Electronic Supplementary Information for

Fluorinated Polyurethane Macroporous Membranes with Waterproof, Breathable and

Mechanical Performance Improved by Lithium Chloride

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Fig. S1 Synthesis strategy of FPU.



Fig. S2 FT-IR spectrum of FPU.

FT-IR spectrum of FPU is presented in Fig. S2. The typical absorption features for carbamate group are found at 3295 cm⁻¹ (N-H), 1713 cm⁻¹ (C=O), 1533 cm⁻¹ (N-H) and 1111 cm⁻¹ (C-O-C), respectively. The -CH₂- specific peak of PTMEG has given their absorption band at 2942 and 2861 cm⁻¹. The stretching vibration for aromatic ring of MDI is found at 1599 cm⁻¹. The stretching vibration from -CF₃ and deformation vibration for CF₂ are found at 1222 and 817 cm⁻¹, respectively.



Fig. S3 ¹⁹F NMR spectrum of FPU.

As show in Fig. S3, the chemical shift for terminal CF₃ appears at 79.89 ppm, while for $-CF_2-CH_2$ appears at 126.77 ppm. The remaining $-CF_2$ - has given their chemical shift from 112.71 to 123.83 ppm. The ¹⁹F NMR spectrum confirmed that the perfluoroalkyl group had grafted on the molecular chain of FPU.



Fig S4 ¹H NMR spectrum of FPU.

Fig. S4 presents the chemical structure and ¹H NMR spectrum of FPU. The chemical shifts for $-CH_2$ -CH₂- in terminal fluorinate segments appear at 2.48 and 3.49 ppm. For PTMEG, TEG and methanol segments, the shifts for $-O-CH_2$ -, $-CH_2$ -CH₂- and $-CH_3$ appear at 3.72, 3.33 and 1.41 ppm, respectively. The signals for aromatic protons of MDI groups appear between 7.15 to 7.35 ppm and for $-CH_2$ appears at 3.63 ppm.

Concentration of PU (wt%)	Concentration of FPU (wt%)	Concentration of LiCl (wt%)	Conductivity (µs/cm)	Viscosity (cps)	Surface tension (mN/m)
14	1.75	0	0.48±0.01	1300±137	23.65±0.21
		0.002	7.23±0.04	1258±129	22.68±0.33
		0.004	15.13±0.02	1276±131	22.60±0.23
		0.006	21.05±0.05	1306±144	21.88±0.51
		0.008	27.53±0.40	1289±110	21.02±0.89
		0.010	34.28±0.42	1255±129	21.96±0.47

 Table S1 Composition and properties of the polymer solutions.



Fig. S5 Preparation methods of aligned FPU/PU fibers.



Fig. S6 FE-SEM images of aligned FPU/PU fibers obtained from from polymers solutions with various LiCl concentrations: (a) 0, (b) 0.002, (c) 0.004, (d) 0.006, and (e) 0.008 wt%, respectively.



Fig. S7 Water contact angle of PU flat film: (a) θ_{adv} and (b) θ_{rec} . Water contact angle of FPU/PU flat

films: (c) θ_{adv} and (d) θ_{rec} .