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A novel approach to the preparation of hollow fiber membranes from heat-resistant polynaphthoylenebenzimidazole

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Materials and Methods

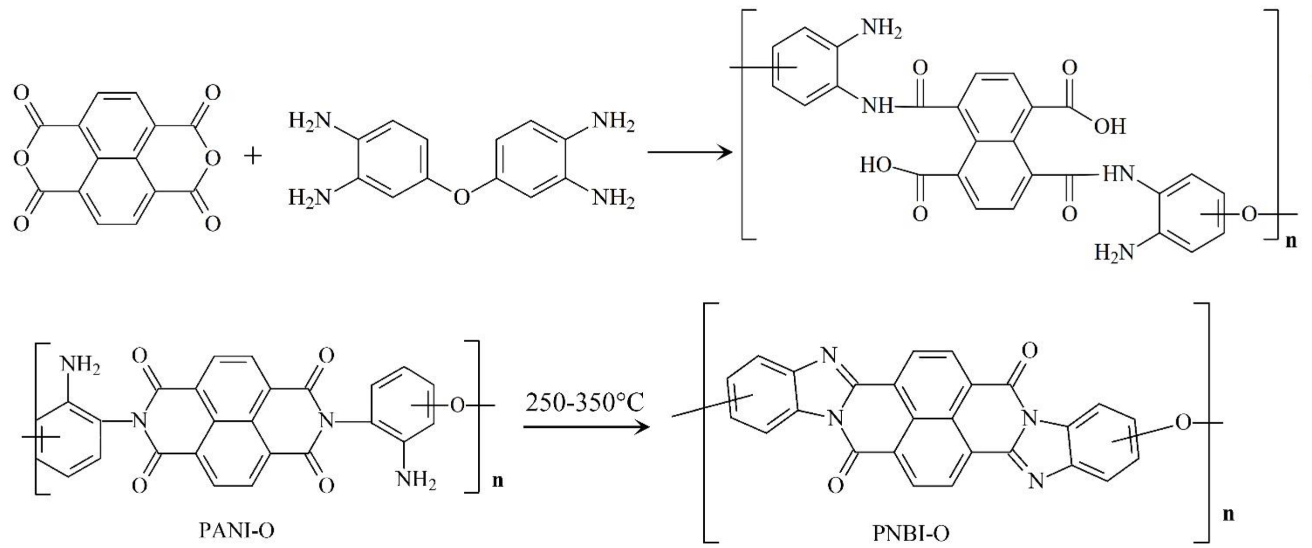
Materials

Monomers and solvents

3,3′,4,4′-tetraaminodiphenyl ether (Rubezhnoe plant, Rubezhnoe, Ukraine) Mp 155–156 °C and 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (VNIPIM, Tula, Russia) were dried at 100 °C under vacuum before use. Benzimidazole, benzoic acid (Thermo Fisher Scientific, Acros Organics, Waltham, MA, USA), NMP and ethanol (Ekos-1, Moscow, Russia) were used as received.

Synthesis of PANI-O

The synthesis of PANI-O was carried out by mixing 9.22 g (0.04 mol) of 3,3′,4,4′-tetraaminodiphenyl ether, 10.727 g (0.04 mol) of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride, 0.96 g (0.00784 mol) of benzoic acid, 0.96 g (0.08 mol) of benzimidazole, 80 ml of anhydrous NMP and 2 ml of toluene in Ar flow for 72 h at room temperature. The resulting solution was diluted with 55 ml of the mixture NMP/ethanol in a ratio of 41.5 ml/13.5 ml and stirred in Ar flow until completely homogenized. Thus, 10 vol% ethanol was present in 135 ml of the mixed solvent. The concentration of the synthesized PANI-O in the reaction solution was 13.7 g/dl.

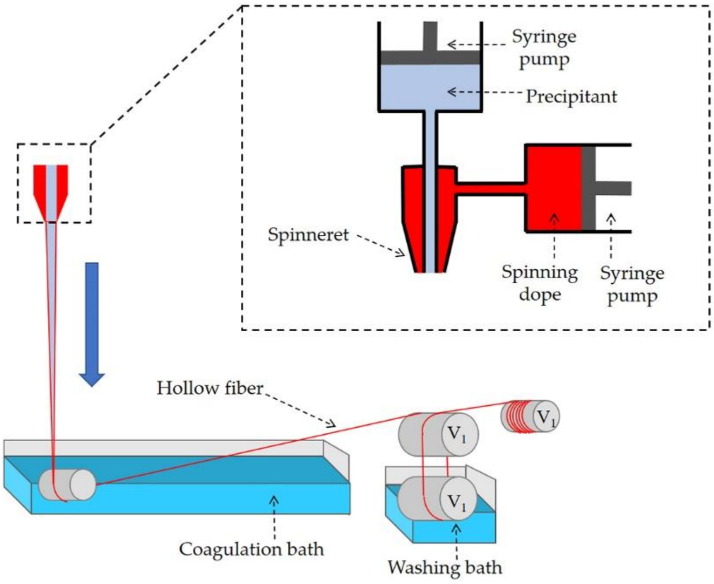


Scheme S1 Scheme of the PNBI-O synthesis, it consists of two stages: The synthesis of the PANI-O prepolymer and its transformations in PNBI at temperatures of 250–350 °C due to the cyclization with removal of water.

Methods

Hollow fiber spinning

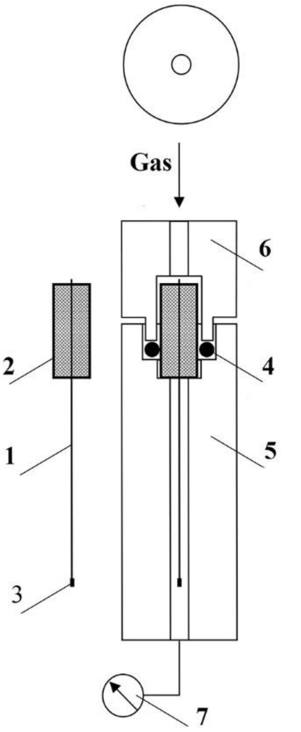
The continuous hollow fiber was spun on a laboratory bench. The spinning solution PANI-O (η = 101 Pa·s) was fed (0.021 ml/min) into a hollow fiber spinneret with inner and outer hole diameters of 250 µm and 900 µm. A precipitant (ethanol) was fed (0.15 ml/min) into the inner cavity, then, after drawing in an air gap (5 cm), the fiber was directed into a precipitation bath containing distilled water.



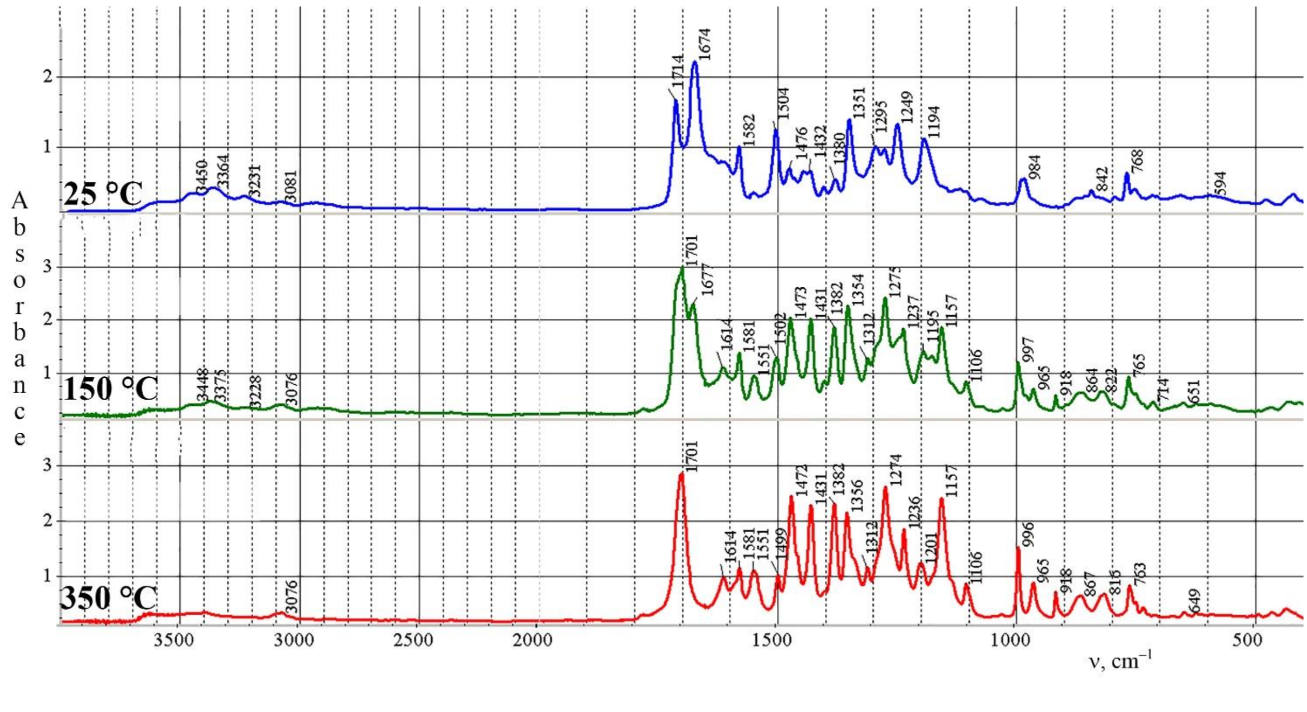
Scheme S2 Scheme of the hollow fiber spinning process.

Measuring the permeability of hollow fibers

A specially developed method was used to measure the permeability of hollow fibers. Hollow fibers were placed in an aluminum hollow cylinder measuring 30 mm in length and 8 mm in diameter with a wall thickness of 1 mm and the inner space of the cylinder was sealed with epoxy glue. After 24 hours, the lower part of the fibers was sealed with cyanoacrylate glue and left in the air for 1 hour. After this, the cylinder with fibers was placed in a special cell for measuring the gas permeability of hollow fibers (Scheme S4) and then an experiment was conducted to determine the permeability of hollow fibers on a barometric setup. Depending on the average fiber wall thickness and the gas type, the measured cell fluxes varied from 0.1 to 0.005 GPU. The ideal separation selectivities $\alpha_{i,j}$ of different gas pairs *i* and *j* were calculated (Table 1). $\alpha i,j = Qi/Qj$, where Q is permeability. $Q=(V/t)/(S*\Delta p)$, where V/t – gas flow through the membrane; S – working area of the membrane; Δp – gas pressure drop across the membrane.



Scheme S3 Scheme of the cell for measuring the permeability of hollow fibers: 1 - hollow fiber; 2 - mandrel (hollow aluminum cylinder into which the fiber is glued with epoxy glue); 3 - mouth of the hollow fiber, sealed with cyanoacrylate glue; 4 - seal; 5 - lower part of the cell for hollow fibers; 6 - upper part of the cell for hollow fibers; 7 - submembrane volume pressure sensor.



Scheme S4 FTIR spectra of initial fibers at 25 °C, heated to 150 °C and obtained after heating to 350 °C.