparation of high permeability, high selectivity, chemically stable, reverse-selective membranes.

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