Technology Offer

Free Standing Dry and Stable Nanoporous Polymer Films Made through Mechanical Deformation

Ref.-No.: 0903-6483-LC

Nanoporous membranes consist of pores with diameters in the range of nanometers and sub nanometers that can separate liquid or gaseous mixtures.

One of the key applications of nanoporous membranes is in water filtration to remove impurities, such as bacteria, viruses, and salts. Nanoporous membranes are also used in energy-related applications, such as gas separation and fuel cells. The membranes can also be used as electrodes in energy storage devices such as batteries and supercapacitors. Other important applications are diagnostics, drug delivery and food processing. According to a 2023 ReportLinker market report the global nanoporous membranes market size reached US$ 816.6 Million in 2022 and is expected to rise to US$ 1,218.7 Million by 2028.

One of the significant challenges is the fabrication and scalability of nanoporous membranes. These membranes require precise control over pore size, shape, and distribution, making their fabrication a complex and expensive process. There is a need for more cost-effective and scalable fabrication techniques to make nanoporous membranes more accessible and practical for widespread use.
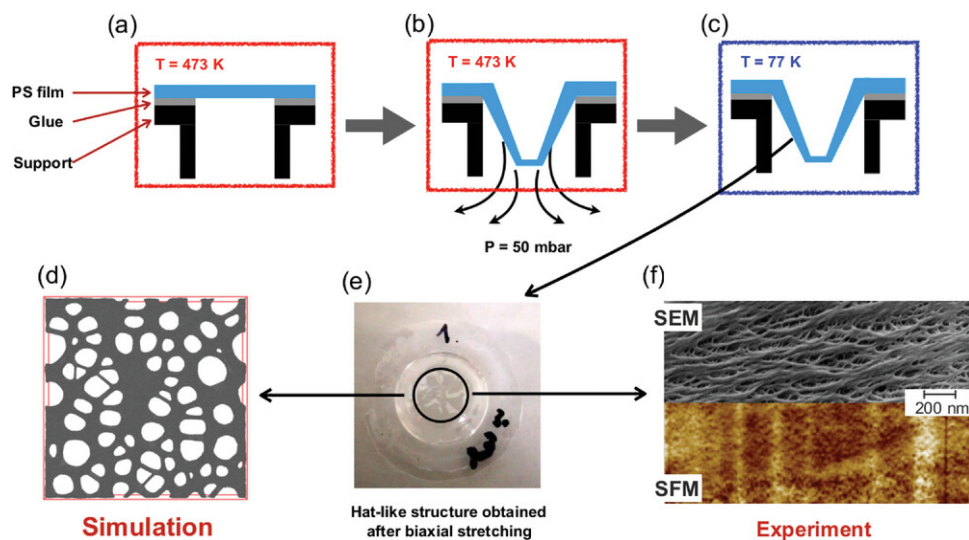
Technology

We offer a new straight forward approach to create nanoporous polymer membranes with well defined average pore diameters between 10 and 50 nm account for more than 70 % of the total pore volume.

The process is based on (fast) mechanical deformation of highly entangled polymer films at high temperatures and a subsequent quench below the glass transition temperature T_g. The methodology does not need any chemical processing, supporting substrate, or self assembly process and is solely based on polymer inherent entanglement effects. The resulting membranes are stable at ambient conditions and display remarkable elastic properties.

Figure 1.
Schematic representation of experimental protocol to deform PS films into "hat" like shape.
a) Pre-heating polymer film at 473 K,
b) applying a pressure of 50 mbar to deform the film into a "hat-like" shape, and
c) the deformed film is fast quenched to 77 K in a liquid nitrogen bath, a
d) applying an analogous protocol (a–c) in MD simulations to produce nanoporous films
e) the hat as it is obtained from experiments after stretching and temperature quench, and
f) SEM and SFM image of the same region of the top part of a hat (side view) of a P-40 film.

Well controlled porous membranes can easily be made from various commodity polymers like polystyrene, polycarbonates, polyetherketones and -sulfones, polyamides, polyesters, polylactic acids, perfluoralkoxyalkanes, polyvinylchloride, polymethacrylamides, poly(meth)acrylates, polyphenyleneethers, -sulfides and -sulfones, polysulfones, styrene-acrylonitriles, polyarylates and cellulose acetates for example. Guidelines to optimize the process parameters based on the used polymer and the wanted product specification is available.

For first laboratory proof of concept experiments monodisperse atactic polystyrene of $M_n = 1 \times 10^6$ Da obtained from Sigma Aldrich was used. Transparent PS films of about 100 µm thickness were prepared by pressing 250 mg of PS under 20 kN load and temperature 433 K (well above Tg = 380 K) for an hour.
To deform the film with a biaxial stress, the PS film was immobilized by the edges over circular aperture of 1.75 cm of diameter and deformed by applying a load using the negative pressure generated by a controlled vacuum of 50 mbar at a temperature of 473 K for different times of duration. Depending on the duration of vacuum pressure applied, different degrees of stretching were achieved in PS films as given in Table 1. To preserve the morphology of the stretched films, they were quenched by dipping them into liquid nitrogen. Computer simulation results reveal that such a quench is not needed and that cooling down below Tg is sufficient. After that films were kept at room temperature without any special conservation precautions.

Sample	Thickness before stretching [µm]	Duration stretching [mins]	Thickness after stretching [µm]	Density ρ [g cm^{-3}]	Effective refractive index n_{eff}	Porosity $\phi^{\#}$	Porosity ϕ^*
P-0	91	0	91	0.98	1.596	0	
P-10	110	15	106	0.94	1.545	0.10	
P-26	80	21	40	0.83	1.464	0.26	
P-40	100	30	12	0.74	1.385	0.40	0.43

Table 1. Samples after different degree of stretching. Film density ρ, effective refractive index n_{eff}, and porosity φ ($\phi^{\#}$ estimated according to $n^2_{eff} = \phi^{\#} n^2_{air} + (1 - \phi^{\#}) n^2_{PS}$ and φ* obtained from BET measurement of examined porous and bulk PS films.

Because it was found that the transversal and longitudinal sound velocities C_T and C_L of the porous polymer films produced with the offered method are higher than the sound velocity of the bulk material, Brillouin Light Spectroscopy (BLS) can be used as a non-contact, non-invasive and zero-strain method for the identification of the nanoporous polymer material claimed by our patent application.

Literature
Kurt Kremer et al: "Free Standing Dry and Stable Nanoporous Polymer Films Made through Mechanical Deformation", *Adv. Sci.* **2023**, *10*, 2207472

Patent Information
EP Priority patent application filed in April 2023.

Contact

Dr. Lars Cuypers
Senior Patent- & License Manager
Chemist
Phone: +49 (0)89 / 29 09 19 - 21
eMail: cuypers@max-planck-innovation.de