



# Mimicking permafrost formation for the preparation of porous polymer membranes



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## ABSTRACT

Here, we demonstrate the fabrication of a microporous membrane and its surface modification via solvent crystallization of a polymer solution under a temperature gradient, similar to the natural process to form permafrost and the subsequent polygonal ground pattern produced during glacier formation. This system was prepared spreading a polyvinylidene fluoride (PVDF) solution on a silicon wafer, followed by crystallization. The solvent crystals were uniformly distributed by applying a directional temperature gradient over a PVDF solution layer. Finally, the microporous membranes were formed by removing solvent crystals via freeze-drying, similar to natural landform formation, such as the patterned ground that arises from permafrost. The introduction of co-solvent systems allowed for the systematic control of the pore morphologies of resulting polymer membranes including pore size, pore wall thickness, and surface topography. Overall, the composition of solvents in the crystallization of PVDF solution was the key factor affecting crystallization behavior, thus determining the morphology, crystallinity, and even polymorph. We believe this bio-inspired approach will open the door to a range of interesting studies related to micro/nano-materials fabrication.

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## 1. Introduction

Polymer materials with highly ordered porous structures can be used as separation media [1], high-surface area adsorbants [2], catalytic supports [3], and platforms for cell cultures [4]. Polymer materials exhibit wide varieties of pore shapes, connectivity, pore wall thickness, and surface morphology, depending on the fabrication methods. Accordingly, efforts have been made to develop a convenient and effective method of preparing porous polymer materials of controlled pore alignment and tortuosity, including chemical etching [5,6], colloidal assembly [7,8], layer-by-layer deposition [9], and template-based techniques [10,11]. However, most approaches are limited by severe conditions, including dangerous chemicals, low processing efficiency, complex devices, and high processing costs. Moreover, most of the existing methods are insufficient to precisely control pore morphologies, and they suffer from poor connectivity.

Recently, we developed highly ordered polymeric membranes with through-thickness nanopores prepared using the nano-frost

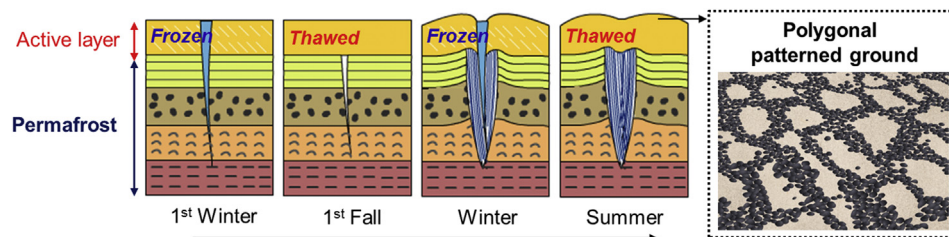
array technique [12]. The formation of nano-frost on polymer surfaces and the subsequent removal of the nano-frost crystals produced nanoporous polymer membranes with an average thickness of 250 nm. The resulting nanomembranes floating on the water surface were easily transferred to various substrates, such as glass, plastic, metal grids, and mica sheets. Although this method is new and it is relatively time consuming, its scale-up is quite challenging. Thus, the availability of the membrane is limited. Moreover, for practical applications, a template-free technique is desirable.

To address these challenges, we hypothesized that directional solvent crystallization in a polymer layer containing co-solvents would create aligned micropatterns similar to natural permafrost and the subsequent patterned ground formation (Scheme 1). Permafrost is defined as ground (soil or rock and the included ice or organic materials) that remains at or below 0 °C. Permafrost was formed during cold glacial periods and has persisted through warmer interglacial periods [13]. In areas not overlain by ice, there exists an active top layer of soil. Since there is a mismatch between the permafrost and the active layer, the soil above the ice-wedges is pushed up, thus forming ridges on the ground, called “ice-wedge polygons”. Water evaporation from the active layer surface induces a much larger mismatch [14].

Inspired by such natural geometry, we developed microporous

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**Scheme 1.** Schematic diagram describing the formation of patterned ground in permafrost areas that are affected by seasonal frost. All schemes were drawn using Adobe Flash CS4 Professional.

polymer membranes with a highly ordered pore pattern. We demonstrate this concept with polyvinylidene fluoride (PVDF) as a model semicrystalline polymer in order to further examine the possibility of controlling the crystallinity and polymorphism of a polymer. Permafrost formation was mimicked by first spreading a PVDF solution onto a silicon wafer. Then, a polymer solution in which PVDF was dissolved in 1,4-dioxane ( $T_m = 11.8^\circ\text{C}$ ) was unidirectionally moved to liquid nitrogen so the 1,4-dioxane could crystallize directionally in the polymer layer. Further, in order to test the controllability of the crystal shape and size in regulating the polygonal pattern, acetone ( $T_m = -95^\circ\text{C}$ ) was added into 1,4-dioxane, thus inducing a non-permafrost zone (active layer) and, subsequently, its evaporation. For the convenience of discussion, the physical properties of the PVDF and solvents are summarized in Table S1. Through this approach, the pore morphologies including pore size, pore wall thickness, and surface topography were tuned through a one-step solvent crystallization of the polymer solution. Additionally, we examined whether co-solvents affected the molecular regularity of resulting PVDF membranes. As far as we know, most research efforts have focused on studying the crystallization of solute, not solvent; moreover, the effect of a co-solvent in crystallization has, to date, seldom been reported. We believe ours is the first demonstration of natural geometry-mimicking co-solvent crystallization in a polymer solution to provide alignment of solvent crystals and subsequent pore patterns in a polymer layer.

## 2. Experimental section

### 2.1. Preparation of porous PVDF membranes

Poly(vinylidene fluoride) (PVDF, average  $M_w = 534$  Kg/mol) was purchased from Sigma–Aldrich (MO, USA) and used as a model semicrystalline polymer. PVDF was dissolved in 1,4-dioxane (Samchun Pure Chemical Co., Ltd) at a concentration of 50 mg/mL. The co-solvent solution consisted of a mixture of 1,4-dioxane and acetone (Sigma Aldrich) and different compositions were

used. The properties of the solvents are summarized in Table S1. Firstly, the PVDF solution was spread onto a silicon wafer (thickness = 50–55  $\mu\text{m}$ , WaferTec, Seoul, Korea). With a homemade device [15], the wafer substrate with a PVDF solution was moved to a liquid reservoir at a controlled speed of 200  $\mu\text{m/s}$ . As the substrate uni-directionally moves, sample was cooled to induce a directional temperature gradient. Thus, the solvent crystal nucleation in a polymer solution start from the bottom and grow along the thickness direction thereby create uniform cylindrical solvent crystals (Scheme 2). After completely crystallizing 1,4-dioxane, the solvent crystals were removed using an FD-1000 freeze-dryer (EYELA, Tokyo, Japan, trap chilling temperature  $-45^\circ\text{C}$ , 5.6 Pa) for 24 h.

### 2.2. Field emission-scanning electron microscopy (FE-SEM)

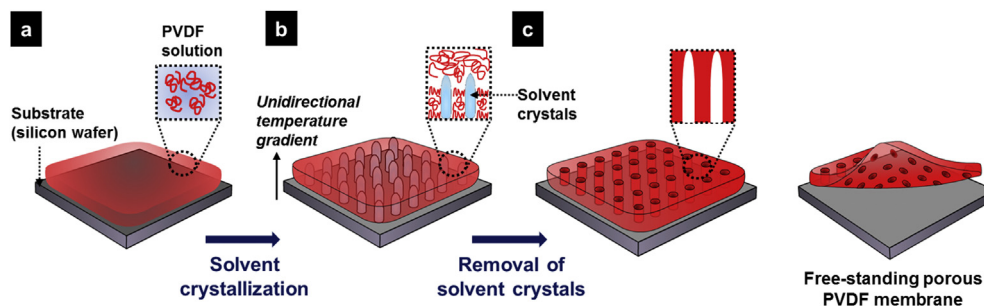
The morphologies of dried samples were investigated by FE-SEM (SIGMA, Carl Zeiss) at an accelerating voltage of 5 kV after coating samples with a platinum layer by ion sputtering (E-1030, Hitachi, Japan). The pore morphologies including pore size, pore wall thickness, and porosity were analyzed by using an Image J. Three images per each condition were analyzed to obtain the mean value.

### 2.3. Atomic force microscopy (AFM)

To characterize the surface topography of pore wall, phase images were obtained on an XE-100 AFM (Park Systems, Korea) in a tapping mode. The silicon cantilever (NSC15, MikroMasch, Spain) with a spring constant of 30.05 ( $\pm 3.7$ ) N/m was used.

### 2.4. Attenuated total reflectance/Fourier transform-infrared spectroscopy (ATR/FT-IR)

ATR/FT-IR spectra were taken on Nicolet 6700 (Thermo Scientific) in order to confirm the polymorphic form of PVDF. The frequency was measured from 550  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$  for 256 times.



**Scheme 2.** (a) The diagram shows presentation of freestanding porous membranes from a polymer solution. (a, b) The solvents are crystallized and aligned by reducing the temperature to below the freezing point of the chosen solvent (here, 1,4-dioxane). (c) The subsequent removal of solvent crystals produces an aligned porous structure. All schemes were drawn using Adobe Flash CS4 Professional.

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