

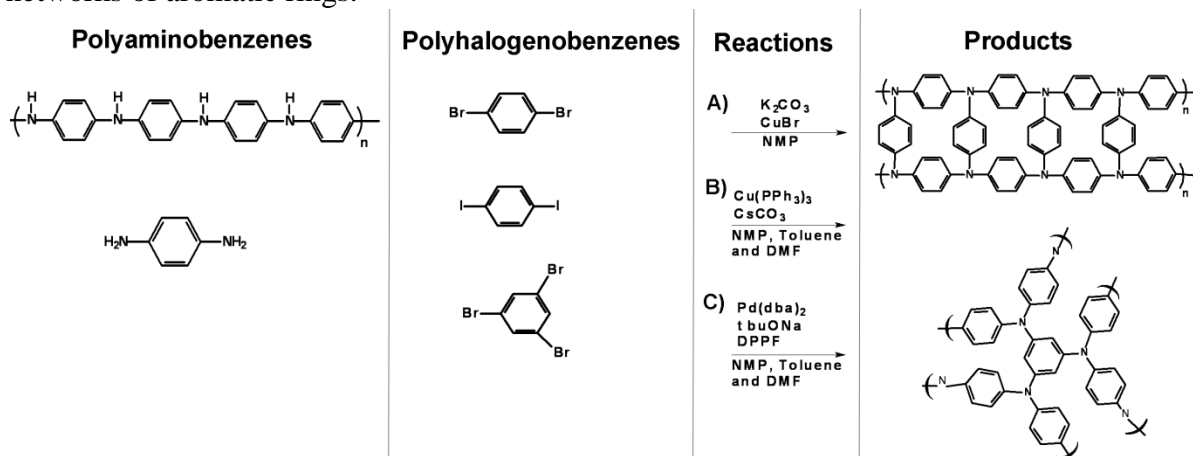
Nanoporous Polymer Networks: Potential Adsorbents for Hydrogen Storage

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Scientific Thrust Area. The use of hydrogen as a fuel and the development of a hydrogen economy have been suggested as means to decrease our dependency on petroleum products worldwide. However, before this vision can be realized, a number of very significant technological hurdles need to be overcome such as the development of safe, compact, and high capacity storage systems for molecular hydrogen. A wide variety of approaches including carbon nanostructures [1], carbon/metal nanostructures [2], carbon aerogels [3], metal-organic frameworks [4], and numerous metal hydrides [5] have been tested to achieve this goal. The first generation of porous polymers found suitable for this application included hypercrosslinked polystyrene-based copolymers with high surface areas exceeding 2000 m²/g [6-10]. For example, our material of this type enabled storage of up to 5.5 wt.% hydrogen [6]. However, this high capacity was only achieved at a temperature of 77 K and a pressure of 80 bar, i.e. at conditions that are difficult to manage in a car. These conditions are necessary though since the enthalpy of adsorption (ΔH) was only 4-6 kJ/mol. Theoretical calculations indicate that ΔH in the range of 15-20 kJ/mol is needed to achieve hydrogen adsorption at room temperature [11]. One option to reach this level is to develop polymeric materials with new chemistries.

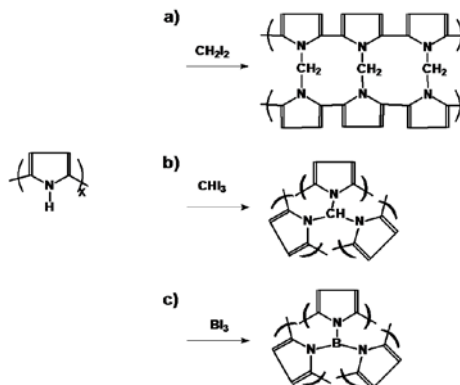
Research Achievement. In this study, we targeted networks consisting of aromatic rings held in a porous framework by the smallest possible linking groups. The simplest approach to forming networks consisting of aromatic rings starts with precursors containing reactive groups directly attached to the aromatic ring such as aryl halides and amines, which can be coupled using a variety of synthetic routes. For example, the Ullman (A, B) and the Buchwald reaction (C) can be used to perform such couplings. As shown in scheme below, we applied both of these syntheses to the crosslinking of aryl amines with polyhalogenobenzenes to form amine-linked networks of aromatic rings.



Low pressure hydrogen adsorption isotherms demonstrate that our new network of aromatic rings with a BET surface area of about 250 m²/g adsorb more hydrogen at low pressures of up to 1.2 bar than hypercrosslinked polystyrenes with surface areas more than seven times as large. In addition, these materials exhibit Langmuir surface areas calculated using H₂ adsorption isotherms larger than those calculated using the BET equation and nitrogen adsorption isotherms.

This unexpected observation and the high hydrogen adsorption at low pressures suggest high H₂-polymer interaction energies in our networks of aromatic rings. Indeed, the enthalpy of adsorption of hydrogen found for most of our polymers is 14 kJ/mol. However, polymer prepared from 1,4-diaminobenzene crosslinked with tribromobenzene features a ΔH of hydrogen adsorption as high as -18 kJ/mol. This value is promising for the adsorption even at room temperature. Another interesting feature of these polymers is that the actual hydrogen storage capacity for most of the networks of aromatic rings in this study exceeds the capacity that could be realized in nitrogen-accessible nanopores. This finding indicates that our networks of aromatic rings include pores that are too small to allow penetration of nitrogen but large enough for hydrogen adsorption.

Using reactions shown in the scheme that are similar to those depicted above, we also prepared nanoporous polypyrroles. The diiodomethane-crosslinked polypyrrole, which exhibits very small pores and remarkably high surface areas of 732 m²/g, reversibly adsorbs 1.6 wt% hydrogen at 77 K and 4 bar. In order to explore the effect of the number of bonds linking the crosslinker with polypyrrole on the porous properties of our materials, we used iodoform. This reaction produced material which reversibly adsorbs 1.3 wt% H₂ at 77K and 4 bar and exhibited surface area of 436 m²/g. A complete novelty is crosslinking of polypyrrole with boron atoms. This process required significant experimentation in order to optimize the choice of both solvent and base. We again prepared polymer with nanoporosity enabling exclusion of gas molecules larger than hydrogen based on their size. This result is important since it may enable selective adsorption of pure H₂ from its mixtures with other gases that are typically present in the industrially produced hydrogen.



Future Work. While we have now available nanoporous polymers with chemistries providing high enthalpy of hydrogen adsorption, their surface areas need to be increased significantly. Optimization of the reaction conditions using methods of combinatorial chemistry and new catalysts to accelerate the crosslinking are expected to provide the high surface area polymers.

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