

Asymmetric Membranes by Wet Phase Inversion of Phenylated Polyphenylene

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ABSTRACT: Asymmetric membranes of phenylated polyphenylene were prepared by wet phase inversion. The polyphenylene ($M_n = 62$ kDa, PD = 2.3) was prepared by Diels–Alder polymerization of 1,4-bis(tetraphenylcyclopentadienonyl)benzene with 1,4-diethynylbenzene at 180°C. Solvents and non-solvents were experimentally identified and solvent : non-solvent systems were evaluated by the quality of the resulting membranes. Cyclohexanone/*n*-butanol (88 : 12) as solvent and *n*-butanol as the non-solvent were found to afford the best asymmetric membranes with minimal defects. Membranes (20–30 μm thick) from coagulating 11.5 wt % polyphenylene from cyclohexanone/*n*-butanol in *n*-butanol baths exhibited 250–300 nm, non-porous skins overlaying 20–30 μm of open-celled, spongiform structure. Due to a relatively high glass transition temperature of 370°C, the phenylated polyphenylene membranes retained their porosity to 200°C higher than polysulfone asymmetric membranes. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: phenylated polyphenylene; asymmetric membrane; phase inversion; Diels–Alder polymerization; morphology; scanning electron microscopy; tensile strength

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INTRODUCTION

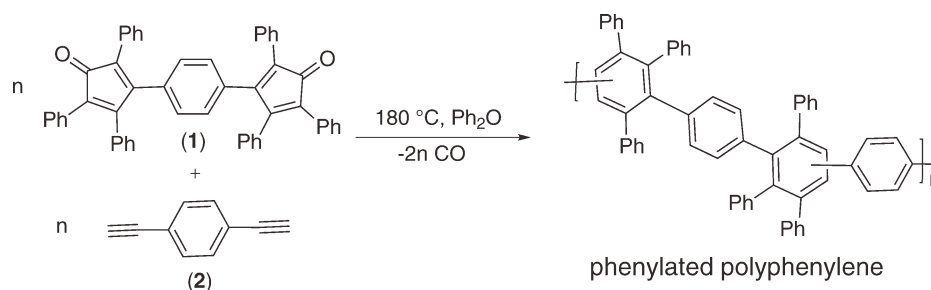
First prepared in the late 1960s, asymmetric polymer membranes are composed of a thin, nonporous layer that controls the selectivity and a relatively thick porous layer that provides mechanical support.¹ Asymmetric membranes are prepared by “wet” phase inversion of a polymer from a thin coating of solution with immersion in a non-solvent.^{2,3} Most asymmetric membranes are made of cellulose acetate or polysulfones, but any polymer that will undergo phase inversion from a thin film of solution with quenching in a non-solvent can be used.³ The nature of the polymer used will affect the gas permeability and selectivity through the dense layer of the membrane and the integrity of the porous structure as a function of temperature, pressure, and plasticization. High performance polymers, such as polysulfones,⁴ polycarbonates,^{5,6} and polyimides,^{6,7} are well suited for asymmetric membranes due to their stability at higher temperatures.

We have been studying gas permeabilities through phenylated polyphenylenes⁸ and their chemical modification to afford fluorine-free, polymer electrolyte membranes for fuel cell applications.^{9,10} These high-molecular weight polymers are prepared by the copolymerization of 1,4-bis(tetraphenylcyclopentadienonyl)benzene with 1,4-diethynylbenzene (Scheme 1).¹¹ The reaction proceeds by the Diels–Alder cycloaddition of a cyclopentadie-

none group with a ethynyl group followed by the cheletropic elimination of carbon monoxide to form an aromatic ring connecting the monomers. The aromatic nature of the polymer backbone provides excellent chemical and thermal stability and introduction of pendant phenyl groups along the polymer breaks up intramacromolecular interactions allowing the polymers to remain soluble and thermally processable.¹² In this article we report the first asymmetric phenylated polyphenylene membranes, prepared by “wet” phase inversion from cyclohexanone : *n*-butanol, their morphology examined with scanning electron microscopy, and characterized by mechanical and thermal analyses. After identifying that cyclohexanone/*n*-butanol : *n*-butanol would be used as the solvent : nonsolvent pair, 25- μm -thick membranes were prepared and compared with asymmetric polysulfone membranes we prepared by phase inversion from *N*-methylpyrrolidinone (NMP) : water.

EXPERIMENTAL

Solvents were obtained from Fisher Scientific (Fairlawn, NJ) and Sigma-Aldrich Chemical Co (St. Louis, MO) and were used as received. 1,4-Bis(tetraphenylcyclopentadienonyl)benzene was prepared from the condensation of 2,2'-(1,4-phenylene)bis(1-phenylethane-1,2-dione) with diphenyl acetone according to literature procedure.⁹ 1,4-Diethynylbenzene was purchased from



Scheme 1. Diels–Alder polymerization of 1,4-bis(tetraphenylcyclopentadienonyl)-benzene (1) and 1,4-diethynylbenzene (2) leading to polyphenylated polyphenylene.

TCI (Portland, Oregon) and was sublimed before use. Polysulfone (poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene]) was obtained from Polyscience Corporation (Niles, IL). Viscosities were measured with a Brookfield viscometer (model LVDV-II; Middleboro, MA) at 60 rpm. Films were prepared using a Specialty Coating Systems (Indianapolis, IN) spin coater. Sample morphologies were examined with a Hitachi S-4800 field emission scanning electron micrograph at 10 kV after coating with platinum (Hitachi, Schaumburg, IL). Cross-section micrographs were obtained by freezing with liquid nitrogen and breaking samples to minimize compression of the open cell pore structures.

Phenylated Polyphenylenes⁹

To a dry round-bottom flask, equipped with a magnetic stir bar, condenser, and a nitrogen adapter, 1,4-bis(tetraphenylcyclopentadienonyl)benzene (17.207 g, 24.9 mmol) and 1,4-diethynylbenzene (3.142 g, 24.9 mmol) were added to diphenyl ether (400 mL). The dark purple solution was heated at 180°C for 5 days under an argon atmosphere before cooling to room temperature and precipitating out the creamy white polymer in acetone (~2 L). Additional purification of the polymer was performed by redissolving dry polymer in tetrahydrofuran and precipitating in methanol (3×). The off-white polymer was collected by filtration and dried in a vacuum oven at 80°C for 24 h; 18.42 g (91% yield); ¹H-NMR (CDCl₃, 400 MHz): δ 7.48–7.40 (m), 7.35–7.31 (m), 7.20–6.55 (m), 6.36–6.17 (m); ¹³C NMR (CDCl₃, 100 MHz): δ 132.4, 131.9, 131.6, 131.6, 130.3, 129.6, 129.3, 127.6, 127.0, 126.7, 125.7, 121.7; ATR–FTIR (neat): 3060–2852 (aromatic C–H stretching, sp³ C–H stretching), 1598, 1073, 1024, 756, and 695 (C=C bending), 836 (aromatic C–H bending) cm⁻¹; gel permeation chromatography (GPC) in tetrahydrofuran (THF) relative to polystyrene, *M_w* = 62,000 g/mol (*M_w*/*M_n* = 2.3); Anal. Calcd: C, 94.68; H, 5.32. Found: C, 88.98; H, 5.15. Solubilities were determined by adding solvent (10 mL) to a few tens of milligrams of polyphenylene in a scintillation vial, stirring for 48 h at room temperature, then heating at reflux for 5 h. Non-solvents: water, methanol, ethanol, *n*-butanol, isopropyl alcohol, acetonitrile, dimethyl sulfoxide, and acetone. Solvents: tetrahydrofuran, NMP, toluene, chloroform, dimethylacetamide, 1,3-dichlorobenzene, and cyclohexanone.

Asymmetric Polysulfone Membrane Preparation

Polysulfone (20 g) was dissolved in NMP (60 g). After heating the solution to 60°C, distilled water (10.9 g) was slowly added with stirring to afford a clear, light yellow, aqueous NMP solu-

tion. Upon cooling, the solution was spun coat (600–700 rpm) onto a glass slide then immediately quenched into deionized water at 23°C to form a white opaque coating that came free of the glass surface spontaneously. The film was soaked in deionized water overnight to remove residual NMP. After drying at room temperature for several hours, the film was dried under dynamic vacuum at 90°C for 18 h resulting in opaque white membranes 2.5 cm × 2.5 cm × 35 cm ± 10 μm thick.

Asymmetric Phenylated Polyphenylene Membrane Preparation

Polyphenylene (13 g) was dissolved in cyclohexanone (87 g) at 70°C. Then *n*-butanol (13 g) at 70°C was added to the solution to give an 11.5 wt % solution in cyclohexanone/*n*-butanol (88 : 12). The viscosity of the phenylated polyphenylene solution in cyclohexanone : *n*-butanol was 2020 centipoise at 23°C. After cooling, 2.0 mL of the clear, tea brown solution was syringed over several seconds time onto a spinning glass slide (600–700 rpm) fixed on the spin coater. The coating was immediately quenched into pure *n*-butanol (200 mL) at room temperature to afford an opaque, light yellow-brownish coating still attached to the glass. After soaking in *n*-butanol for 2 h, the slide was removed from the non-solvent solution and the membrane was carefully peeled free, air dried at room temperature for 2 h, then dried under dynamic vacuum at 90°C for 18 h. This resulted in membranes that were 2.5 cm × 2.5 cm × 25 cm ± 10 μm in thickness.

RESULTS AND DISCUSSION

Discovering conditions for wet phase inversion of polyphenylenes require identification of miscible solvent : non-solvent pairs for the polymers. Phenylated polyphenylene is less soluble in polar solvents than polysulfone, but we did find that it would dissolve in NMP, one of the most commonly used solvents for making asymmetric polysulfone membranes.⁴ Unfortunately, the maximum concentration of polyphenylene in NMP and toluene solutions was less than <10 wt % and the resulting membranes were too thin and fragile. Therefore, we screened solvents by finding those that would allow solutions with more than 10 wt % polyphenylene to be dissolved. THF and chloroform were good solvents, but too volatile to give defect-free membranes. Cyclohexanone and 1,3-dichlorobenzene were found to give solution concentrations higher than 10 wt % polyphenylene and had sufficiently low volatility to spin coat membranes for phase inversion. Solvent : nonsolvent pairs were screened by coating

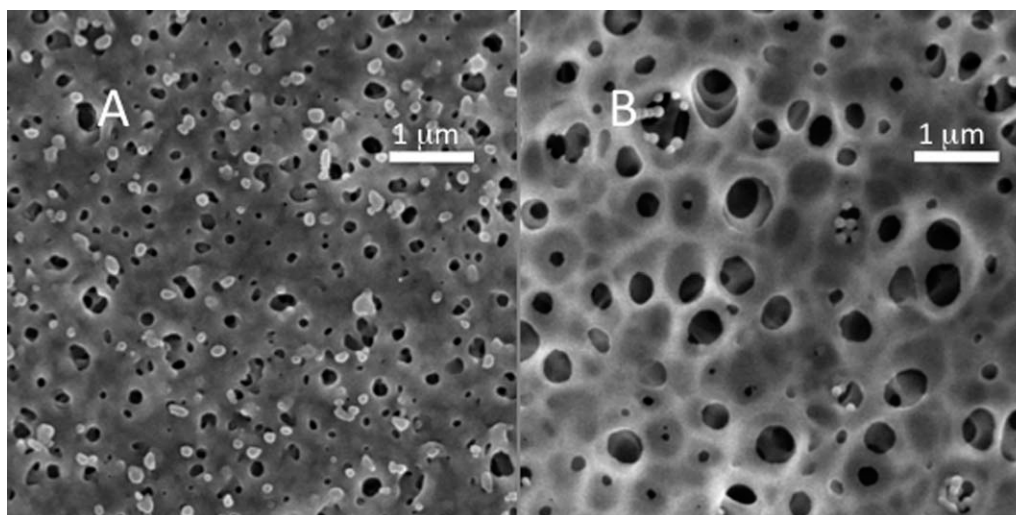


Figure 1. Scanning electron micrographs of the porous, bottom surface of polyphenylated polyphenylene (A) and polysulfone (B) membranes.

slides with the solution and immersing in the candidate non-solvents. Membranes with porosity developing from phase inversion scattered light and generally appeared opaque while generally those without porosity were transparent. After screening a relatively large number of solvent mixtures, two different solvent : nonsolvent pairs were found to be suitable for phase inversion synthesis of polyphenylene asymmetric membranes, 1,3-dichlorobenzene/isopropyl alcohol and cyclohexanone :

butanol. Unfortunately, membranes prepared by phase inversion from 1,3-dichlorobenzene : isopropyl alcohol adhered strongly to the glass and could not be removed without damaging the membrane. Examination of the resulting membranes revealed a dense skin making up half of the membrane with the remaining half consisting of open cell porosity. Fortunately, cyclohexanone : *n*-butanol proved to be a more suitable solvent pair. However, cyclohexanone by itself was too good a solvent. Membranes

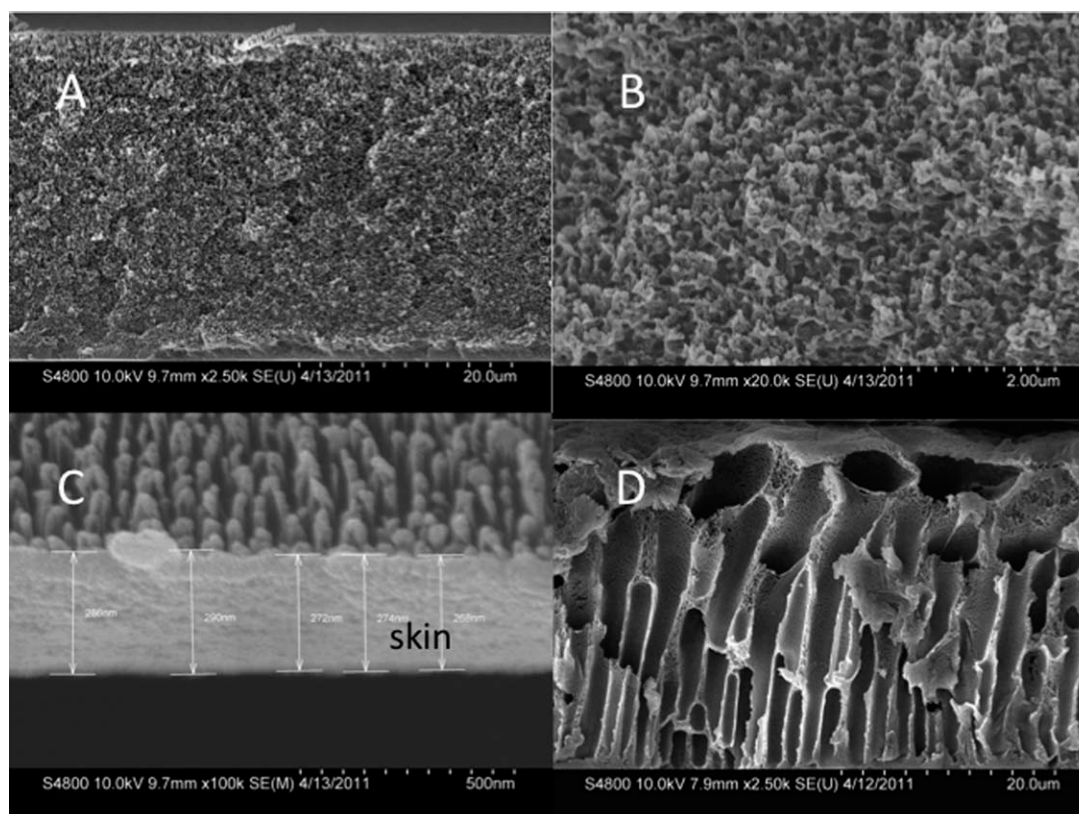


Figure 2. Scanning electron micrographs of cross-section of polyphenylated polyphenylene asymmetric membrane (A), its porous interior (B), its non-porous skin (C), and the cross-section of an asymmetric polysulfone membrane (D).

from quenching 14 wt % polyphenylene in cyclohexanone in *n*-butanol had very thick skins (10 μm) in a 20 μm thick asymmetric membrane. We lowered the solubility of the polyphenylene by adding small amounts of *n*-butanol until phase inversion gave a reasonably thin skin. Dilution with 12 wt % *n*-butanol gave a solvent that would dissolve over 11.5 wt % polyphenylene but would allow coagulation of the polymer with immersion into pure *n*-butanol and formation of opaque membranes with skin layers less than 500 nm in thickness. Unlike those membranes made with dichlorobenzene, these were easily lifted free of the glass substrate.

Scanning electron microscopic examination of the surface of the polyphenylene membrane that had been exposed to the non-solvent, *n*-butanol, was riddled with pores between 50 and 250 nm in diameter [Figure 1(A)]. The opposite side, originally attached to the glass surface was non-porous and relatively smooth. The non-solvent side of our polysulfone membrane had large pores between 50 and 800 nm in diameter [Figure 1(B)]. The cross-section morphology was examined by freeze fracturing the membrane [Figure 2(A)]. Scanning electron microscopy revealed that the skin on the polyphenylene membrane appeared to be 250–300 nm thick and non-porous [Figure 2(B)]. Below the skin, the membrane appears to be porous with a sponge-like texture consistent with slow precipitation¹⁵ and pores \sim 100 nm in diameter [Figure 2(C)]. In contrast, the polysulfone membranes made by phase inversion from NMP look like previously reported membranes with long finger-like macrovoids, several μm in diameter and nearly the thickness of the membrane in length, oriented perpendicular to the thin non-porous skin on the side that was exposed to the non-solvent [Figure 2(D)].⁴

For asymmetric glassy membranes to retain their porosity, they must be used at temperatures below their glass transition temperature (T_g). Polysulfone has a T_g of 185°C.^{4,14} Phenylated polyphenylene has been reported to have a T_g of 388°C.⁹ Differential scanning calorimetry of our polyphenylene membrane revealed a slightly lower T_g of 368°C. In a more practical demonstration, we slowly heated an asymmetric polyphenylene membrane while monitoring its temperature and appearance. The opacity of the membranes comes from light scattering from the μm -sized pores. At 370°C, the polyphenylene asymmetric membranes turned transparent as the pores collapsed.

The tensile strength of the asymmetric polyphenylene membranes was found to be 16 MPa, compared to 10 MPa for our polysulfone asymmetric membranes of similar thickness. The polyphenylene membrane tensile strain was 6–7% while that of the polysulfone membrane was 23%. Asymmetric membranes with spongiform morphologies typically have higher tensile strength and elongation than those with asymmetric morphologies with

macrovoids,¹⁵ but there is insufficient information on this polyphenylene to ascertain the relative contributions of composition and morphology to mechanical properties.

CONCLUSIONS

Phenylated polyphenylene, prepared by Diels–Alder polymerization, can be fashioned into asymmetric membranes through wet phase inversion. After surveying a number of solvent : non-solvent systems, we found that cyclohexanone : *n*-butanol gave the membranes with the greatest integrity and a spongiform porous structure with nonporous skin. Phenylated polyphenylene membranes were shown to retain their porous structure to 370°C, over 200°C higher than those made from polysulfone. Since such enhanced thermal stability would be useful for some gas separations, our next goal is to study the gas permeabilities of these asymmetric membranes and to develop complete solubility phase diagrams for the cyclohexanone–*n*-butanol solvent : nonsolvent system.

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