



Hollow fiber spinning of block copolymers: Influence of spinning conditions on morphological properties

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ABSTRACT

The self-assembly of block copolymers proposes interesting strategies for design and fabrication of ordered nano/microdomain structures. Recently, large attention has been given to the preparation of integral asymmetric flat sheet membranes with cylindrical domains forming an isoporous top layer. In this work, this strategy is extended to the formation of nanoporous hollow fiber membranes from polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) solutions via phase inversion process. In this way, the self-assembly of block copolymers into an ordered morphology via solvent evaporation is combined with microdomain alignment by shear flow in the die. The influence of the experimental parameters on the morphology of the hollow fiber is discussed, such as solution concentration and viscosity, extrusion pressure within the spinneret and air gap distance between the spinneret and the precipitation bath (evaporation time). The evaluation of the surface morphology of the membranes by scanning electron microscopy (SEM) confirms the strong effect of shear flow and solution viscosity on the formation of nanoporous structures in hollow fiber spinning.

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1. Introduction

New materials and procedures have been developed to present alternative routes for the preparation of well-ordered nanostructured membranes [1]. The self assembly of block copolymers offers an attractive strategy to fabricate nanoporous membranes by choosing appropriately designed block chemistries, compositions and processes [2]. Recently, block copolymer based membranes with nanoscale pores, high porosity, narrow pore size distributions, highly selective separation and tunable chemical and mechanical properties have received large attention both from the scientific and the application viewpoint [1]. Block copolymers consist of two or more chemically incompatible blocks that are covalently joined. They can self-assemble into a variety of periodic arrays of spherical, cylindrical, or lamellar microdomains depending on the volume fraction of the blocks [1–3]. In solution, microphase separation can also occur and the block copolymers assemble into micellar structures, depending on the thermodynamic incompatibility between their chemically dissimilar segments, the selectivity of the solvent and the polymer concentration [3].

From a nanotechnological viewpoint, the self-assembly of block copolymers into regular crystal-like structures is very interesting as

length scales can be obtained, which are not so easy to achieve by other methods. Many techniques have been developed to induce the alignment and control of the arrangement of microdomains in block copolymer films by coupling with external fields [4]. Solvent evaporation is one of the strong directional fields to kinetically freeze nanostructures under proper preparation conditions. Cylindrical microdomains vertically orientated to the film surface are a result of the maximized solvent concentration gradient along the direction perpendicular to the surface [5–7]. The typical domain sizes of cylinders or gyroidal networks formed by block copolymers make them interesting candidates not only as templates for nanolithographic applications, but also for ultrafiltration membranes. Cylinders vertically aligned to the plane of a substrate are useful to fabricate nanochannel structures and isoporous membranes, while those parallel aligned to the plane of substrate are also motivating in nanolithography [8].

Thin film morphologies have been widely studied for numerous block copolymers and post treatment effects such as thermal or solvent vapor annealing to remarkably improve the ordering of block copolymer morphologies [5,9–12]. However, large scale defect-free block copolymer morphologies with perfect periodic domain ordering are difficult to obtain without the application of, for example, external forces or a well-designed surface topography. Researchers have applied external force for alignment of cylindrical phase block copolymer bulk materials to achieve defect-free orientations and to control lateral ordering of the nanoscopic domains

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[13]. Recently, a few studies have focused on the effect of shear flow [14–16], solution extrusion [17], and solvent evaporation coupled with flow through a channel [7] to align cylindrical block copolymer domains in solution.

One of the straight forward and most important industrial procedures for fabrication of integral asymmetric membranes is the non-solvent-induced phase separation (NIPS), where a cast film of a polymer solution is immersed in a precipitation bath. Combined self-assembly of block copolymers with non-solvent induced phase separation, now referred to as the SNIPS method, directly enhances formation of uniform pore sizes in the selective layer of membranes [18]. This one step novel procedure was established a few years ago [19] to prepare a nanoporous asymmetric membranes of a PS-*b*-P4VP diblock copolymer. The well-ordered nanoporous structure on the top layer of the block copolymer membranes is achieved by controlling the kinetic factors influencing self-assembly prior to reaching the thermodynamic equilibrium state. More studies on integral asymmetric block copolymer membranes from the same type of block copolymer (PS-*b*-P4VP) have been reported since then [11,12] and the concept could be extended to other stimuli-responsive membranes like PS-*b*-P2VP [12] and also postfunctionalized block copolymer membranes [20].

Hollow fiber membranes are generally used in many membrane applications ranging from gas separation to microfiltration. Compared to other membrane configurations, the main advantage of hollow fiber geometry is that it provides a high ratio of membrane area to module volume, and therefore higher productivity per membrane module. However, formation mechanism for hollow fiber membranes in which the polymer solution is extruded through a spinneret into a nonsolvent bath is more complex than in the case of integral asymmetric flat sheet membranes because of a larger number of morphology controlling factors during processing and phase inversion. The hollow fiber membranes fabricated via phase inversion by two internal and external coagulants have an asymmetric structure with a thin separating layer on the both inner and outer surface. The internal coagulant controls the inner skin morphology, while the external coagulant controls the outer skin morphology [21,22]. The addition of another evaporation step prior to precipitation in wet-phase inversion processes (dry/wet phase inversion) improves preparation of defect-free and ultrathin skinned asymmetric membranes [23].

However, in dry-jet wet-spinning processes, other factors such as extrudate swell, relaxation, gravitation and spinning-line stress in the air gap region along the distance between spinneret and precipitation bath can influence the membrane morphology and performance. Two dominant factors, elongational and shear stresses have a dramatic effect on the polymer segmental orientation and relaxation at the outer surface of the fiber [24–28]. The rheology of many polymer solutions is associated with a non-Newtonian behavior such as shear-thinning [27]. The segmental orientation induced by the shear flow within the spinneret relaxes in the short air gap region if the elongational stress caused by gravity along the spin line is small. However, the elongational stress caused by gravity becomes more prominent with increasing air gap distance which might enhance the spin line orientation [24,28]. The defect-free thin skin with nanoscale pores in narrow-sized distribution can develop the performance of the resultant membranes in selectivity and permeability. Block copolymers are able to implement this superior facility by self-assembly of well ordered nanoscale domains on top of the skin layer.

In the present work, we focus on the self-assembly of asymmetric PS-*b*-P4VP diblock copolymers (where P4VP forms cylinders in the bulk morphology) during hollow fiber spinning. To our knowledge, our experiments for the first time establish the manufacturing of nanostructured hollow fiber membranes by phase

inversion dry-wet jet spinning of diblock copolymers which form cylindrical morphology. In this way, the self assembly of block copolymers into an ordered morphology induced by solvent evaporation is coupled with the alignment of cylindrical domains through shear flow. The hollow fibers are spun from the concentrated solutions of PS-*b*-P4VP in different mixtures of solvents (THF and DMF). The block copolymer undergoes microphase separation at a certain solution concentration and composition during solvent evaporation. The influence of effective parameters of shear stress, solution viscosity and evaporation time on the formation of regular nanoporous structures in hollow fiber was evaluated by variation of the block copolymer concentration, the pressure gradient within the spinneret and air gap distance between the spinneret and the precipitation bath.

2. Experimental section

2.1. Material

ULTEM® 1000 Polyetherimide (PEI) resin purchased from General Electric Company, USA, was used in this study. The weight average molar mass, $M_w = 5.8 \times 10^4$, and $M_w/M_n = 1.92$ were determined by gel permeation chromatography (GPC) (Waters 2410 refractive-index detector) at 50 °C calibrated against polystyrene standards. N, N-dimethylformamide (DMF) and tetrahydrofuran (THF) were used as received.

2.2. Synthesis of PS-*b*-P4VP

PS-*b*-P4VP diblock copolymers with two different compositions were synthesized by sequential anionic polymerization following the procedure described elsewhere [19]. The polymerization of styrene as the first block was initiated with *s*-butyl lithium suspended in cyclohexane. After 2 h, 4-vinylpyridine monomer was added and the temperature of –62 °C was maintained for a further period of 2 h. The polymerization was quenched with argon saturated methanol. After the addition of a few crystals of 2, 6-di-*tert*-butyl-4-methyl-phenol (to prevent thermal decomposition), half of the THF was removed by distillation at reduced pressure. The block copolymer was obtained by precipitation of the solution into a 10-fold excess of a 1:1 (v/v) methanol/water mixture with a typical yield of 60–70% [19].

The PS-*b*-P4VP compositions were determined by means of ¹H NMR spectroscopy in deuterated chloroform as solvent. ¹H NMR spectra were recorded on a Bruker advance 300 NMR spectrometer at 300 MHz with internal standard DMSO-*d*₆. The molecular weights of the precursors and molecular weight distributions were measured by GPC at 30 °C calibrated against polystyrene standards. Two different types of PS-*b*-P4VP diblock copolymers were used in this study which we refer to “PSP4VP-A” and “PSP4VP-B”. The molecular characteristics of the block copolymers are listed in Table 1.

2.3. Production of hollow fiber membranes

The copolymers were dissolved in mixtures of DMF and THF at room temperature for about 24 h under agitation with a magnetic

Table 1
PS-*b*-P4VP block copolymers characteristics.

Block copolymer code	Block copolymer type	Molecular weight (kg/mol)	Polydispersity index	P4VP content (wt %)
PSP4VP-A	PS _{83.3} - <i>b</i> -P4VP _{16.7}	198	1.07	16.7
PSP4VP-B	PS ₈₁ - <i>b</i> -P4VP ₁₉	167	1.06	19.0

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