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The first example of hollow polynaphthoylenebenzimidazole fiber preparation

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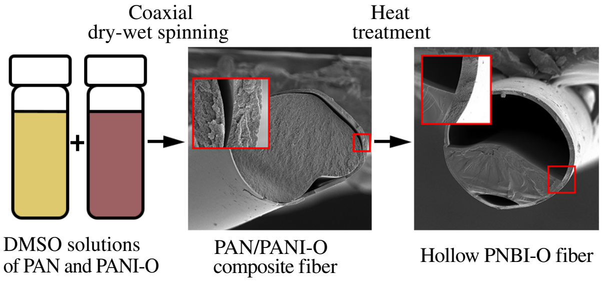
A new unique two-stage method for spinning hollow polynaphthoylenebenzimidazole (PNBI) fibers has been proposed. Polyacrylonitrile (PAN) fiber having a porous morphology was coated with poly(*o*-aminophenylene)-naphthoylenimide (PANI-O) precursor to form a composite fiber with a core–shell structure and subsequently this composite fiber precursor was heat treated in air. The inner PAN fiber underwent oxidative cyclization, accompanied by its high shrinkage, while the PANI-O shell, due to heterocyclization, turned into a PNBI-O shell, and the inner space of the hollow fiber was only partially filled with cyclized PAN.



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Owing to their geometric configuration, hollow fibers as membrane materials have a significant advantage over films and traditional fibers in that they have a larger surface area. This attribute has caused increased interest in them.[1] Fire-resistant and chemically stable, hollow fibers stand out in their potential applications due to their distinctive thermophysical properties.[2] These fibers provide exceptional thermal insulation while being lightweight, making them highly promising for high-temperature applications. Furthermore, their chemical resistance ensures stable operation even in aggressive environments. This makes them ideal for creating efficient filtration systems[3] and developing the membranes.[2,4]

Polynaphthoylenebenzimidazoles (PNBIs) are ladder and semi-ladder polyheteroarylenes distinguished by their exceptional thermal and interesting optical properties.[5,6] Remarkably, PNBIs retain 90% of their mass after exposure to 400 °C for 10 h.[6] Along with their thermal stability, PNBIs have high chemical and fire resistance, exhibiting a limited oxygen index ranging from 56% to as high as 83%.[7,8] Their membrane gas separation properties are particularly outstanding, lying close to the upper bound of the Robeson diagram for gas pairs such as O_2/N_2, H_2/N_2 and H_2/CH_4.[9] Additionally, PNBIs exhibit high mechanical properties, for example, PNBI containing an –O– bridge group (PNBI-O) achieves tensile strengths of up to 174 MPa for films[9] and an impressive 500 MPa for fibers with a diameter of 40 μm.[8] PNBI hollow fibers are still unknown.

The standard approach to producing hollow fibers from solutions typically requires the use of dual coagulants for the inner and outer surfaces.[10] These coagulants induce phase separation, which determines the morphology of the inner and outer layers of the fiber. However, during the spinning, there exist challenges in achieving a thin wall while maintaining the desired shape and strength. These parameters are crucial to prevent potential collapse of hollow fibers both during manufacturing and during operation. Consequently, this requires special conditions for the spinning solution. Here, rheological properties[11] play a key role in maintaining the fiber shape and preventing post-coagulation deformation, especially after removal of the internal coagulant. Such prerequisites influence the minimum achievable diameter and wall thickness of hollow fibers.[10] This prompts the search for new ways to produce hollow fibers, including from melt or without the use of an internal coagulant.[12]

In our previous work,[8] we used poly(*o*-aminophenylene)-naphthoylenimide (PANI-O) in dimethyl sulfoxide (DMSO) solution as a PNBI-O precursor to produce PNBI-O fibers. When exposed to air in the temperature range of 250–350 °C, this polymer undergoes heterocyclization and transforms into PNBI-O (Scheme 1). We have shown that to obtain fiber, a PANI-O solution must be aged or a small amount of non-solvent added to it, which improves the viscoelastic properties necessary for stable jet formation in dry or dry-wet spinning processes.

In this work, the use of a supporting core made of a PAN solution, known for its excellent spinnability, made it possible to employ a PANI-O solution of low concentration and low viscosity for the outer layer, which does not inherently form fibers on its own. Notably, this technique eliminates the need for an internal coagulant during fiber spinning. For this research, we used a 15.5 wt% solution of PANI-O in DMSO with an intrinsic viscosity of polymer equal to 0.8 dl g^{-1}. The preparation of this solution was carried out strictly according to the method described earlier.[8] The purity of monomers and polymers was monitored using NMR and FTIR spectroscopy. Additionally, a 27 wt% solution of PAN in DMSO was prepared and used.[†]

Before spinning, the solutions were characterized by determining their viscosity and viscoelastic properties in the range of linear viscoelasticity (Figure 1).

Concentrated PAN solutions are prone to gelation at low temperatures.[13] Therefore, a solution preheated to 70 °C was used for spinning, while the PANI-O solution was spun at 25 °C. The choice of this temperature regime is explained by the fact that when heated, PANI-O tends to cyclize even in solutions.[8] Under these conditions, the PANI-O solution is characterized by a low viscosity of 1 Pa s and does not exhibit elasticity [Figure 1(*a*), curve *3*]. At 70 °C, the PAN solution, on the contrary, demonstrates the properties of a viscoelastic fluid, including the existence of a region of Newtonian viscosity behavior and the intersection of the graphs of the frequency dependence of the moduli, which indicates the dominance of elasticity over viscosity at an angular frequency of about 1000 rad s^{-1} [Figure 1(*b*), curves *2* and *5*]. When the PAN solution is cooled to 25 °C within the spinneret, its viscosity increases almost tenfold, and the point of intersection of the module graphs shifts to a frequency of 10 rad s^{-1} [Figure 1(*b*), curves *1* and *4*]. Such conditions ensure a consistent flow of viscous solution from the spinneret, preventing capillary instabilities until the coagulation process begins.

The hollow fibers were spun using the dry-wet spinning method.[‡] The specificity of this process is the rapid coagulation of the PANI-O solution, followed by slow interdiffusion of the coagulant into the PAN solution and DMSO from the PAN solution through the coagulated PANI-O shell. This induces mild coagulation, resulting in the formation of a composite fiber consisting of a porous PAN fiber core covered with a dense PANI-O shell. The resulting fibers were rinsed in distilled water for an hour and then dried at 25 °C for 24 h to achieve equilibrium residual moisture.

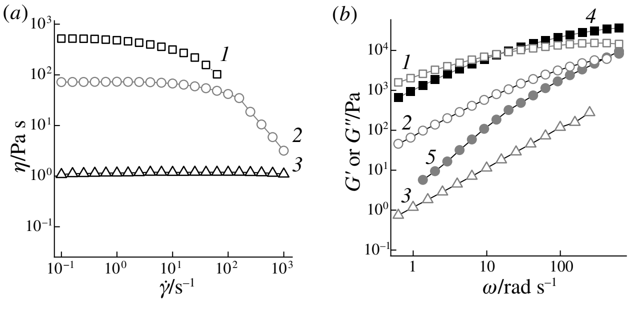


Figure 1 Rheological behavior of solutions of (*1*),(*2*),(*4*),(*5*) 27% PAN–DMSO and (*3*) 15.5% PANI-O–DMSO at (*1*),(*3*),(*4*) 25 and (*2*),(*5*) 70 °C: (*a*) flow curves and (*b*) frequency dependences of (*4*),(*5*) the elasticity modulus G' and (*1*)–(*3*) the loss modulus G''.

Subsequent heat treatment of the composite fiber was carried out in a tubular furnace with gradual heating to 300 °C at a rate of 5 °C min^{-1}, followed by exposure for 3 h. This treatment promoted oxidative cyclization of nitrile groups in the PAN core, accompanied by its shrinkage, resulting in the formation of a hollow fiber partially filled with a squeezed PAN residue [Figure 2(*b*)], with an outer circular layer of PANI-O converted to PNBI-O. Interestingly, the initially imperfectly round composite fibers [Figure 2(*a*)] took on a round shape after heat treatment [see Figure 2(*b*)]. This transformation is apparently associated with the 'inflation' of the shell due to the boiling off of solvent residues or gaseous products released during chemical transformations of PAN,[14] and the stabilization of the shape after the subsequent heterocyclization of PANI-O into PNBI-O. The degree of transformation of PANI-O into PNBI-O shells was assessed by changes in the characteristic bands of the IR spectra of the fiber surface recorded by FTIR spectroscopy (Figure 3).

The transformation of PANI-O into PNBI-O fibers was assessed by monitoring changes in the intensity of characteristic bands in the FTIR spectra of fibers taken before and after heating. Intensity changes are observed at 1714 and 1674 cm^{-1}, corresponding to the valence vibrations of the unassociated C=O group and the second carbonyl group stretching towards the

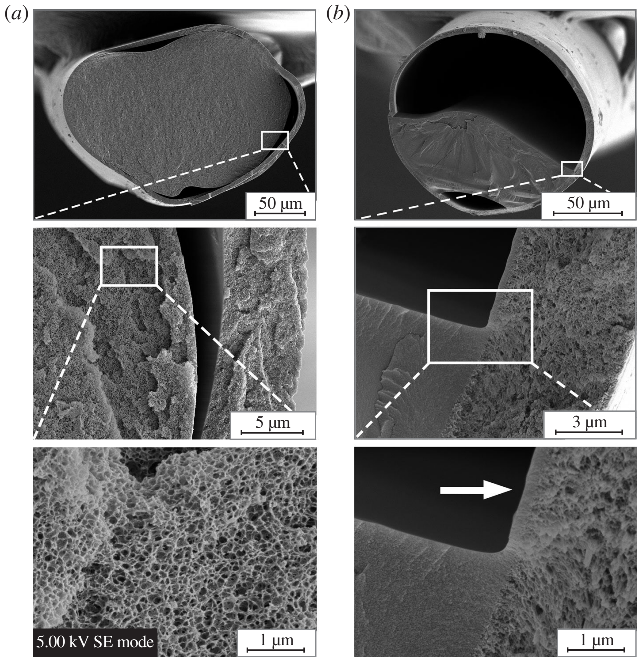
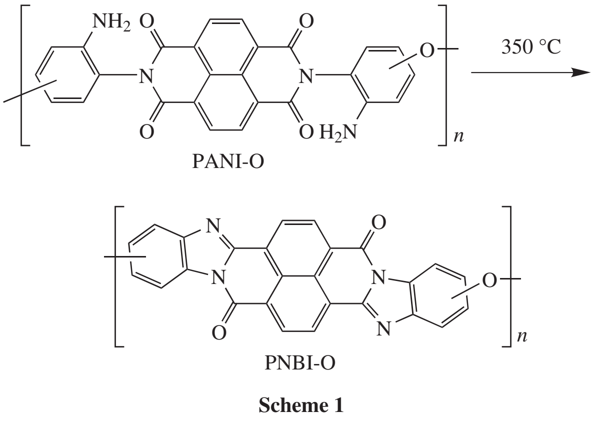


Figure 2 SEM images of (*a*) the precursor composite fiber and (*b*) the annealed hollow fiber at various magnifications as indicated by the scale bar.



Scheme 1

[†] PAN powder (Good Fellow Co., UK) with a molecular weight of 85 kg mol^{-1} and a polydispersity index of 2.1 consisted of 93.8% acrylonitrile, 5.8% methyl acrylate, and 0.3% methyl sulfonate. DMSO (99.6%) was produced by EKOS-1 (Russia).

[‡] Hollow fibers were spun through a coaxial spinneret with inner and outer orifice diameters of 250 and 900 µm, respectively (25G + 18G needles). In this case, instead of the internal coagulant, a PAN–DMSO solution heated to 70 °C was fed into the central channel of the spinneret, while the outer channel was filled with a PANI-O solution at a temperature of 25 °C. The air gap between the spinneret and the coagulation bath was 40 mm. Distilled water at a temperature of 25 °C was used as the coagulant.

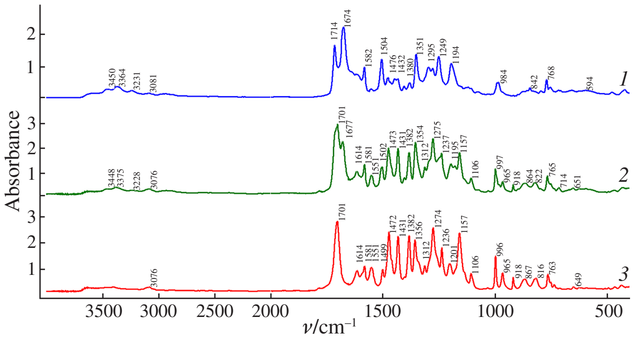


Figure 3 FTIR spectra of (*1*) initial PANI-O fibers at 25 °C, (*2*) PANI-O fibers heated to 150 °C and (*3*) PNBI-O fibers obtained after heating to 350 °C.

nearby NH_2 group, respectively. In the spectrum of the initial PANI-O fibers, narrow bands are observed in the region of 3450, 3364 and 3231 cm^{-1}, corresponding to the stretching vibrations of NH_2 in PANI-O, which disappear as intramolecular cyclization occurs and a polyconjugated C=N–C=C bond is formed.

The use of a supporting inner core based on the viscoelastic PAN solution allowed us to obtain a thin layer of low-viscosity PANI-O solution, which by itself is not capable of forming fibers. This makes it possible to form a thin PANI-O shell with a thickness of about 7 μm on the PAN surface [see Figure 2(*b*)]. After heat treatment, the fiber diameter was ~150 μm, and the thickness of the PNBI-O shell/fiber wall, which surrounds the dense layer of cyclized PAN and the void space, was ~6.5 μm.

The conducted research showed that the precursor composite fiber has a finely porous PAN core with a pore diameter of 30 to 120 nm and a continuous PANI-O shell that delaminates from PAN. PAN undergoes cyclization during heat treatment in air with a reduction in volume, leaving a monolithic phase that partially fills the volume of the hollow PNBI-O fiber. The resulting fibers are brittle with a critical bending radius of about 130*d*, where *d* is the fiber diameter. The tensile strength is 40 ± 10 MPa with a relative elongation at break of ~1% during stretching.

A new approach to the production of hollow PNBI-O fibers with thin walls and small diameter from a solution of its precursor PANI-O has been successfully implemented. The developed method has a number of important advantages. Firstly, it is suitable for spinning fibers from low-viscosity PANI-O solutions, resulting in a strong thin layer (up to 10 μm). Secondly, the method eliminates the need for an internal coagulant, which greatly simplifies the process of producing hollow fibers. Thirdly, the PAN core acts as a support during spinning, preventing instability and keeping the shell from collapsing, and then during heat treatment it helps straighten the shell for obtaining round hollow PNBI-O fiber. The results obtained show the significant potential of the presented method for producing thin-walled hollow fibers for various applications.

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