Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Swelling-Induced Pore Generation in Fluorinated Polynorbornene Block Copolymer Films

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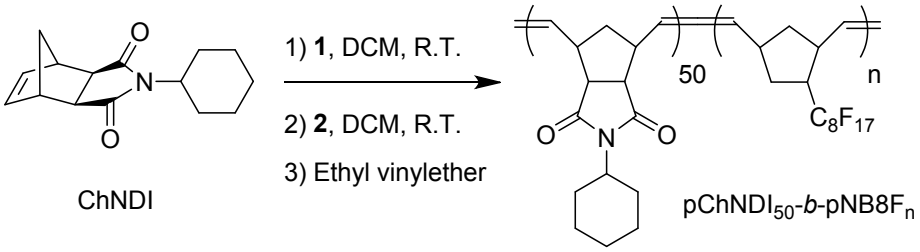
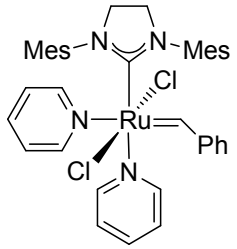
1. Procedure for the Synthesis of pChNDI-*b*-pNB8F



ChNDI

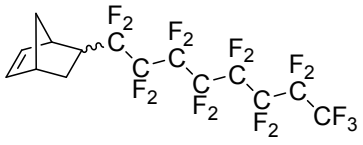
$pChNDI_{50}$-*b*-$pNB8F_n$

1



Grubbs 3rd Generation Catalyst

2

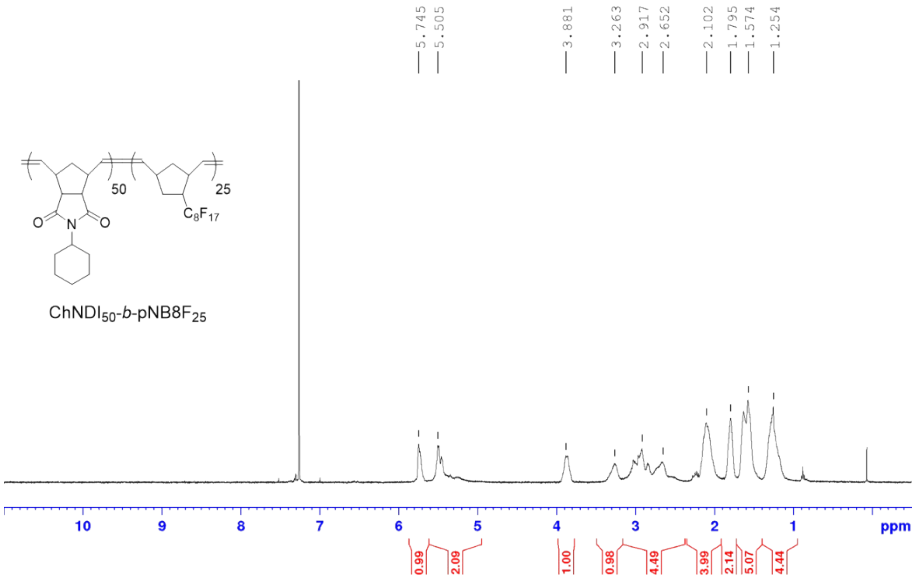


NB8F

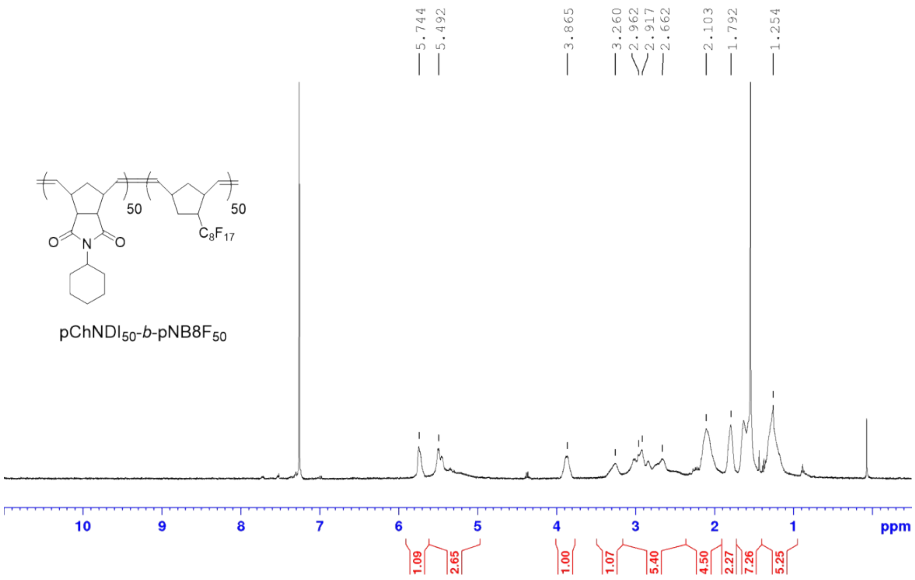
N-Cyclohexyl-*exo*-norbornene-5,6-dicarboxyimide (ChNDI)[1, 2] and 5-(perfluorooctyl) norbornene (NB8F)[3] were synthesized following previously reported procedures. ChNDI (50.6 mg, 0.206 mmol) and Grubbs 3rd generation catalyst (3.00 mg, 0.00413 mmol) were separately weighed in 5 mL vials and subsequently evacuated and backfilled with argon three times. Anhydrous dichloromethane (DCM) (0.5 mL each), degassed through three freeze-pump-thaw cycles in a separate Schlenk flask, was then added to each vial. In another vial, NB8F (52.9 mg, 0.103 mmol for 50:25 / 105.7 mg, 0.206 mmol for 50:50 / 158.5 mg, 0.309 mmol for 50:75) was weighed out and dissolved in anhydrous DCM (1 mL). The solution was subsequently degassed by three freeze-pump-thaw cycles. The polymerization was initiated by adding the ChNDI solution to a vigorously stirred solution of the Grubbs third generation catalyst at room temperature. Reaction mixture was stirred additionally for 30 minutes at a room temperature during which complete conversion of ChNDI was observed. NB8F solution was then added dropwise to the reaction mixture. After an hour of additional stirring, the reaction was terminated by adding 1 mL of ethyl vinylether and stirring for 20 minutes. Precipitation of the reaction mixture into methanol followed by overnight drying

under ambient conditions yielded the desired block copolymer, pChNDI-*b*-pNB8F, as a white powder.

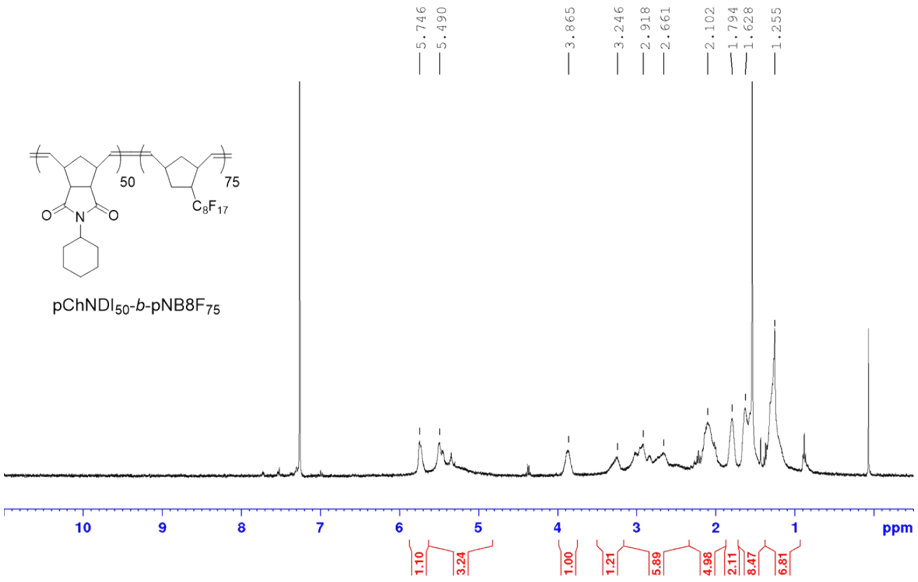
pChNDI$_{50}$-*b*-pNB8F$_{25}$: 74 mg (Yield: 72 %)



pChNDI$_{50}$-*b*-pNB8F$_{50}$: 130 mg (Yield: 83 %)



pChNDI$_{50}$-*b*-pNB8F$_{75}$: 165 mg (Yield: 79 %)



2. Supporting Information Figures

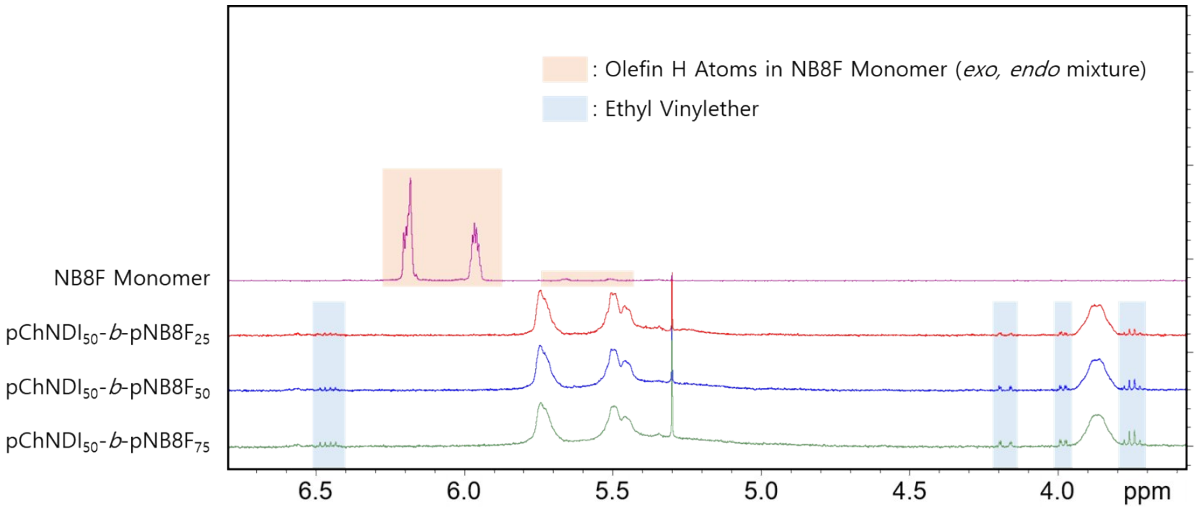


Fig. S1 NMR spectra of NB8F monomer and polymerization mixtures after termination.

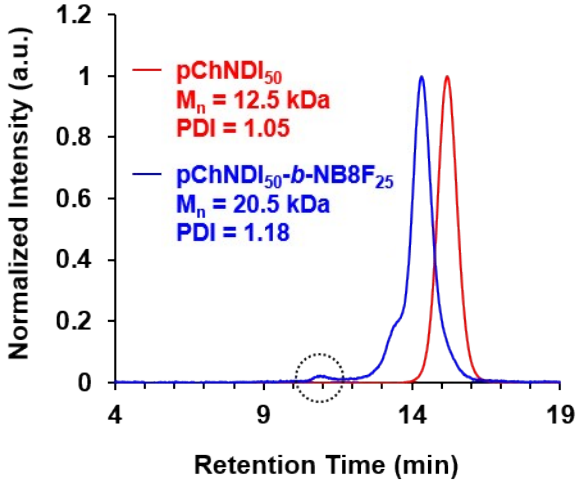


Fig. S2 SEC traces of $pChNDI_{50}$ (red) and 50:25 BCP (blue). Additional peak from BCP micelles (Dotted circle).

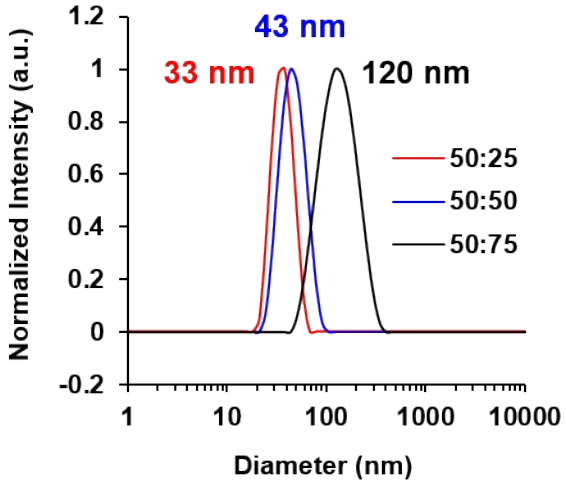


Fig. S3 DLS traces of 50:25 (red), 50:50 (blue), 50:75 (black) BCPs in THF.

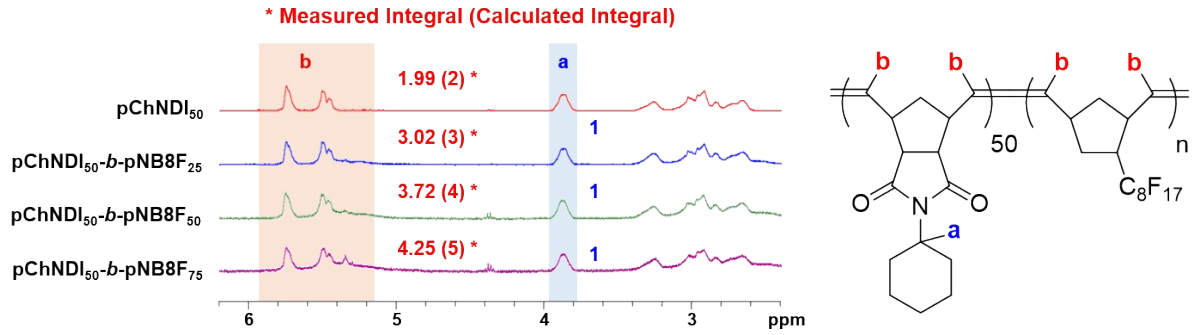


Fig. S4 NMR spectra of $pChNDI_{50}$ (red) 50:25 (blue), 50:50 (green), 50:75 (purple) BCPs. Resonance of a hydrogen within cyclohexyl group (blue a) was used as a reference, and the integrals of peaks corresponding to the olefin hydrogens in the BCP backbone (red b) were measured. The numbers shown in red are the measured integral values of the olefin hydrogens, and those in brackets show calculated values assuming that all BCPs exist as solvated unimers.

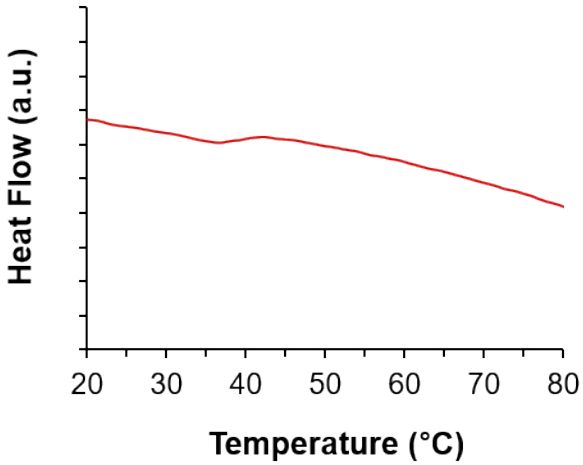


Fig. S5 DSC thermogram of pChNDI$_{50}$-*b*-pNB8F$_{75}$ from 3rd cycle of scanning at 5 °C/min heating rate (endotherm up).

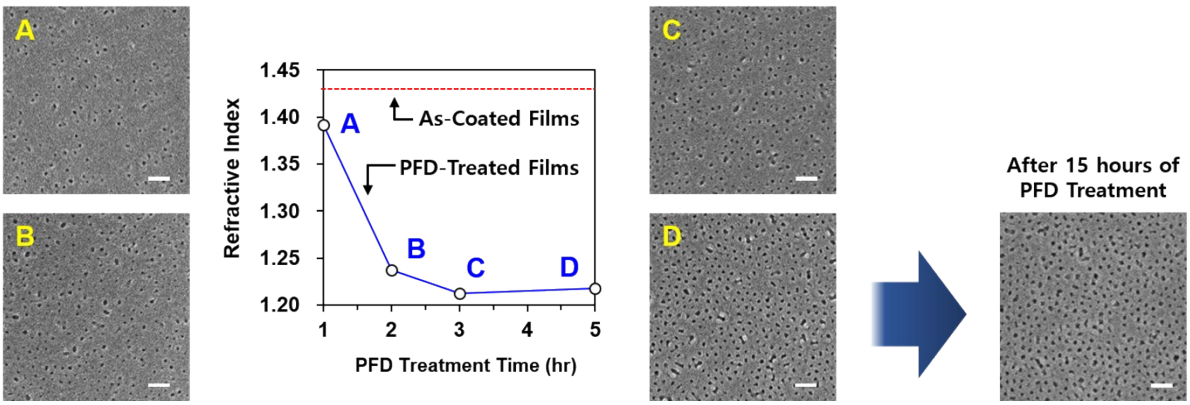


Fig. S6 Time-dependent changes in the film pore morphology (A, B, C, and D), and refractive index of 50:75 BCP films. All scale bars correspond to 100 nm. Although almost no additional decrease in the RI was observed after 3 hours of PFD treatment, further swelling yielded higher number density of surface pores (From C to D). We attribute this observation to a greater degree of plastic deformation on the film surface at longer swelling durations without significant changes in overall porosity. Further PFD treatment beyond 5 hours did not lead to significant changes in pore morphology.

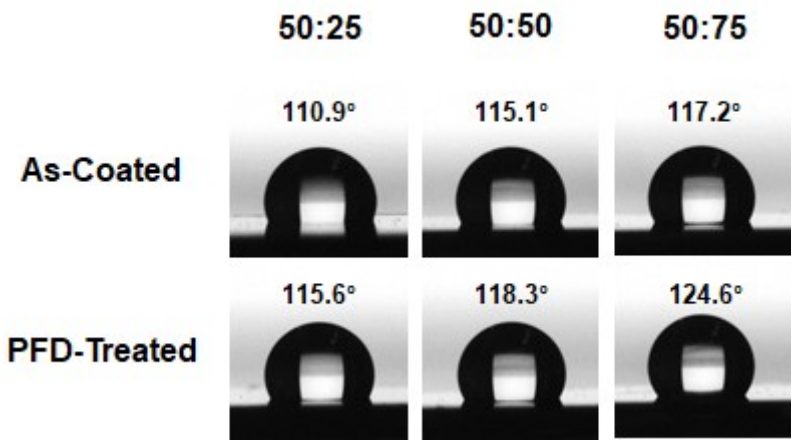
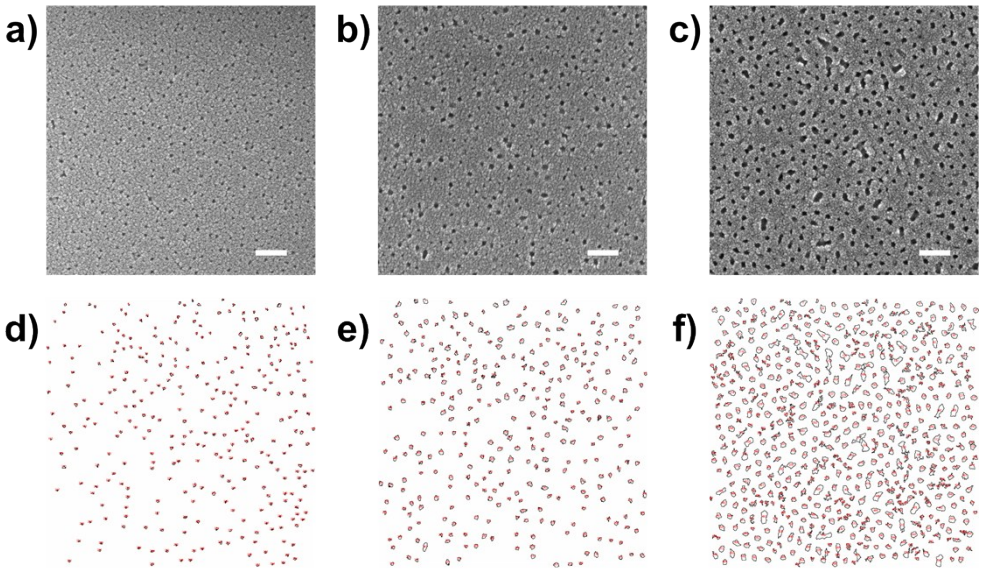


Fig. S7 Water contact angle measurements of various BCP films before and after PFD treatment. The ratios show the degree of polymerization of pChNDI and pNB8F block, respectively.



pChNDI-*b*-pNB8F	50:25 (a, d)	50:50 (b, e)	50:75 (c, f)
Number of Detected Pores	305	322	607
Average Pore Size (nm^2)	30 ± 13	101 ± 45	180 ± 113
Areal Fraction of Pores (%)	1.2	4.5	15.1

Fig. S8 Number, average size, and areal fraction of pores from Fig. 3a-c SEM data obtained by image analysis. Standard deviations of pore size are calculated.

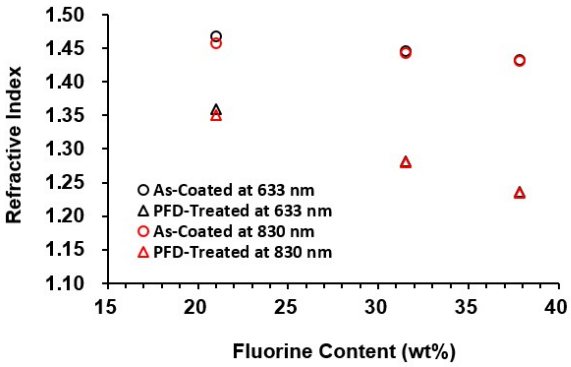


Fig. S9 Refractive indices of as-coated and PFD-treated films of pChNDI-*b*-pNB8F at two wavelengths (633 nm and 830 nm).

3. Supporting Information References

1. K. F. Castner and N. Calderon, *J. Mol. Catal.*, 1982, **15**, 47-59.
2. A. P. Contreras, M. A. Tlenkopatchev, M. D. Lopez-Gonzalez and E. Riande, *Macromolecules*, 2002, **35**, 4677-4684.
3. E. Perez, J. P. Laval, M. Bon, I. Rico and A. Lattes, *J. Fluorine Chem.*, 1988, **39**, 173-196.