Mendeleev Communications

Mendeleev Commun., 2025, **35**, 334–336

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

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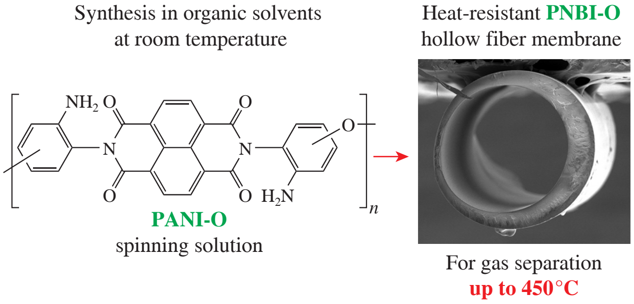
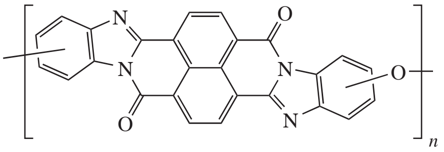
DOI: 10.71267/mencom.7658

For the first time, hollow fiber polynaphthoylenebenzimidazole (PNBI) membranes were obtained by a two-stage acid-free method through a precursor fiber made of poly(*o*-aminophenylene)naphthoylenimide (PANI-O) by its subsequent heat treatment, leading to the formation of PNBI. The gas separation characteristics of such fiber at room temperature for H_2, He, O_2 and CO_2 were studied by an integral method. It was shown that PNBI is one of the most promising polymers for the manufacture of thermally stable gas separation membranes with high productivity.



Keywords: poly(*o*-aminophenylene)naphthoylenimide, polynaphthoylenebenzimidazole, hollow fiber, membrane, gas separation characteristics, rheology.

Polynaphthoylenebenzimidazoles (PNBI) are promising high-performance polymers belonging to the polyheteroarylenes family and characterized by extremely high for organic polymers thermal stability (450–600 °C), as well as chemical, radiation, UV and fire resistance.[1–4] These characteristics, combined with promising gas separation properties,[5] make PNBI a likely competitor to polybenzimidazole (PBI) fibers (Celazole®, PBI Performance Products, Inc.)[6,7] in the field of high-temperature membrane separation. For example, unlike existing polymer analogs, PNBI membranes would allow hydrogen to be separated from gas mixtures formed during steam reforming of methane followed by water gas reaction at an operating temperature of 190–350 °C.[8] Today, hydrogen extraction requires cooling gas mixtures to room temperatures,[9–12] which leads to additional energy costs. Therefore, a search is underway to increase the operating temperature range of polymer membranes,[13,14] and PNBI membranes could solve this problem in the future. The membrane characteristics of various PNBIs have been studied for films at 35 °C and it turned out that they have very promising gas separation properties.[5] At present, a new technology for obtaining PNBI-O (Scheme 1) through the stage of the precursor polymer poly(*o*-aminophenylene)naphthoylenimide (PANI-O) has been developed at INEOS RAS.



PNBI-O

Scheme 1 Structure of the polymer PNBI-O.

PANI-O is synthesized in organic solvents at room temperature.[15] An important advantage of this method is the possibility of producing various products, including films, fibers and hollow fibers, from solutions in organic solvents. Compared to the processing of non-melting PNBI-O, soluble in concentrated sulfuric and polyphosphoric acids, the processing of PANI-O is technologically and economically feasible. When processed in an air atmosphere at a temperature of 250–350 °C, PANI-O is converted into PNBI-O.[16] Previously, the properties of PANI-O solutions were studied in detail and it was shown that these systems remain 'alive' after synthesis and continuously change their properties, since intramolecular cyclization and polymerization reactions continue to occur in them,[17] the intensity of which depends on the temperature. It was possible to identify the temperature and time window in which the rheological properties of solutions are achieved, allowing the formation of fibers and films. In addition, such an important aspect of spinning technology as the process of interaction with the precipitant[18] was thoroughly studied, which made it possible to develop a laboratory technology for spinning PANI-O fibers. Due to the introduction of original developments into the practice of molding, it became possible to carry out the dry-wet molding process using a simple technological precipitator, which made it possible to obtain fibers with high strength (up to 600 MPa) and outstanding heat resistance (up to 600 °C).[16] In continuation of the conducted research, the present work is focused on the development of a laboratory technology for the production of hollow fiber membranes by the dry-wet method from PANI-O solutions in *N*-methylpyrrolidone.

Before forming hollow fibers, in order to controllably change the rheological properties, the synthesized PANI-O solution (for details, see Online Supplementary Materials) was kept at a temperature

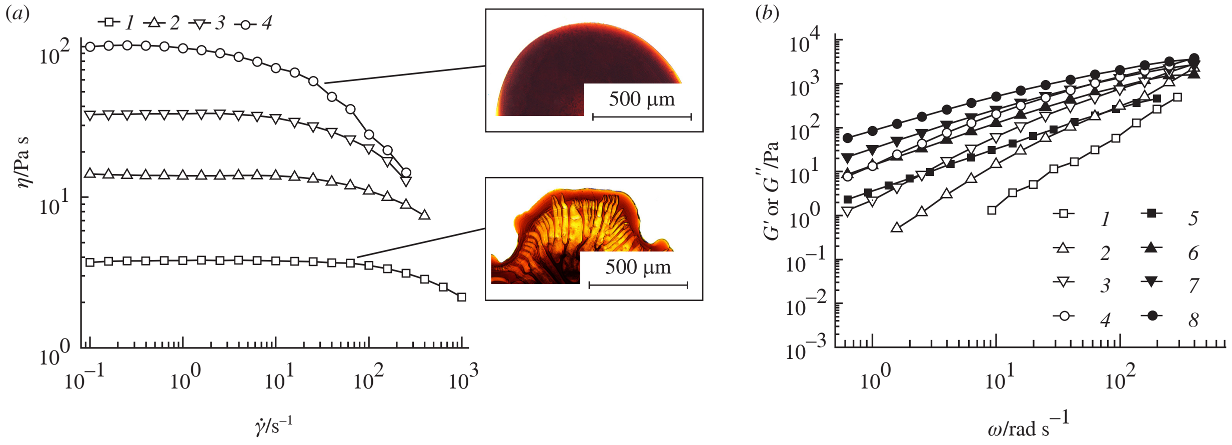


Figure 1 Rheological behavior of PANI-O solutions aged at 70 °C for (*1*),(*5*) 0, (*2*),(*6*) 5, (*3*),(*7*) 10 and (*4*),(*8*) 16 h: (*a*) flow curves and (*b*) frequency dependences of (*1*)–(*4*) the elastic modulus G' and (*5*)–(*8*) the viscosity modulus G''. (*a*) Morphology of droplets precipitated with water from PANI-O solutions with $\eta = 101$ Pa s (upper inset) or $\eta = 3.7$ Pa s (lower inset), aged at 70 °C for 16 or 0 h, respectively.

of 70 °C with constant stirring. During the heating process, a part of the solution was collected to determine the change in viscoelastic properties (Figure 1). For solutions with different rheological behavior, the process of precipitation with water on a drop was simulated, the corresponding micrographs of which are also shown in Figure 1. A detailed description of the drop method was published earlier.[18]

Initially, the solution is an abnormally viscous liquid with a viscosity value $\eta = 3.7$ Pa s in the Newtonian flow region [Figure 1(*a*), curve *1*]. The elastic modulus G' is weakly manifested and cannot be registered at low frequencies of action [Figure 1(*b*), curve *1*]. Such a solution is not capable of stably forming a fiber. When flowing out of the spinneret, the stream breaks up into drops and sedimentation occurs with deformation of the drop shape and the formation of multiple defects [Figure 1(*a*), lower inset]. It is impossible to obtain a hollow fiber from the initial solution, since it is impossible to fix and maintain its shape in a solid state. To continue the chemical processes in the prepolymer, leading to an increase in the viscosity of the solution and its viscoelastic properties, the solution was thermostated at 70 °C with constant stirring for 16 h. During this period of time, the solution changed its rheological properties sufficiently to form a hollow fiber. After 16 h of thermostating, the viscosity value increased almost 30 times, reaching a value of 101 Pa s [Figure 1(*a*), curve *4*]. Proportionally to the increase in viscosity, the viscoelastic properties also increased significantly, and for the frequency dependences of the elastic modulus G' and the viscosity modulus G'', an intersection point appeared at a frequency of 396 rad s^{-1} [Figure 1(*b*), curves *3 vs. 7* and *4 vs. 8*]. Simultaneously with the change in rheological characteristics, the sedimentation of model droplets proceeded practically without the formation of defects [Figure 1(*a*), upper inset].

Hollow fibers of PNBI-O were prepared in two stages. In the first stage, continuous PANI-O hollow fiber was spun using the dry-wet method (for details, see Online Supplementary Materials). In different experiments, the temperature of the precipitation bath was varied from 10 to 70 °C. The fibers were then washed in wash bath with distilled water and dried at 25 °C for 24 h until equilibrium moisture content was reached. The resulting PANI-O hollow fibers were heat treated in a tube furnace with gradual heating (5 °C min^{-1}) to 300 °C and holding at this temperature for 3 h.

The transformation of PANI-O into PNBI-O was previously studied using FTIR spectroscopy[19] (for spectra, see Online Supplementary Materials). It was found that in the spectrum of the initial PANI-O fibers, signals were observed in the region of 3200–3500 cm^{-1}, corresponding to the stretching vibrations of NH_2 in PANI-O, which disappeared as heating proceeded and intramolecular cyclization occurred with the formation of polyconjugated bonds C=N–C=C, and a transformation of the doublet at 1670–1700 cm^{-1} into a singlet at 1700 cm^{-1} was also observed, which corresponds to the stretching vibrations of the non-associated C=O group and the second carbonyl group, stretching towards the nearby NH_2 group, respectively.

The surface morphology of the PNBI-O fiber cross-cleavage made in liquid nitrogen was studied using scanning electron microscopy (SEM). Figure 2 shows the SEM image of the fiber cleavage and cross-sections of the fibers prepared under different conditions near the outer (skin) and inner (core) surfaces at higher magnification. The outer diameter of the fibers obtained under all conditions is ~500 μm, and the wall thickness varies in the

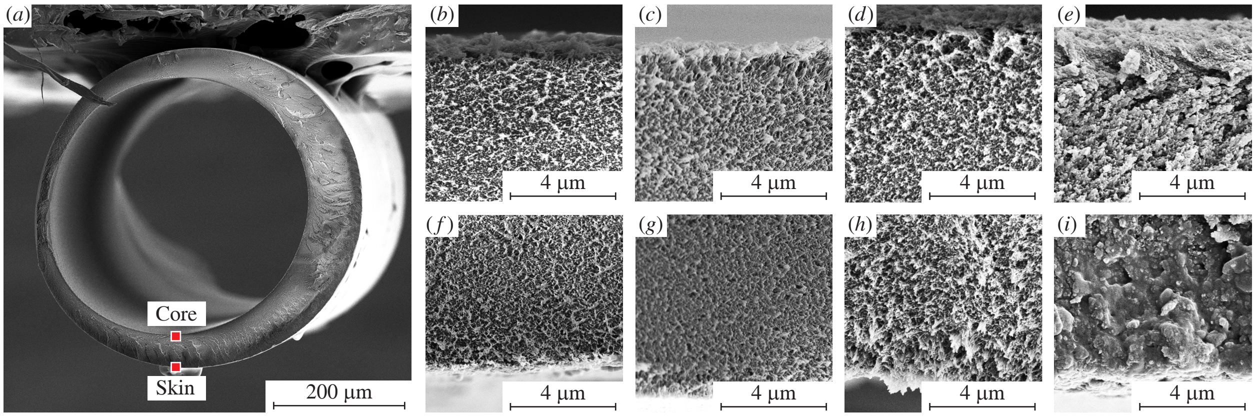


Figure 2 SEM images of (*a*) PNBI-O hollow fiber spun at 10 °C and fiber morphology spun at precipitation bath temperatures of (*b*),(*f*) 10, (*c*),(*g*) 25, (*d*),(*h*) 50 and (*e*),(*i*) 70 °C near the (*b*)–(*e*) inner (core) and (*f*)–(*i*) outer (skin) surfaces at higher magnification.

Table 1 Ideal separation selectivities α of various gas pairs for PNBI-O fibers and films.

Gas pair	Selectivity α	
	Fiber (22 ± 2 °C)	Film (35 °C)[a]
H_2/CO_2	4.7–5.1	4.7
CO_2/O_2	4.5–4.6	4.8
H_2/He	1.2–1.3	1.2
He/CO_2	3.9–4.1	4.1
He/O_2	17.0–18.0	19.0

[a] Data taken from ref. 6.

range from 20 to 80 μm. With increasing precipitant temperature, the morphology of the hollow fiber walls becomes increasingly loose, but changing the precipitant temperature does not lead to the appearance of an asymmetric structure. In all cases, the fibers obtained are monolithic, according to SEM data.

The gas separation characteristics of the PNBI-O hollow fibers were investigated using a barometric setup (for details, see Online Supplementary Materials), and the ideal separation selectivities α were calculated (Table 1). The hollow fibers exhibit significant selectivity, which is within statistical error in line with PNBI-O films.[5] However, the low fluxes through the fibers (around 0.2 GPU for hydrogen) combined with the studied morphology suggest that most of the fiber wall is monolithic.

As a result of the conducted research, the technology of manufacturing the hollow fiber PNBI membrane through the stage of preparing the precursor PANI-O hollow fiber with its subsequent heat treatment at 300 °C in air was successfully developed for the first time. The outer diameter of the resulting PNBI-O fiber was 500 μm, and the wall thickness was 20–80 μm. The new synthesis technology allows spinning hollow fibers from a solution of PANI-O in *N*-methylpyrrolidone. The produced hollow fiber membranes have very promising gas transport and gas separation characteristics. The combination of these advantages together with the outstanding heat resistance of the polymer (up to 600 °C) allows considering PNBI-O as a promising polymer for producing heat-resistant gas separation membranes.

The synthesis and fiber spinning were carried out with the financial support from the Russian Science Foundation (grant no. 23-19-00222). The study of the rheological properties of solutions was carried out on the equipment of the 'Shared Analytical Research Center of Deep Oil Processing and Petrochemistry' within the framework of the State Program of TIPS RAS. SEM images were obtained using the equipment of the Resource Center of Probe and Electron Microscopy (Kurchatov Complex of NBICS-Natural-like Technologies, NRC 'Kurchatov Institute'). The contribution of Center for Molecule Composition Studies of INEOS RAS is gratefully acknowledged.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7658.

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Received: 17th October 2024; Com. 24/7658