Fabrication and Scale-Up of Porous Polybenzimidazole (PBI) Supports for Gas Separation Composite Membranes

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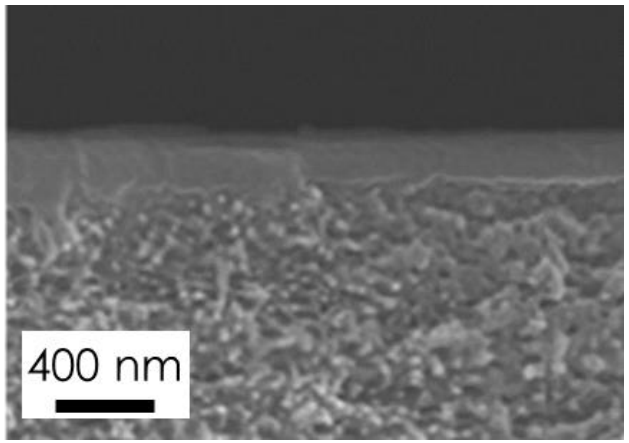
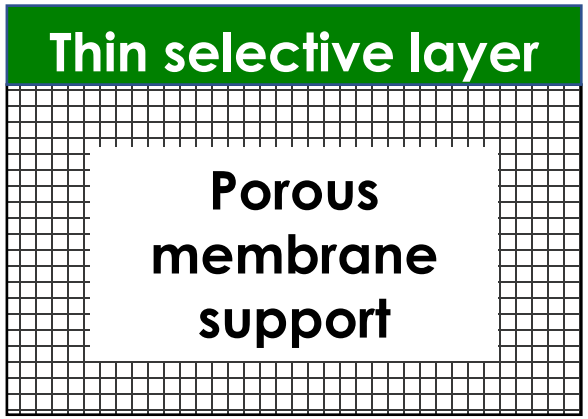
Outline

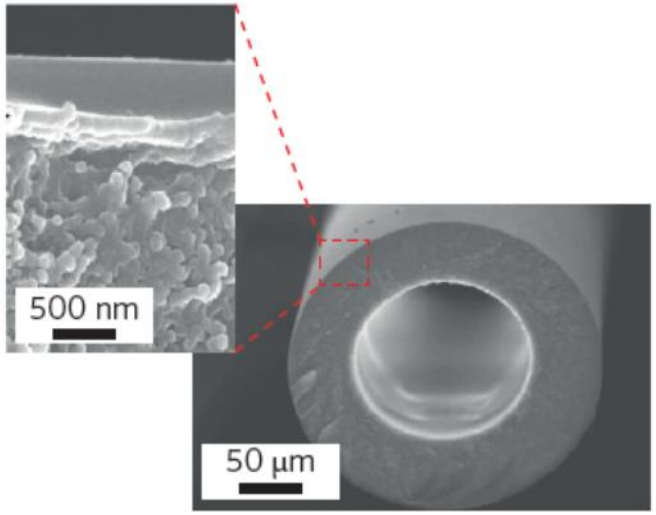
- Importance of porous membrane supports
- Membrane fabrication via phase inversion
- Membrane characterization
  - Gas permeance
  - Surface pore structure
  - Chemical and thermal stabilities
- Supporting performance in composite membranes
- Scale-up fabrication
- Conclusions
- Acknowledgments

Gas Separation Often Relies on Thin Film Composite (TFC) Membranes



Flat-sheet

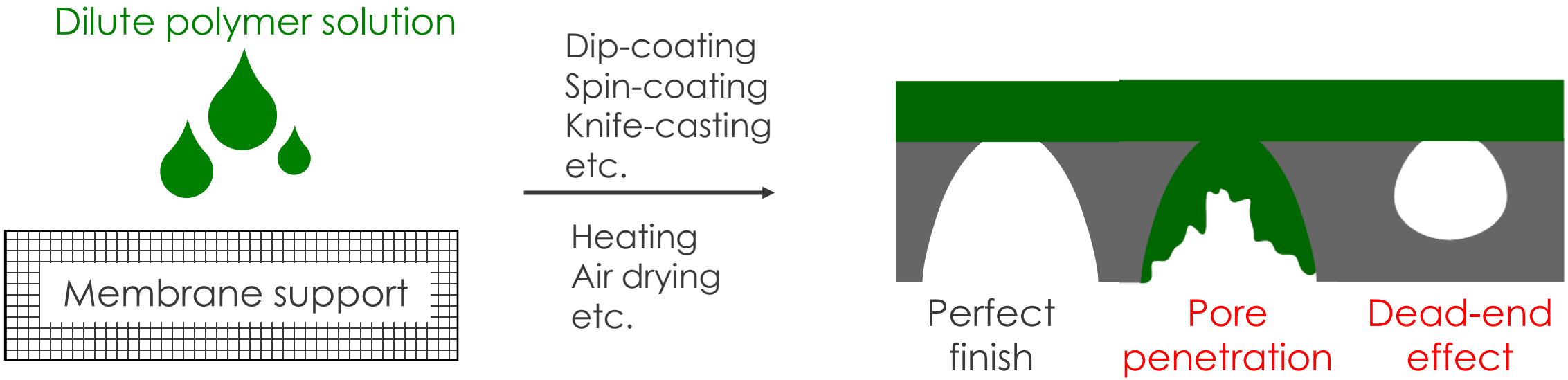




Hollow fiber

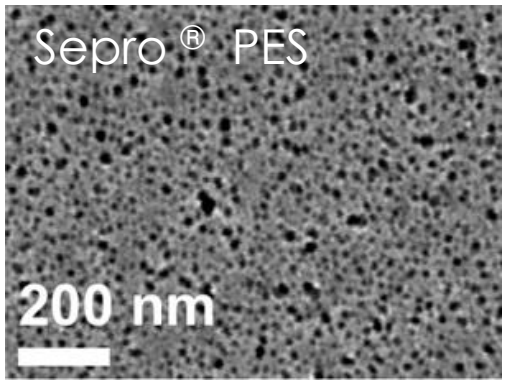
Koros et al, *Nature Materials*, 2017, 16, 289.

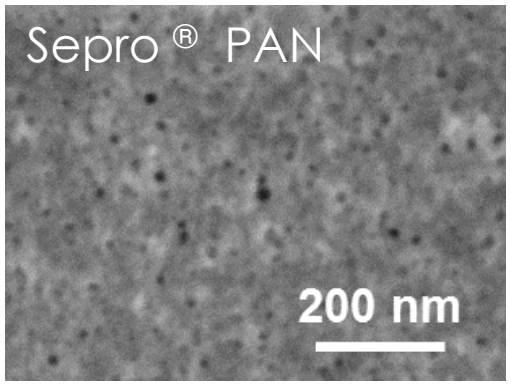
Promising Porous Membrane Supports

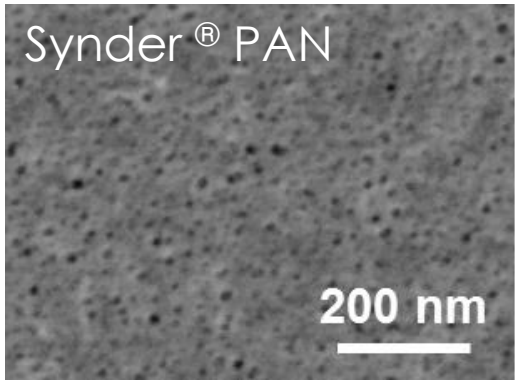


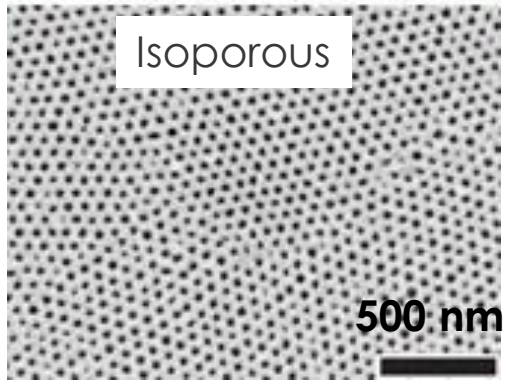
- **High (effective) porosity (>10%)** - to provide sufficient permeance
- **Small pore size (10-50 nm)** - to ease pore penetration effect
- **Chemical stability** - to tolerate aggressive coating solvents
- **Thermal stability** - to withstand harsh drying conditions

Membrane Supports in the Market and Other Labs





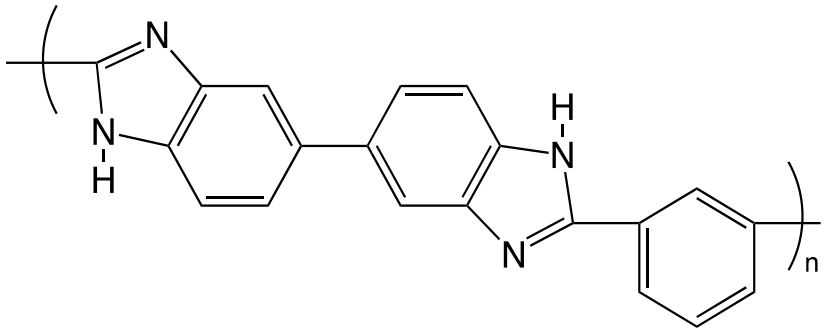




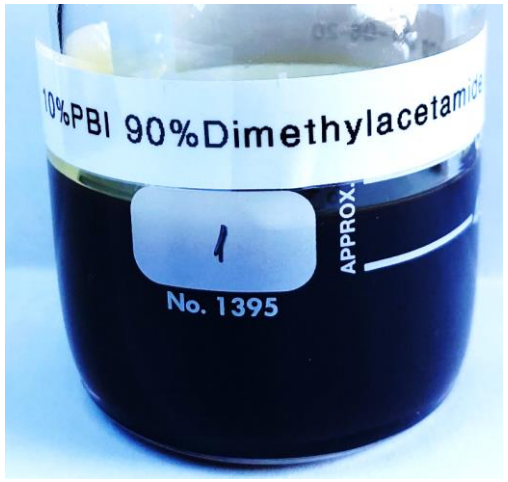
Materials	Glass Transition Temp.(°C)*	Solvent Resistance (R: Resistant/N: Not resistant)				
		Alcohol (ethanol)	Ketone (acetone)	Aromatic (toluene)	Cyclic ether (tetrahydrofuran)	Halogenated (chloroform)
Polyacrylonitrile (PAN)	82 to 145	R	R	R	R	R
Polyethersulfone (PES)	158 to 228	R	N	N	N	N
Polysulfone (PSF)	179 to 194	R	N	N	N	N
Polyvinylidene fluoride (PVDF)	-67 to 5	R	N	R	N	N
Polystyrene-block-poly(4-vinylpyridine) (PS-*b*-P4VP)	100 to 148	R	N	N	N	N

* www. polymerdatabase.com, accessed on 10/20/2019; #Peinemann et al, *Nature Materials*, 2007, 6, 992.

Polybenzimidazole (PBI) as a Support Material



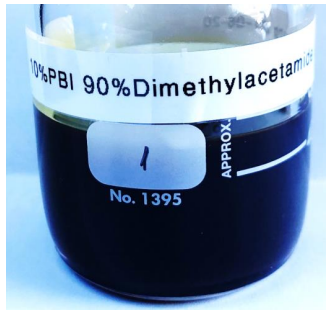
PBI powder



PBI solution

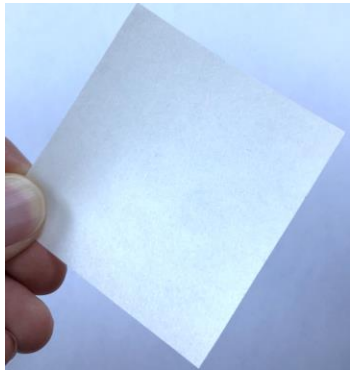
- High glass transition temp.: 425 °C
- Dissolution in very few polar solvents under heat: dimethylacetamide (DMAc)
- Membrane applications: hydrogen separation, organic solvent nanofiltration
- PBI solution: commercially available

Phase Inversion to Prepare PBI Supports



PBI-DMAc solution

Non-woven fabric substrate



Knife casting
20-30 °C

Supported PBI wet film

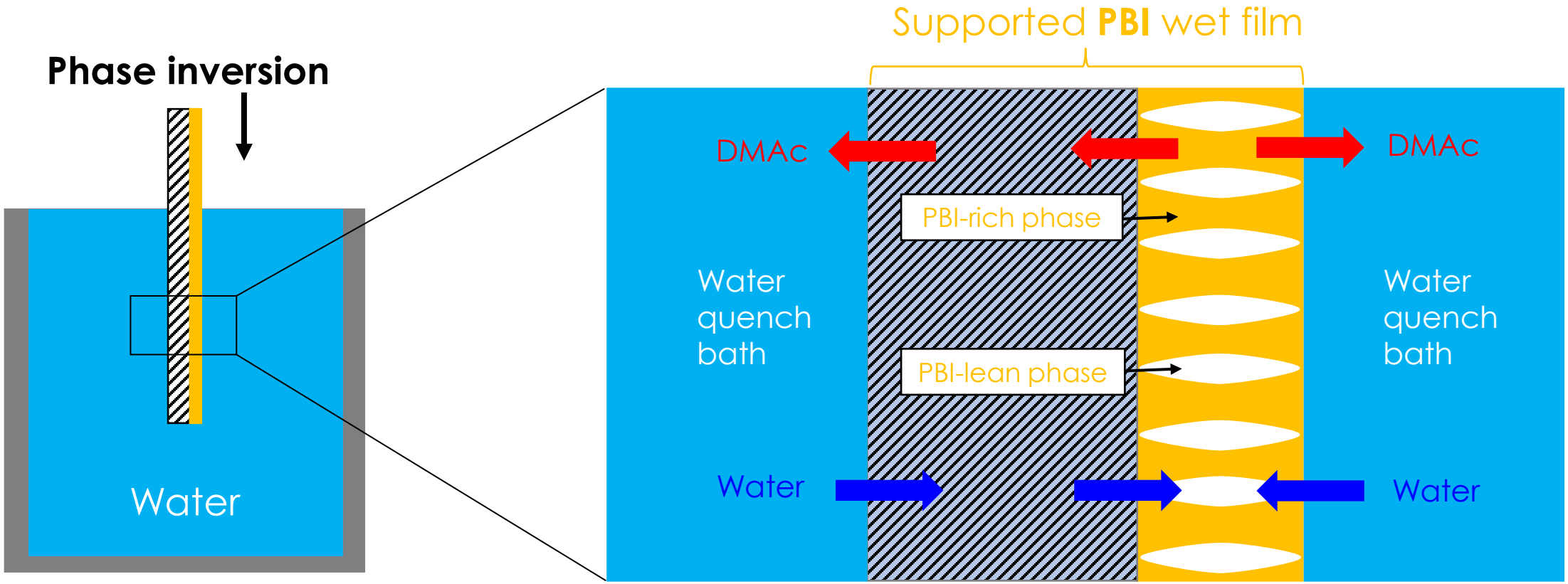
Phase inversion
Water bath
20-60 °C

Wet porous PBI support

Wash in water
Dry at 20-100 °C

Porous PBI support

Pore Morphology Determined by Solvent Exchange Process

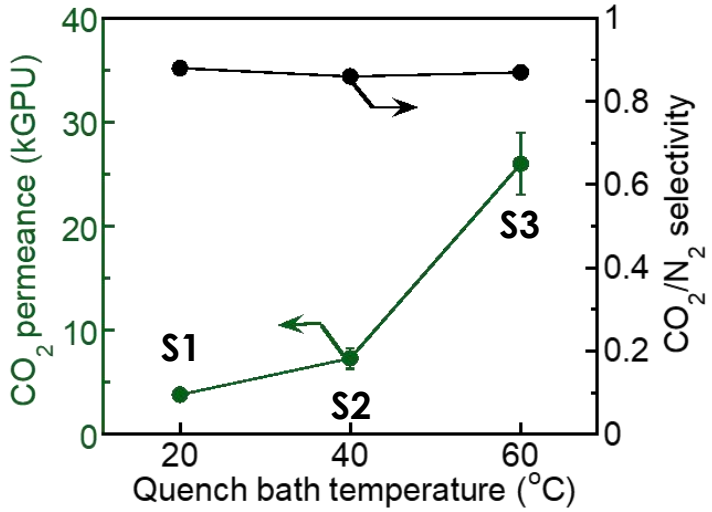


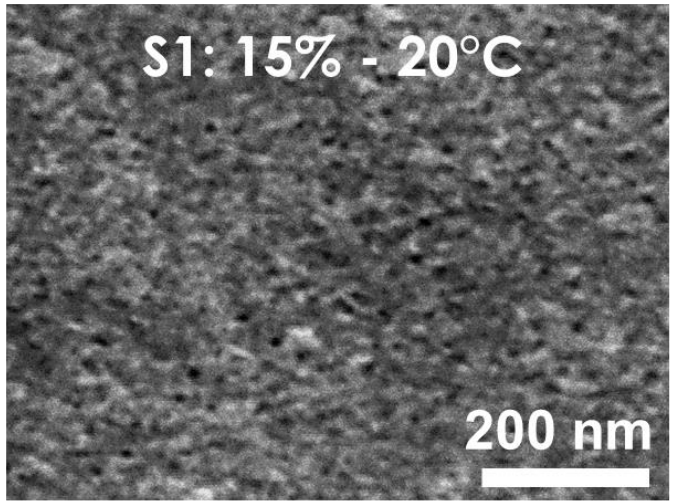
- Vigorous DMAc(solvent) - water exchange leads to pore formation
- **PBI dope concentration (DMAc content)** and **water quench bath temperature** significantly affect the solvent exchange process

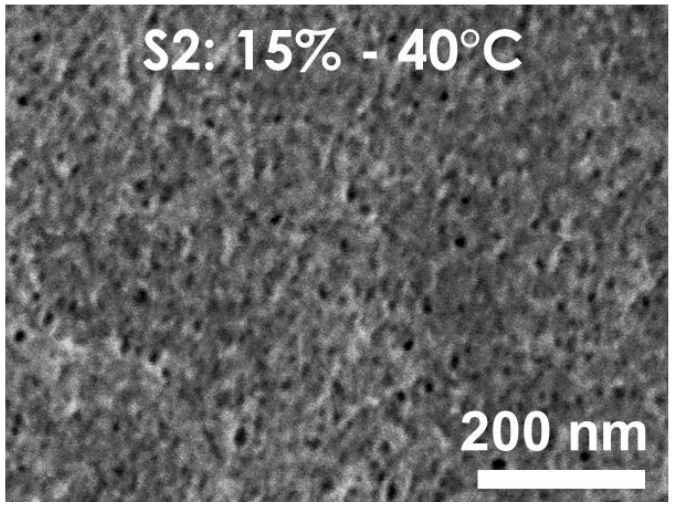
Varying Quench Bath Temp. and PBI Conc. to Achieve Different Pore Morphologies

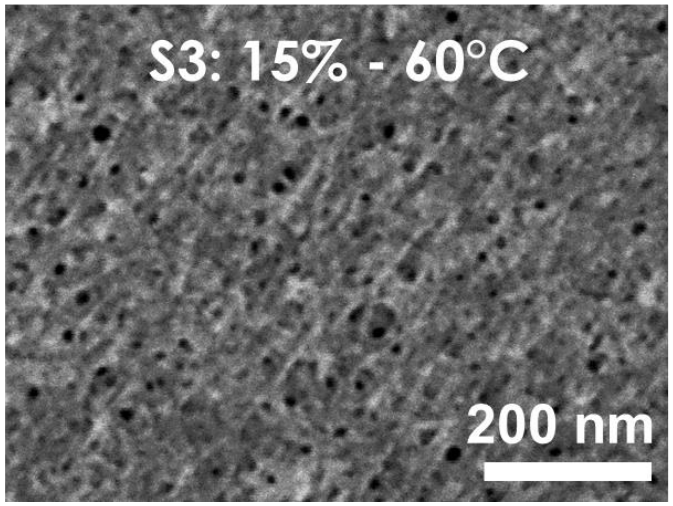
Sample	PBI (wt.%)	DMAc (wt.%)	Quench Bath Temp. (°C)	Alternative Name
PBI-S1	15	85	20	PBI-15%-20C
PBI-S2	15	85	40	PBI-15%-40C
PBI-S3	15	85	60	PBI-15%-60C
PBI-S4	12.5	87.5	60	PBI-12.5%-60C
PBI-S5	11	89	60	PBI-11%-60C
PBI-S6	10	90	60	PBI-10%-60C
PBI-S7	9	91	60	PBI-9%-60C

Effect of Bath Temp. on CO_2 Permeance and Pore Structure

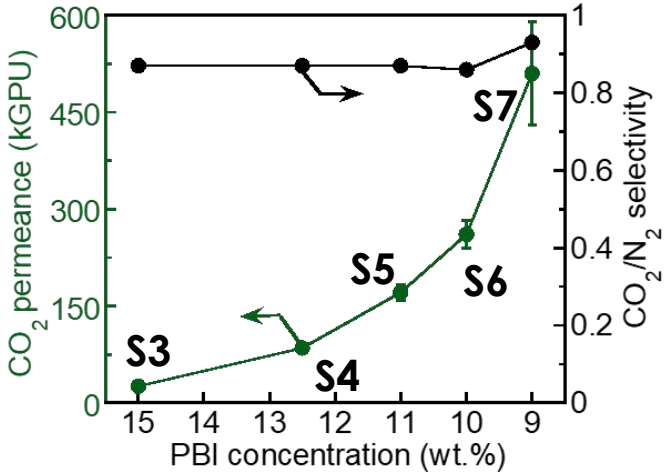


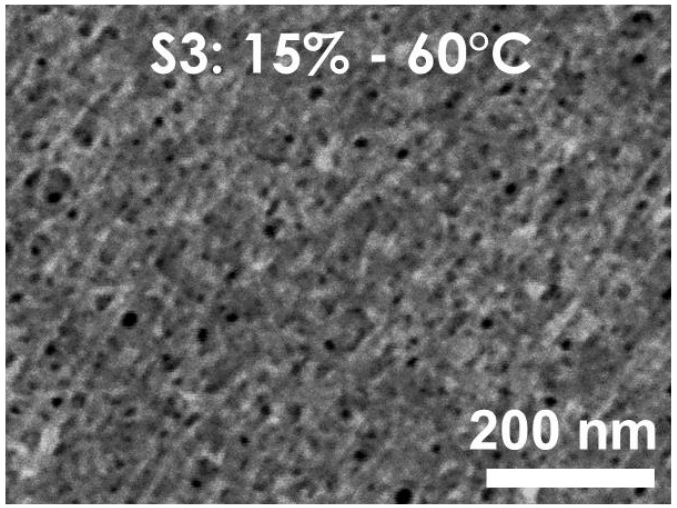


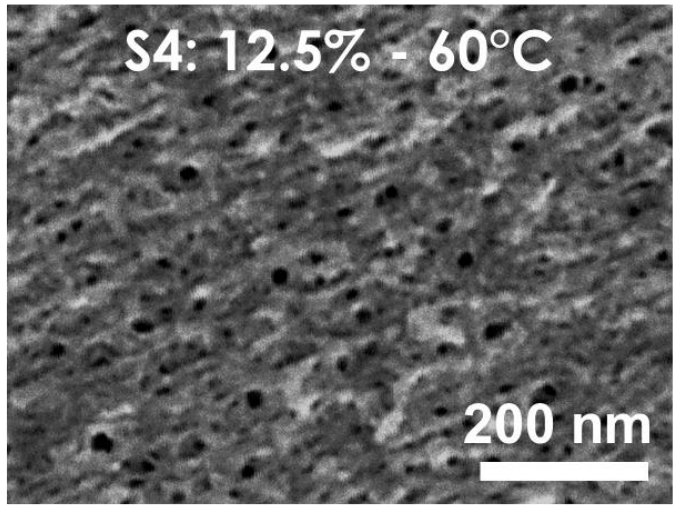


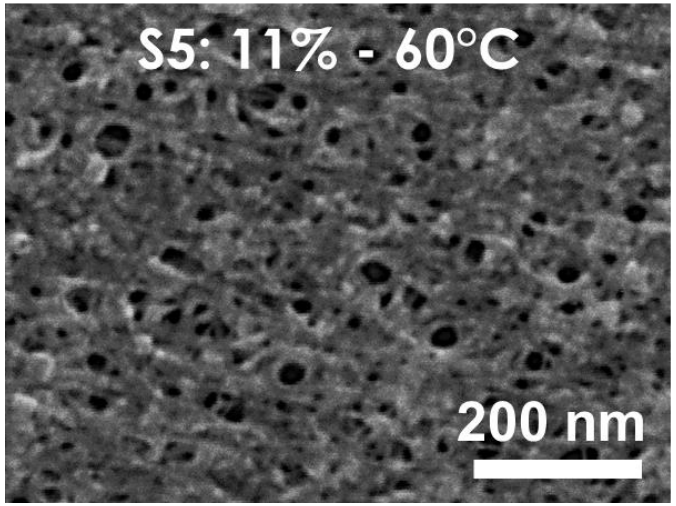


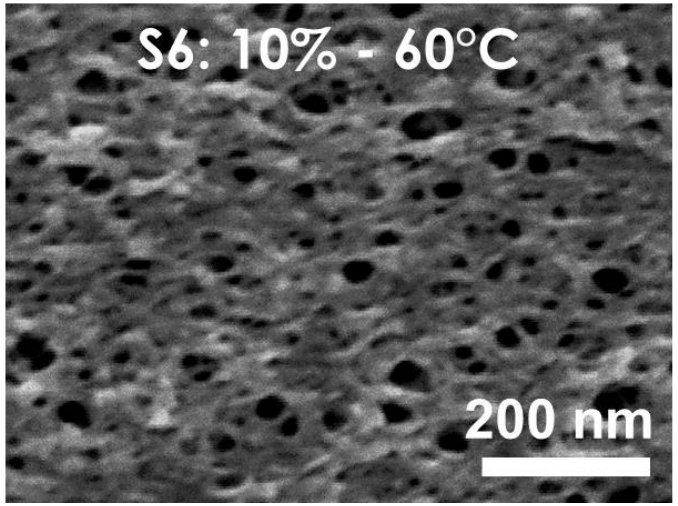
Effect of PBI Conc. on CO_2 Permeance and Pore Structure

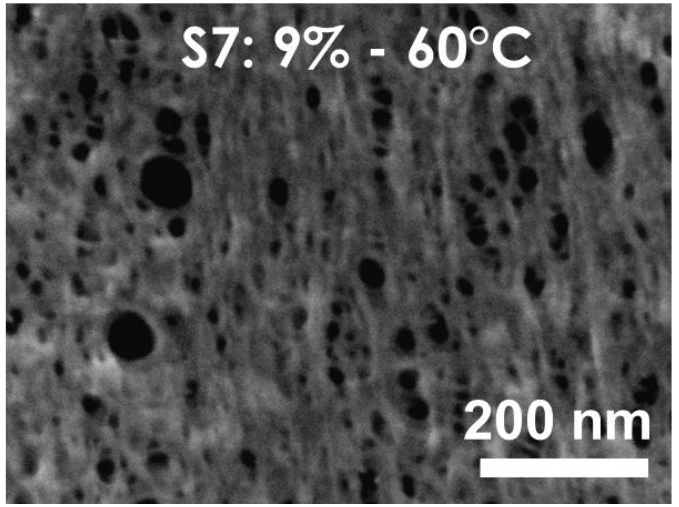




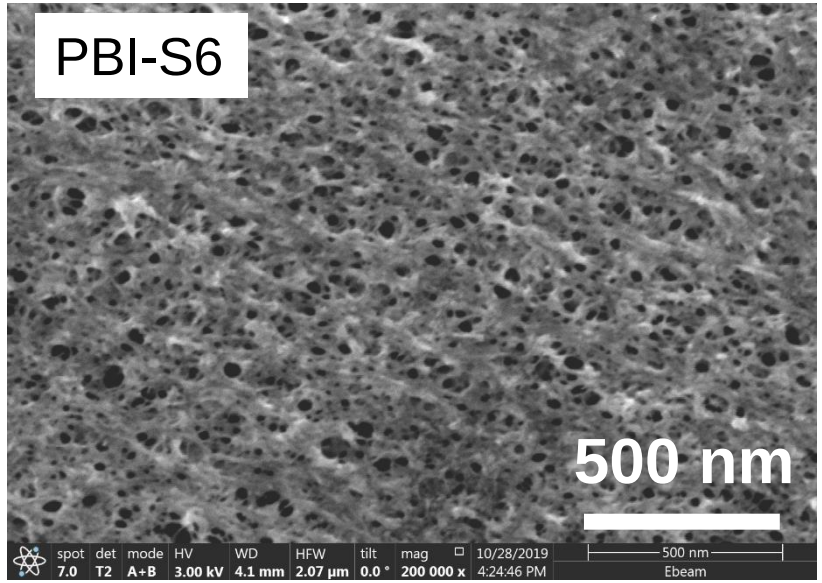


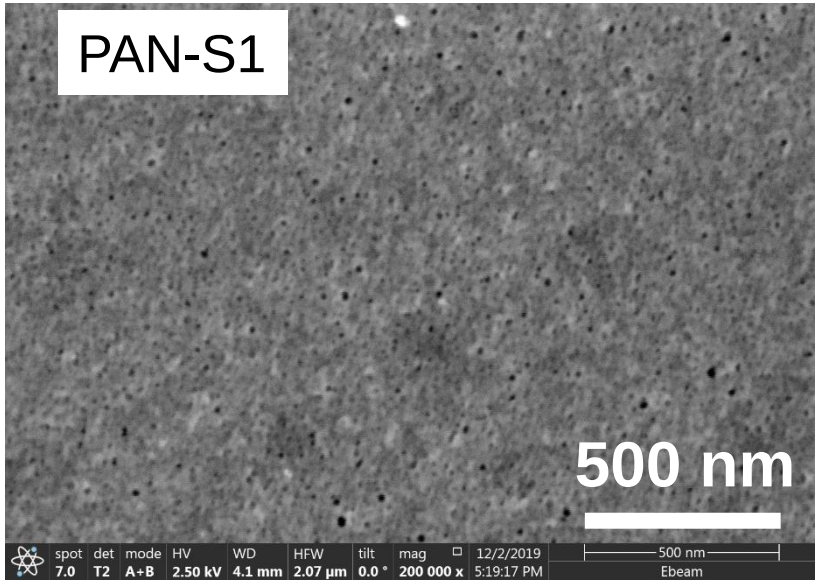


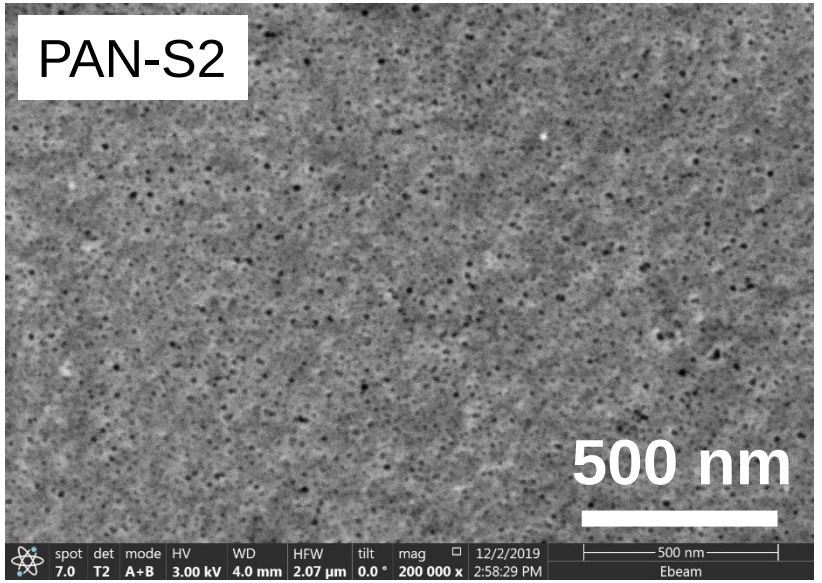




PBI Supports *vs.* Commercial PAN Supports



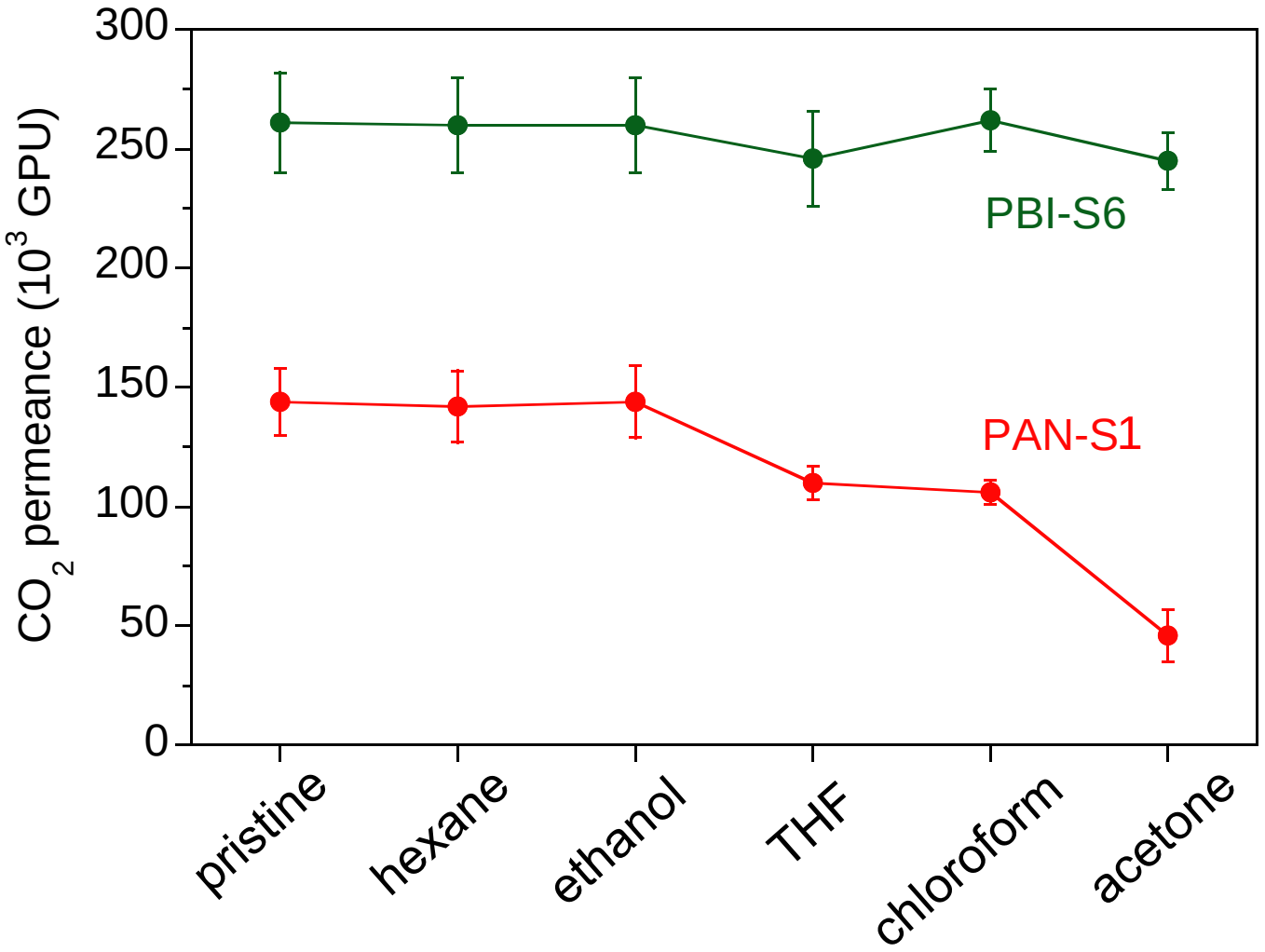


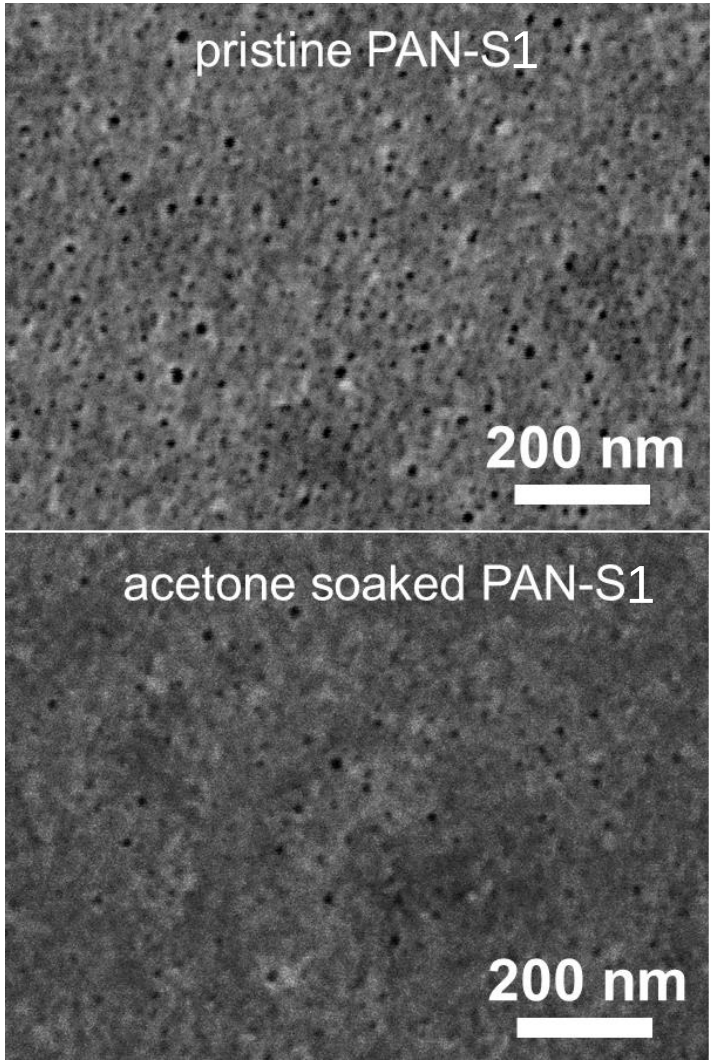


	PBI-S6	PAN-S1 (ULTURA™)	PAN-S2 (Synder®)
CO_2 permeance[1] (kGPU)	260 ± 20	138 ± 13	53 ± 1
Pore size (dia, nm)	5 - 42	≤ 20	≤ 22
Surface porosity (%)	22 ± 2	6 ± 1	8 ± 1

1. Determined at a pressure drop of 1 bar and 22 °C.

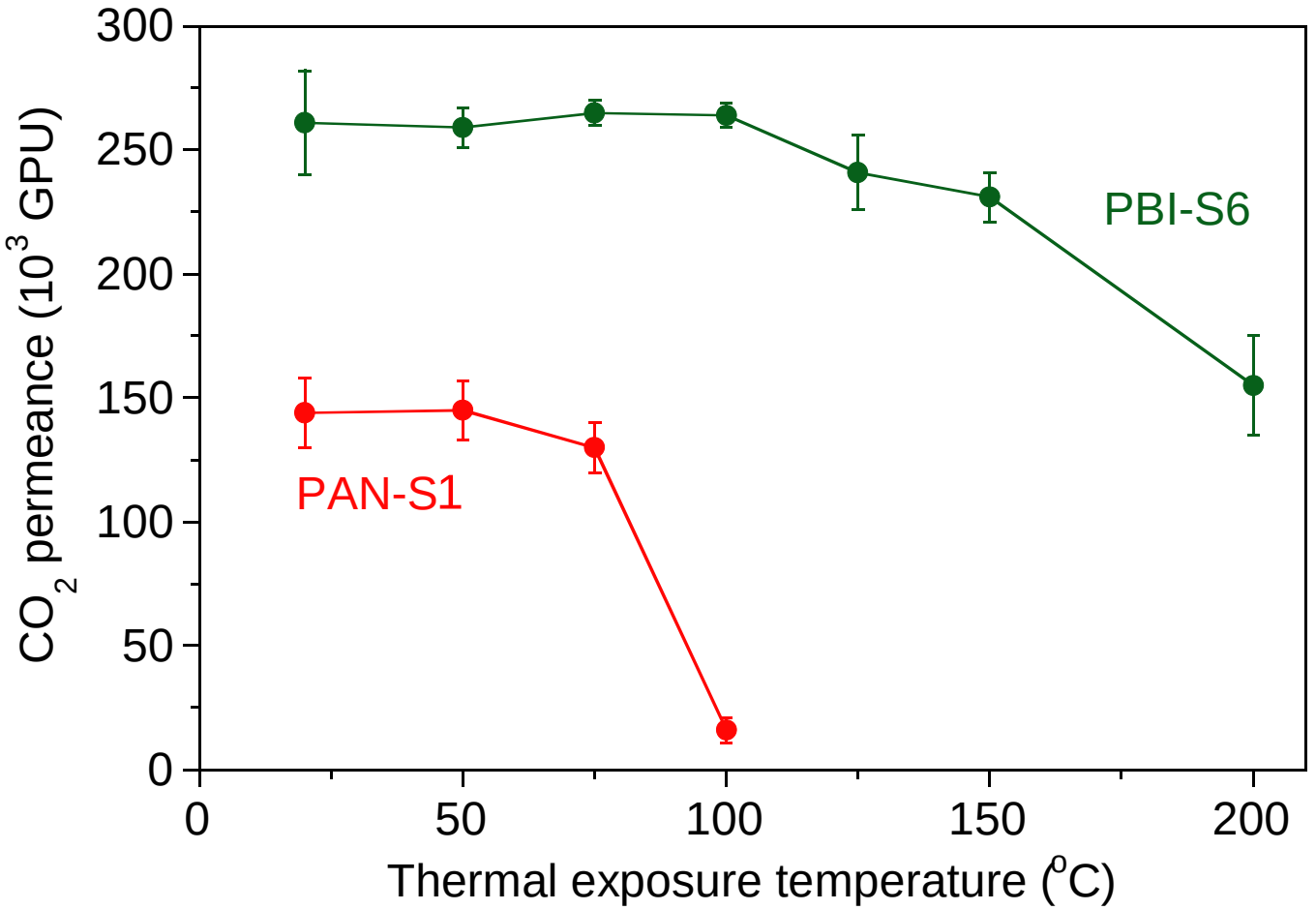
Effect of Solvent Immersion on Gas Permeance

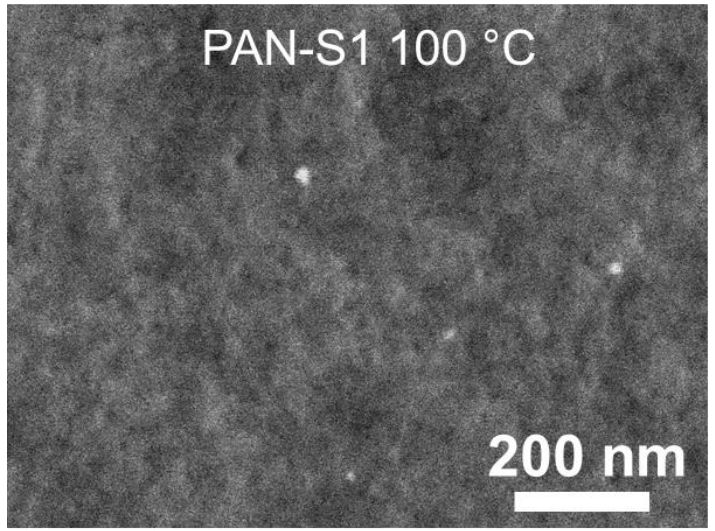


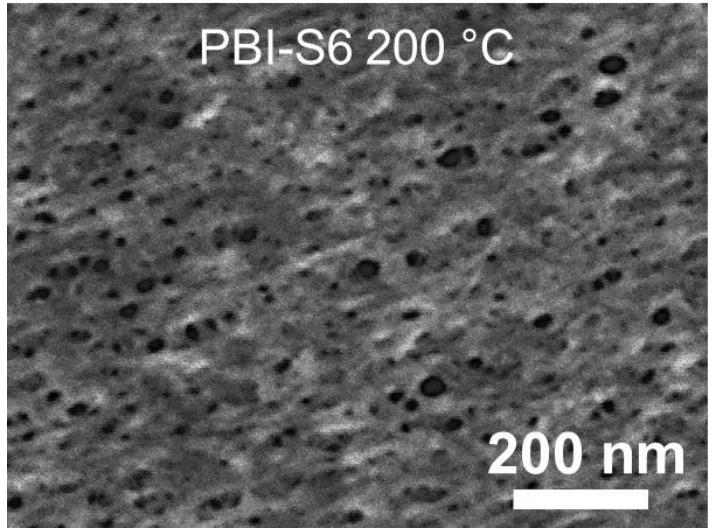


Prior to gas permeance test, each sample was immersed in a given solvent for 1 hour, followed by room temperature drying.

Effect of Thermal Exposure on Gas Permeance

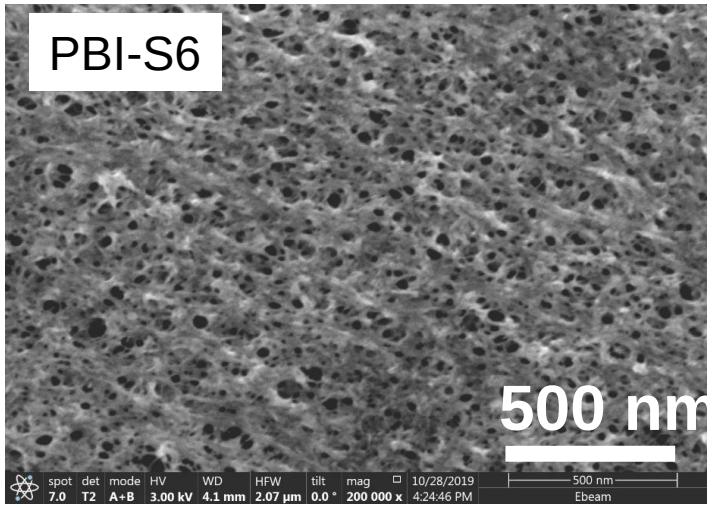


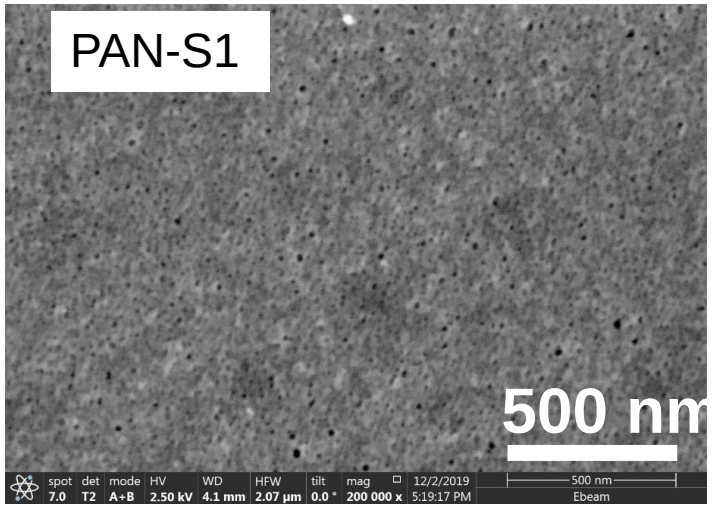


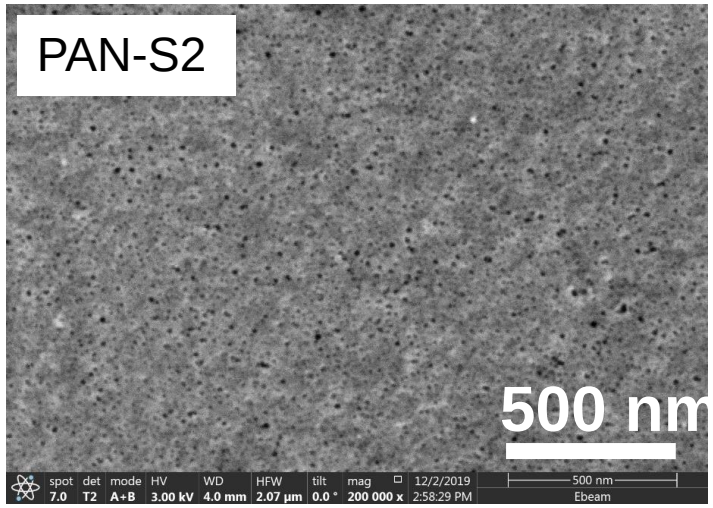


Prior to gas permeance test, each sample was thermally treated for 1 hour at a given exposure temperature.

PBI Supports *vs.* Commercial PAN Supports





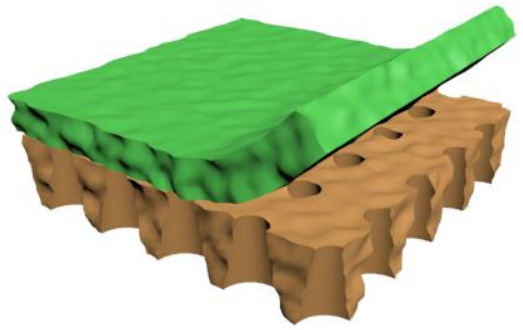


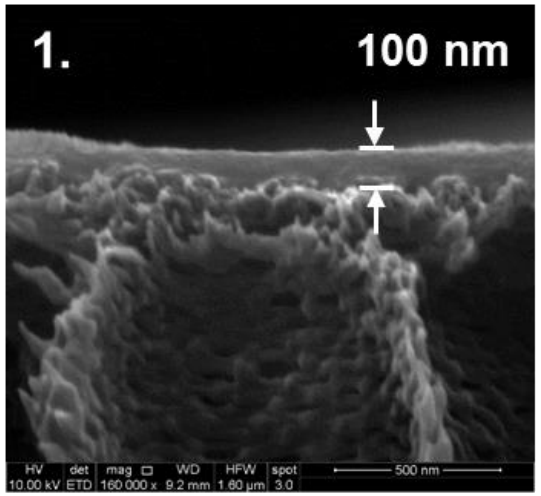
	PBI-S6	PAN-S1 (ULTURA™)	PAN-S2 (Synder®)
CO_2 permeance[1] (kGPU)	260 ± 20	138 ± 13	53 ± 1
Pore size (dia, nm)	5 - 42	≤ 20	≤ 22
Surface porosity (%)	22 ± 2	6 ± 1	8 ± 1
Operation temperature (°C)	≤ 200	≤ 75	≤ 75
Solvent resistance	Excellent[2]	Good[3]	Good[3]

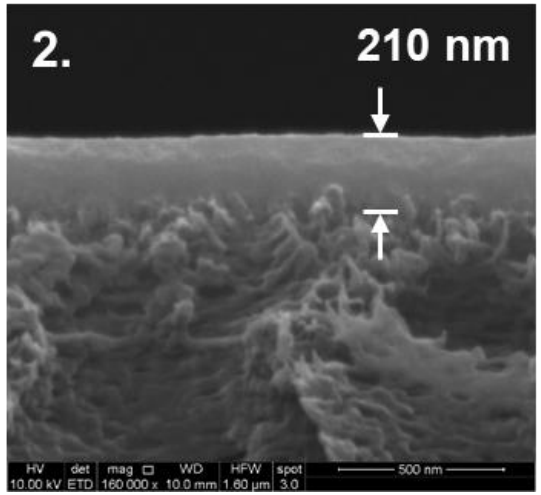
1. Determined at a pressure drop of 1 bar and 22 °C. 2. Neither dissolved or swollen in common thin film coating solvents like acetone, tetrahydrofuran (THF), and chloroform. 3. Not dissolved but swollen in common solvents.

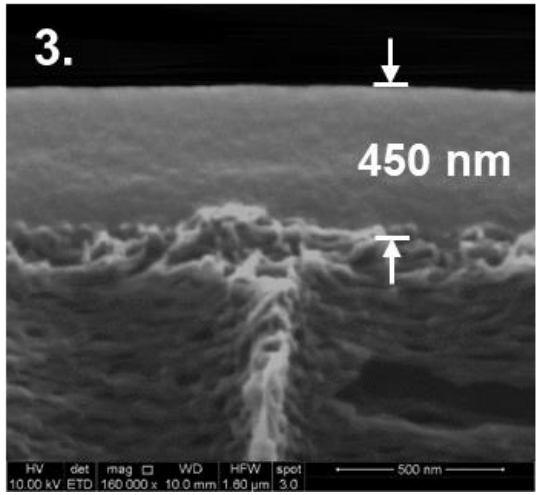
Supporting Performance in Two-Layer Composite Membranes

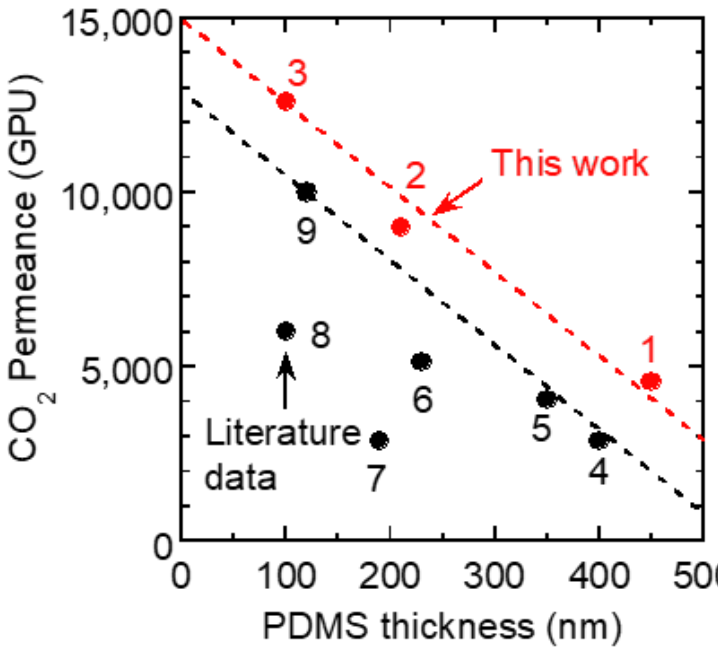
Polydimethylsiloxane (PDMS) knife-casting







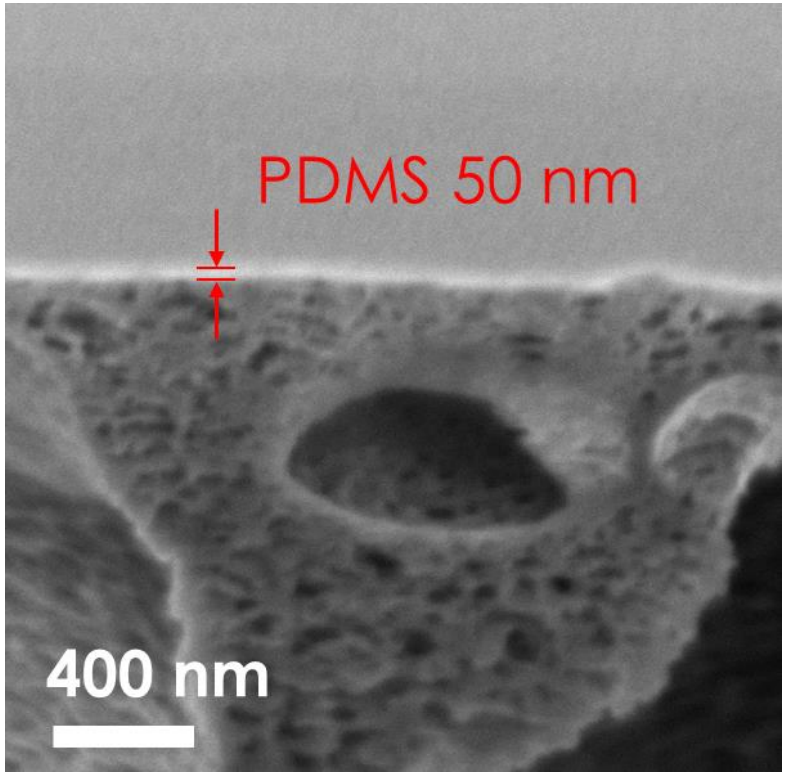




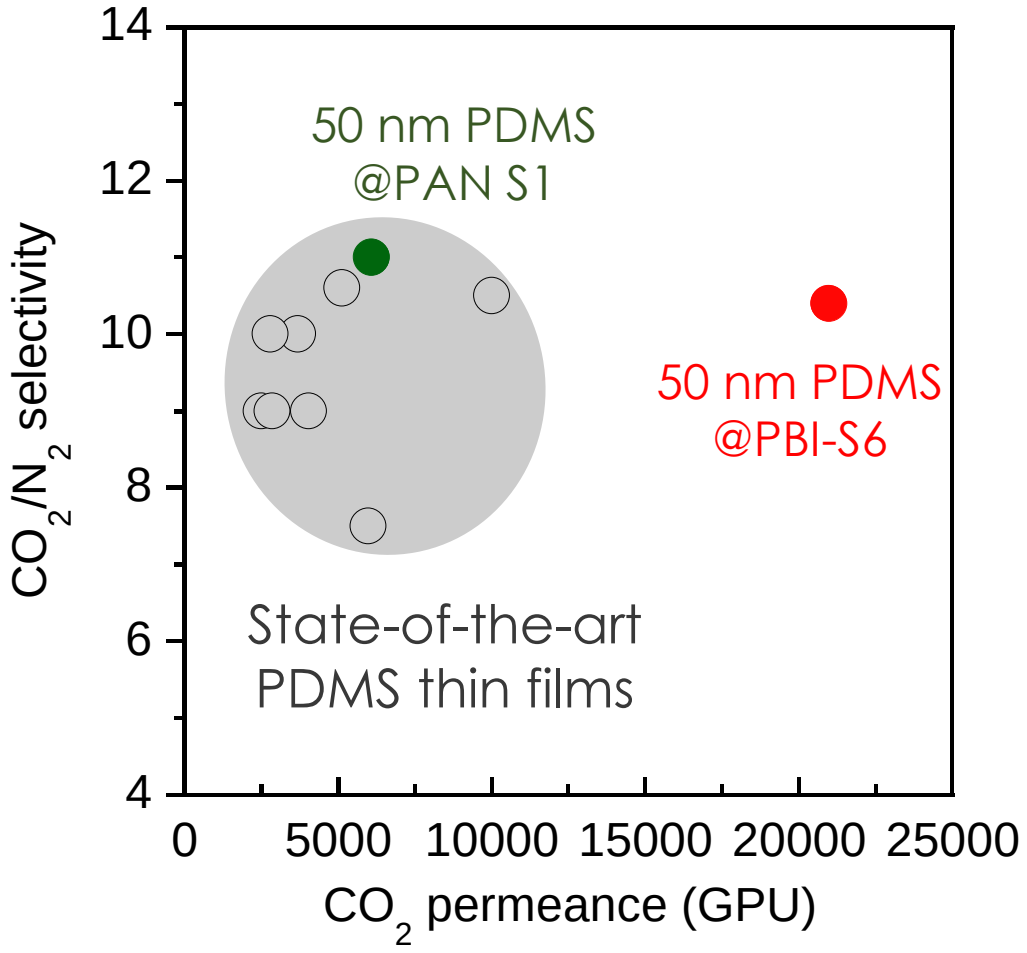
#	Substrate	CO_2/N_2	Ref.
1		11.5	
2	PBI-S6	11.6	This work
3		11.7	
4	PAN	9.0	a
5	PAN	9.0	b
6	PAN	10.6	c
7	PAN	10.0	d
8	PSF	8.0	e
9	PSF	10.5	f

References:
(a) Nanoscale, 8 (2016) 8312;
(b) J. Membr. Sci., 499 (2016) 191;
(c) J. Membr. Sci., 541 (2017) 367;
(d) Energy Environ. Sci., 9 (2016) 434;
(e) Sep. Purif. Technol., 239 (2020) 116580;
(f) ACS Appl. Mater. Interfaces, 7 (2015) 15481.

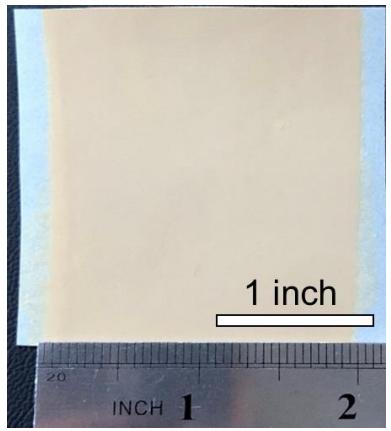
Supporting Performance in Two-Layer Composite Membranes



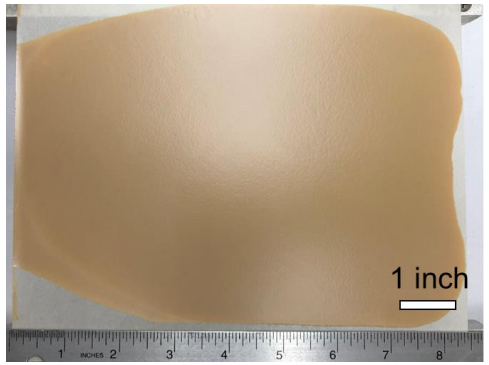
Ultra-thin PDMS film prepared by a modified coating method.



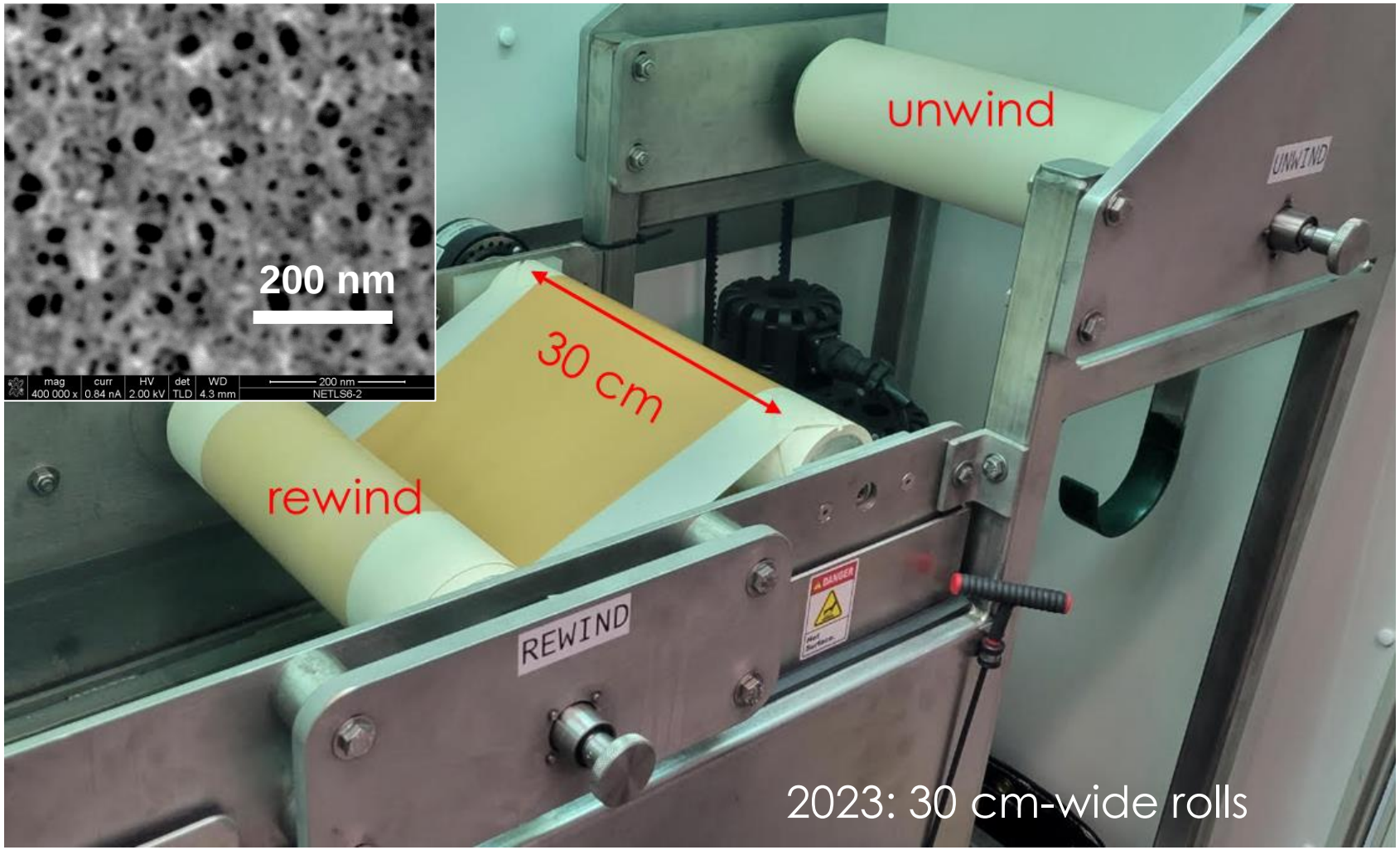
Scale-Up Fabrication via a Roll-to-Roll Process



2020: 40 cm^2



2021: ~200 cm^2



Conclusions

- **Developed scalable PBI supports with:**
  - **High porosity** (up to ~20%)
  - **Tunable pore size** (13 to 42 nm)
  - **Excellent thermal stability and solvent resistance**
  - **Demonstrated highly permeable and ultra-thin film coatings on PBI supports**
  - **Minimum waste treatment cost:** Our polymer dope only consists of PBI and DMAc, so the generated waste water (from quench bath) only contains DMAc contaminant.
- **Scaled up PBI support fabrication from the bench-scale hand casting to roll-to-roll continuous production**

Acknowledgments

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Victor Kusuma
Thien (James) Tran
Fangming Xiang
James Baker

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