HYDROGEN GAS SEPARATIONS USING A HIGHLY MICROPOROUS POLYMER

Chad L. Staiger, Chris J. Cornelius & David R. Wheeler

Chem & Biotechnologies/Micro Analytical Systems Departments
Sandia National Laboratories, PO Box 5800, MS 0888
Albuquerque, NM 87185-0888 e-mail: clstaig@sandia.gov

Introduction

Increasing interest by governmental entities to realize a future in which hydrogen is a dominating fuel source has spurred great interest in all aspects of hydrogen production, storage and utilization. Currently, hydrogen is produced by reforming fossil fuels (natural gas, oil, and coal). The capital and energy intensive reforming step does not produce pure hydrogen, but a mixture of light gases (syngas). Current methods for hydrogen purification/separation include pressure swing adsorption or cryogenic technologies. While these technologies work well, membranes for hydrogen separation represent an attractive alternative to further reduce the costs of hydrogen production. Recently, McKeown et al reported a series of highly porous polymers (1) which have good thermal and mechanical stability.1,3 The bisspiroindane ring system induces an extreme amount of contortation into the polymer backbone. Rotational freedom in the polymer backbone is limited because of the ladder structure. The contortion and rigidity allow a high degree of void volume to exist. High polymer void volumes typically lead to increased gas throughput (permeability), however selectivity can be negatively affected.1,3 We have prepared one of these microporous polymers and evaluated its permeability and selectivity for use in hydrogen and other light gas separations.

Scheme 1. Preparation of spiro polymer 1.

Experimental

All solution NMR spectra were recorded on a Bruker Avance DRX spectrometer. Proton spectra were obtained at an operating frequency of 400 MHz. Infrared spectra (FTIR) were obtained using a Perkin Elmer Model 1600 FTIR spectrometer. Thermal analyses were performed on a Perkin Elmer TGA 7 and a TA 2010 DSC. Size exclusion chromatography was performed using a Polymer Labs PL-GPC210 operating at 40 °C equipped with RI detection. The mobile phase was THF at a flow rate of 1.00 mL/min. Separation was affected using two 300 × 7.5 mm PLgel 5 µm mixed-C columns. Calibration curves were generated using polystyrene standards. Surface area and pore analysis obtained by N2 adsorption at 77 K using a Quantachrome Autosorb 6B. Membrane permeabilities were obtained using a home made permeation apparatus described elsewhere.5 Reagents and anhydrous grade solvents (Aldrich or Acros) were used as received unless otherwise stated.

Poly(3,3',3''-tetramethyl-1,1''-spirobisindane-5,5',6,6'-tetrol-co-2,3,5,6-tetrafluorophthalonitrile) (1). A mixture of K2CO3 (6.91 g, 50.0 mmol), 3,3',3''-tetramethyl-1,1''-spirobisindane-5,5',6,6'-tetrol (3.40 g, 10.0 mmol) and 2,3,5,6-tetrafluorophthalonitrile (2.00 g, 10.0 mmol) were stirred in DMF (50 mL) at 80 °C for 72 h. The heterogeneous solution was cooled to room temperature and then poured into rapidly stirred H2O (300 mL). The solid was collected by vacuum filtration and washed with MeOH (2 × 100 mL). The bright yellow solid was taken up in a minimum amount of THF (~25 mL) and precipitated into rapidly stirring MeOH (400 mL). The polymer was collected by vacuum filtration and dried under vacuum (0.1 mm Hg @ 50 °C) to give 4.07 g (88%) of a bright yellow solid. 1H NMR (400 MHz, CDCl3) δ6.90-6.70 (br s, 2H), 6.60-6.30 (br s, 2H), 2.70-1.90 (br m, 4H), 1.70-0.80 (br m, 12H). IR (KBr) ν 2959, 2235, 1538, 1314, 1011 cm⁻¹. GPC: Mw=90,010; Mw=30,800; PDI = 2.92. BET surface area = 818 m²/g.

Film preparation of spiro polymer 1. Spiro polymer 1 (550 mg) was dissolved in CH2Cl2 (15 mL) and filtered (2 µm glass microfiber). The filtered solution was pouring into a flat Petri dish (12 cm dia.) and then placed in a vacuum desiccator with the gas inlet open to the atmosphere. The solution was allowed to evaporate for 4 days. The dish was removed and the clear yellow film released from the glass using H2O.

Results and Discussion

A prototypic microporous polymer 1 was prepared by heating a DMF solution of 3,3',3''-tetramethyl-1,1''-spirobisindane-5,5',6,6'-tetrol and 2,3,5,6-tetrafluorophthalonitrile at 80 °C for 72 h in the presence of K2CO3 (Scheme 1). After cooling the solution, polymer 3 was precipitated by pouring into water. The bright yellow polymer was further purified by dissolving in THF and reprecipitated by pouring into methanol. Yields of the polymer 1 after drying under vacuum were generally in excess of 85%. Size exclusion chromatography revealed a molecular weights typically greater than 100,000 (Mw) with a PDI's of 3 to 3.5. The thermal stability of spiro polymer 1 was investigated using DSC and TGA under an atmosphere of nitrogen. The DSC was unremarkable with the exception of a decomposition event with an onset of 395 °C. There was no discernable glass transition (Tg) present. The TGA showed the onset of weight loss at 484 °C and by 800 °C had only lost 55% of the original mass. The high thermal stability of spiro polymer 1 can be attributed to its ladder structure, since two bonds must be broken to cleave the polymer backbone.

Surface area analysis of spiro polymer 1 by N2 adsorption/desorption revealed a highly porous structure. The surface area, calculated from BET, was 818 m²/g. The pore volume at 0.99 relative pressure (P/P0) was 1.06 cc/g. The pore size distribution (BJH Desorption) suggested a significant number of pores between 20 and 30 Å. The microporosity of the material (pore size < 20 Å) is currently being evaluated.

Spiro polymer 1 films were cast into free standing films (~60 µm thick) from CH2Cl2 and then subjected to gas permeability

measurements. Single gas permeabilities were measured for helium, hydrogen, carbon dioxide, oxygen, nitrogen and methane at 35 °C using the time lag method (Table 1). Spiro polymer 1 showed high permeability for each gas, with H₂ having the highest permeability of 1763 Barrers. In addition, permselectivities were particularly good for O₂/N₂, H₂/CH₄ and CO₂/CH₄ with respect to there permeabilities.

**Table 1. Single gas permeabilities and ideal permselectivities of spirom polymer 1.** Permeabilities are the average of two different films.

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<th>Permeability at 35 °C (Barrers)</th>
<th>Ideal Permselectivity</th>
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<tr>
<td></td>
<td>He</td>
<td>H₂</td>
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<tr>
<td>He</td>
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**Conclusion**
A highly contorted ladder polymer was prepared and evaluated for gas transport. The membrane permeabilities were consistent with those of a polymer containing large amount of free volume. While permeabilities were high, permselectivities were also good, particularly for O₂/N₂, H₂/CH₄ and CO₂/CH₄ separations. Manipulating polymer functionality or structure in this class of polymers may allow for increased permeabilities and permselectivities.

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**References**