Supporting Information

Substrate-independent Three-dimensional Polymer Nanosheets Spontaneously Induced by Solution Casting

Cheol Hun Park,[a] Eun Min Go,[b] Kyung Min Lee,[b] Sang Kyu Kwak,[b,*] Jong Hak Kim[a,*]

[a] Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea

[b] Department of Energy Engineering, School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea

[*] To whom correspondence should be addressed

E-mail: skkwak@unist.ac.kr or jonghak@yonsei.ac.kr

Figure S1. SEM images: (a) Pt-sputtered 3D PEGBEM-POEM (7:3) nanosheets; (b) magnified image of (a); (c) nanosheet structure after ethanol treatment; (d) nanosheet structure after calcination at 500 °C.

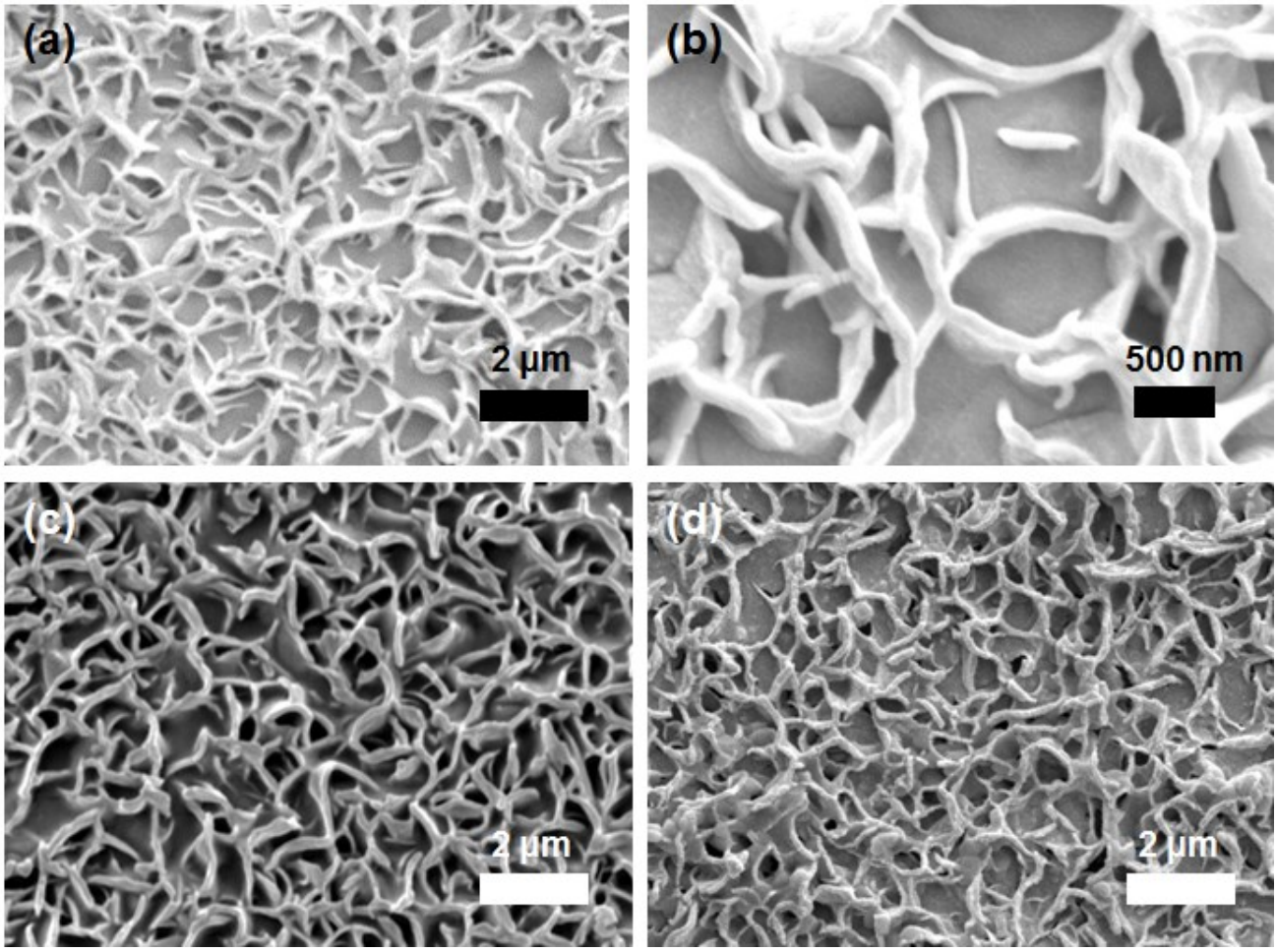


Figure S2. SEM images of the surface structure of various polymers prepared by solution casting onto porous polysulfone membrane: (a) poly(1-trimethylsilyl-1-propyne) (PTMSP); (b) poly(ether-block-amide) (PEBAX); (c) poly(ethylene oxide) (PEO); (d) PEGBEM-PHMEP (3:7); (e) PEGBEM-POEM (10:0); (f) PEGBEM-POEM (5:5); (g, h) highly magnified images of the non-flat regions of PEGBEM-POEM (10:0) and PEGBEM-POEM (5:5), respectively.

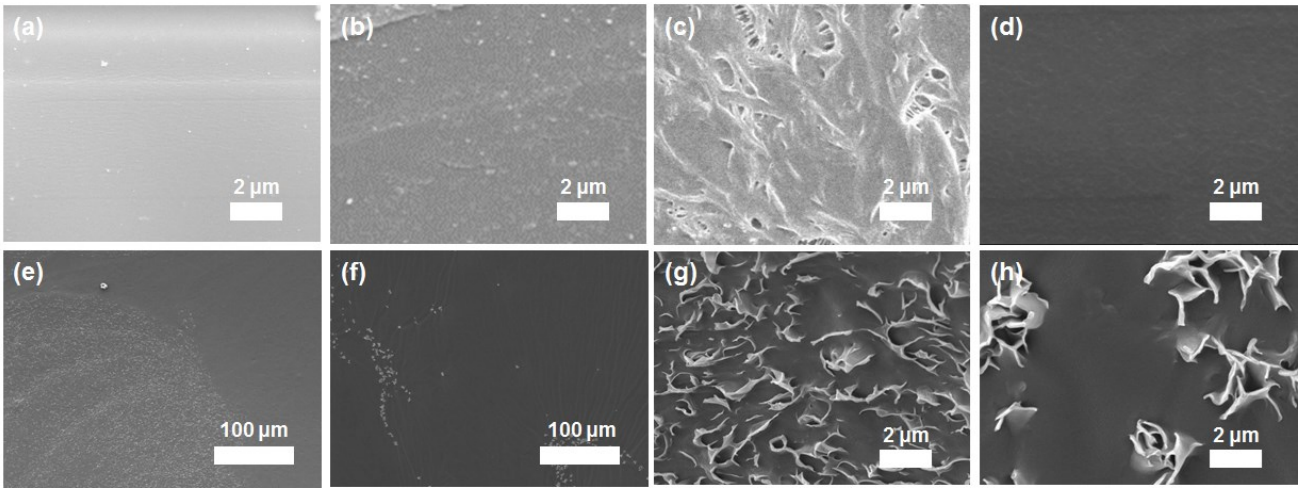


Figure S3. Effect of temperature on the development of 3D polymer nanosheets. Casted polymer solution dried at high temperature (50 °C); (a) low magnification, (b) high magnification, and low temperature (15 °C); (c) low magnification, (d) less dense regions at high magnification, (e) more dense regions at high magnification.

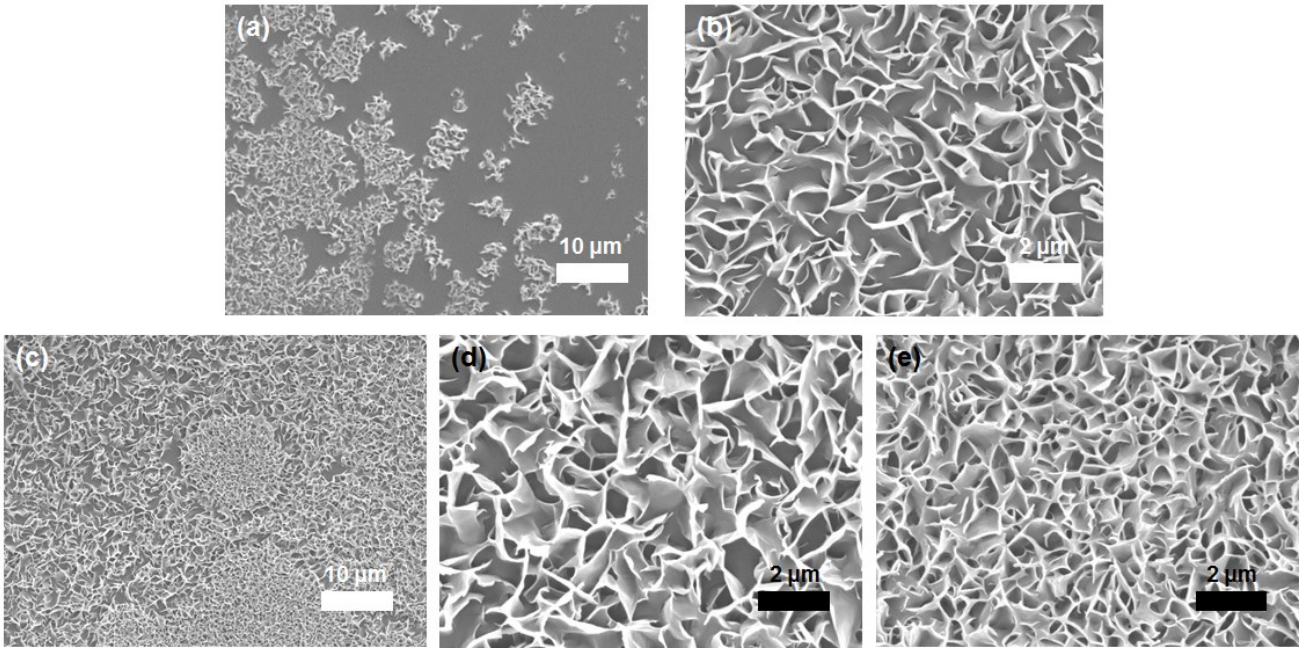
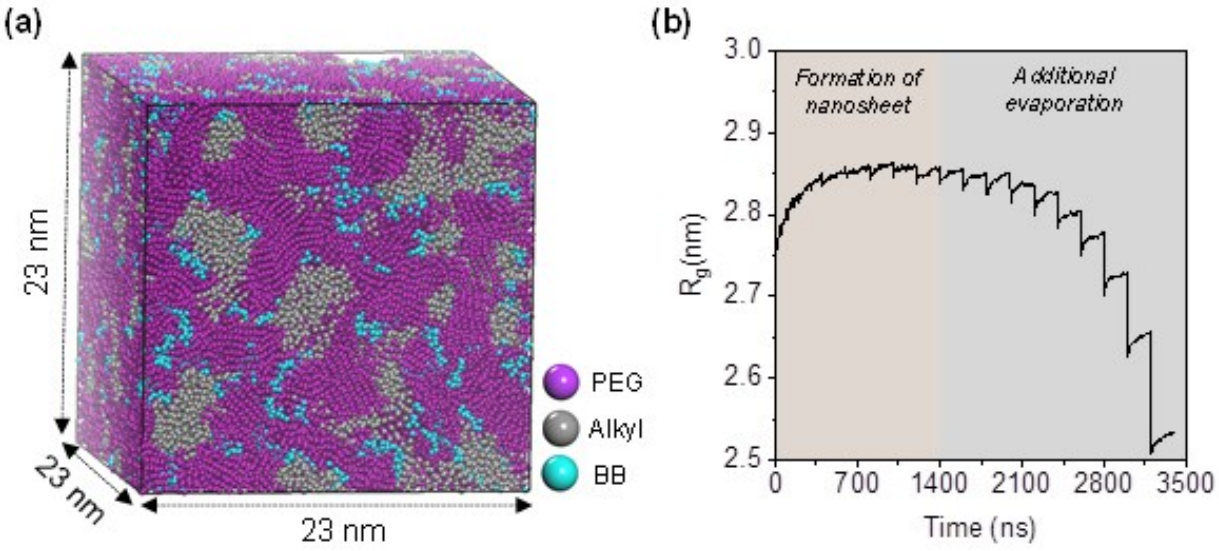


Figure S4. (a) Final configuration of PEGBEM-POEM obtained using a constant evaporation rate of the solvent after the formation of nanosheets. (b) radius of gyration (R_g) of PEGBEM chain during the transformation from nanosheets to homogeneous structures owing to additional evaporation of the solvents.



Supplementary Note. We found that the evaporation rate of the solvent affected the structural stability of the nanosheets. To maintain a stable structure, the evaporation rate of ethanol should be increased after the formation of nanosheets. When the evaporation rate was constant, the nanosheets were transformed into homogeneous structure after 50% of the solvent was evaporated, while the PEGBEM chains were bent (see Supporting Information **Figure S4**). This indicates that the nanosheets probably formed in beneath the surface with slow evaporation of the solvent; after their formation, the solvent evaporated rapidly from the surface of film. Contrarily, homogeneous structures are easier to form by the rapid aggregation of PEGBEM-POEM comb copolymer.

Figure S5. Formation of nanosheets by slow evaporation of the solvent (i.e., ethanol). The solvent is not shown in the simulation boxes for clarity; note that the final configuration has no solvent, as it has evaporated. The simulation boxes in all the configurations are cubes with equal lengths along the *x*-, *y*-, and *z*-axes.

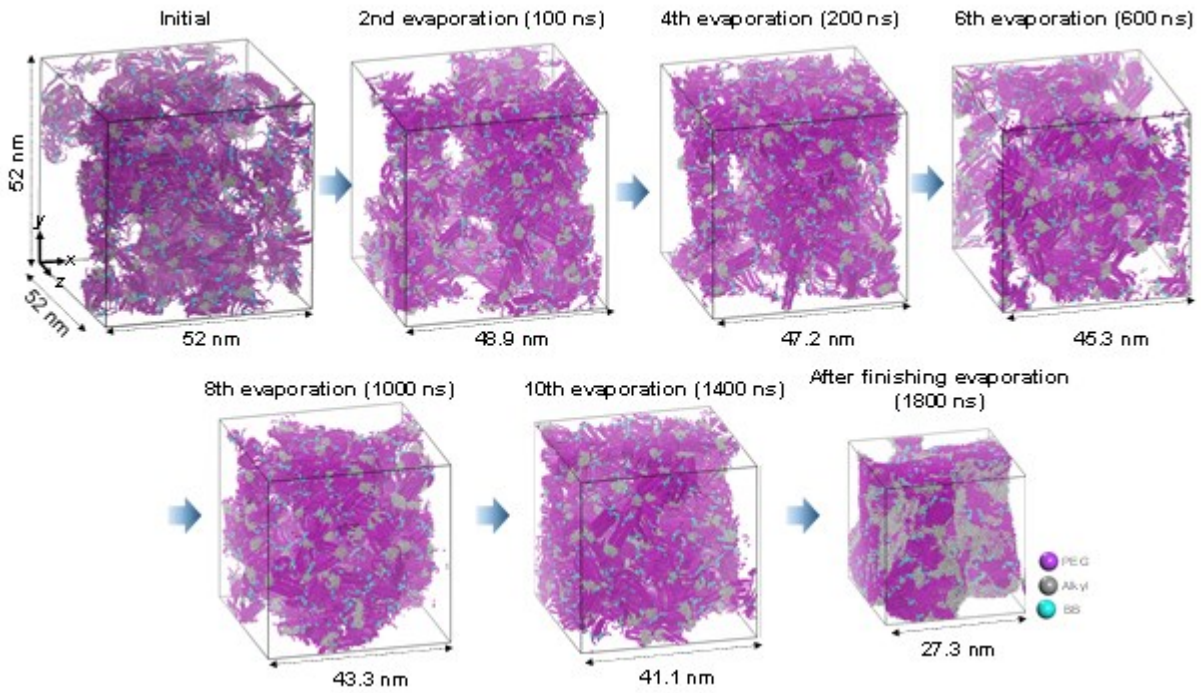


Figure S6. Formation of dense structures by fast evaporation of the solvent. The solvent is not shown for clarity except for in the 5th configuration; note that the final configuration has no solvent, as it has evaporated. The simulation boxes in all the configurations are cubes with equal lengths along the *x*-, *y*-, and *z*-axes, and the initial state is the same as in Figure S4.

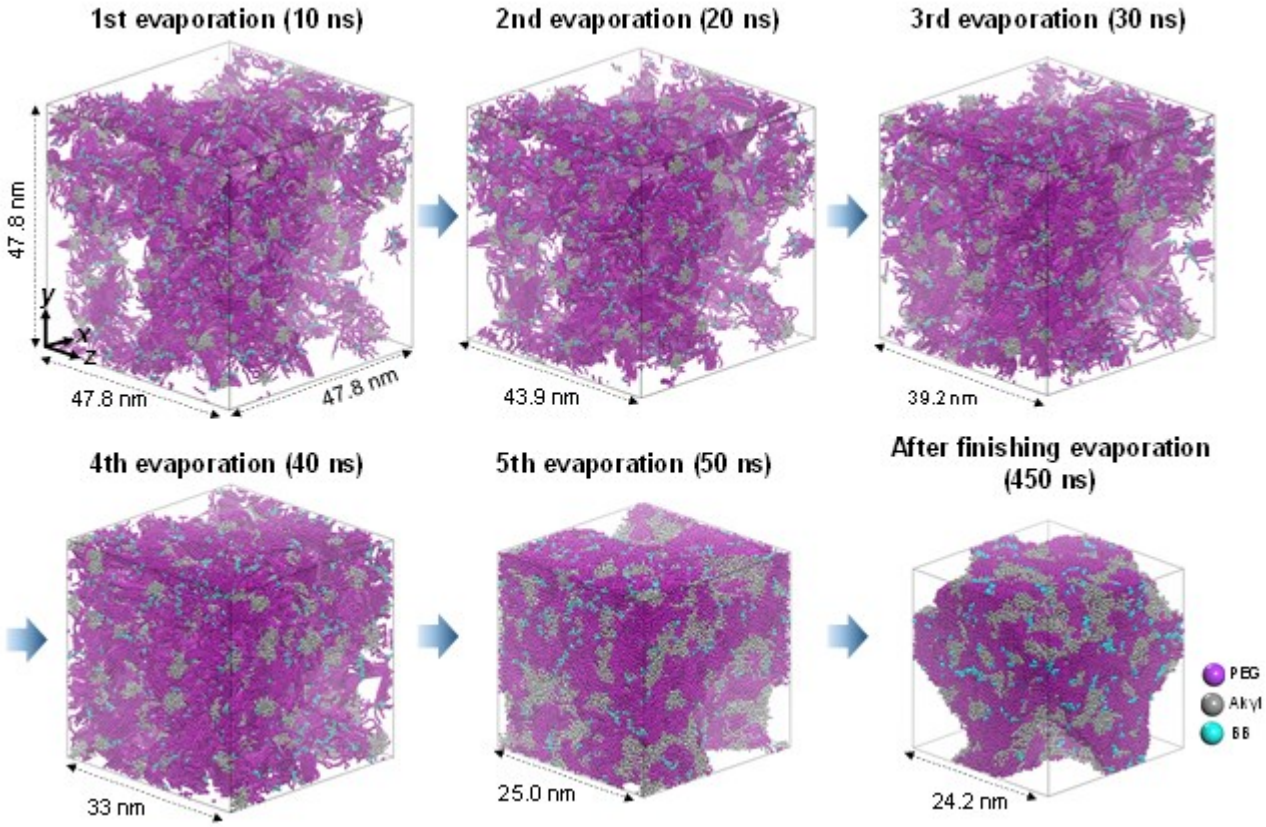


Figure S7. End-to-end distance of the PEGBEM chain in (a) nanosheets and (b) dense structures. Note that the rapid decrease in the end-to-end distance at 40 ns for the dense structures was owing to the removal of the solvent.

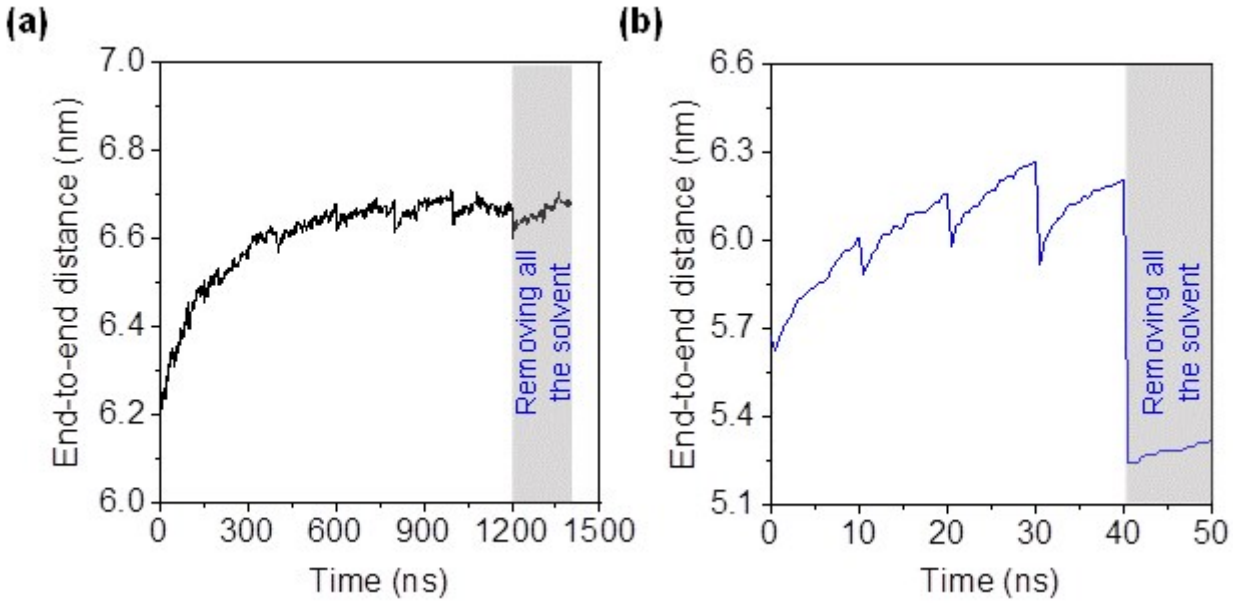


Figure S8. Solvent accessible surface area (SASA) of alkyl groups in nanosheets and dense structures.

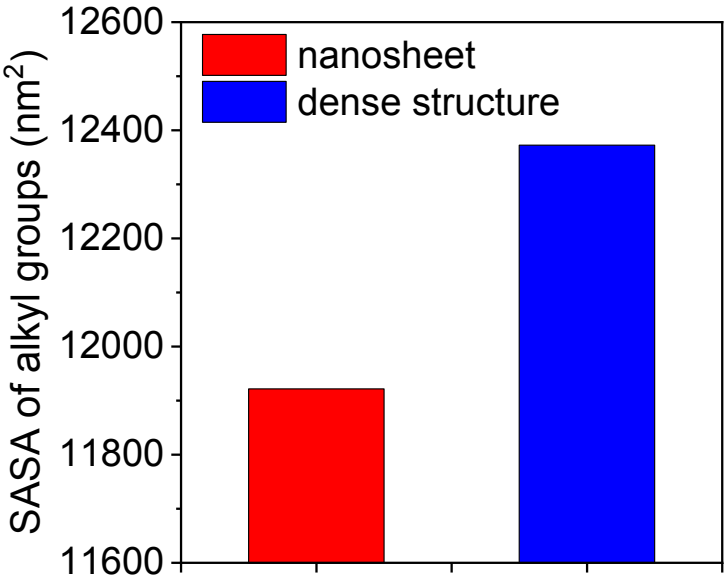


Figure S9. SASA of alkyl groups in the nanosheet and dense structures as a function of the simulation time. Inset shows SASA of alkyl groups in the dense structure. The SASA was estimated by averaging over the trajectories of the evaporation simulations every 50 ns for the nanosheet and 5 ns for the dense structures.

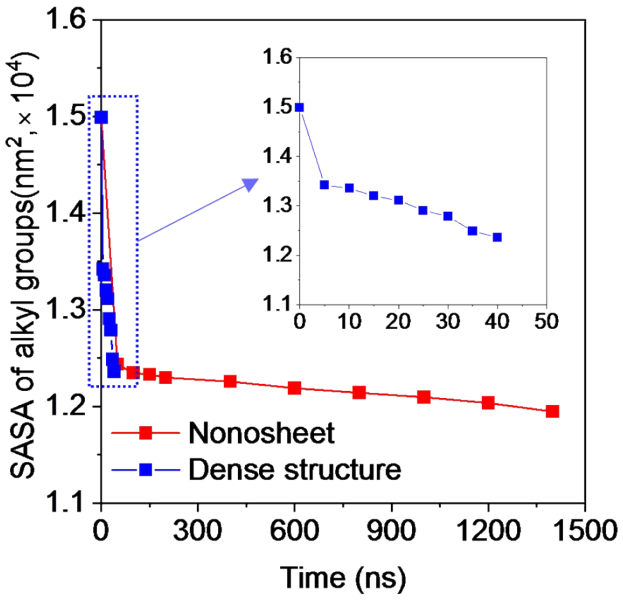


Figure S10. Water contact angle measurement: (a) PEGBEM-POEM (10:0); (b) PEGBEM-POEM (7:3); (c) PEGBEM-POEM (5:5). Oil contact angle measurement: (d) PEGBEM-POEM (10:0); (e) PEGBEM-POEM (7:3); (f) PEGBEM-POEM (5:5). The volume of water and oil used for the contact angle measurements was 2 µl, and the digital photographs were obtained 1s after the liquid was dropped.

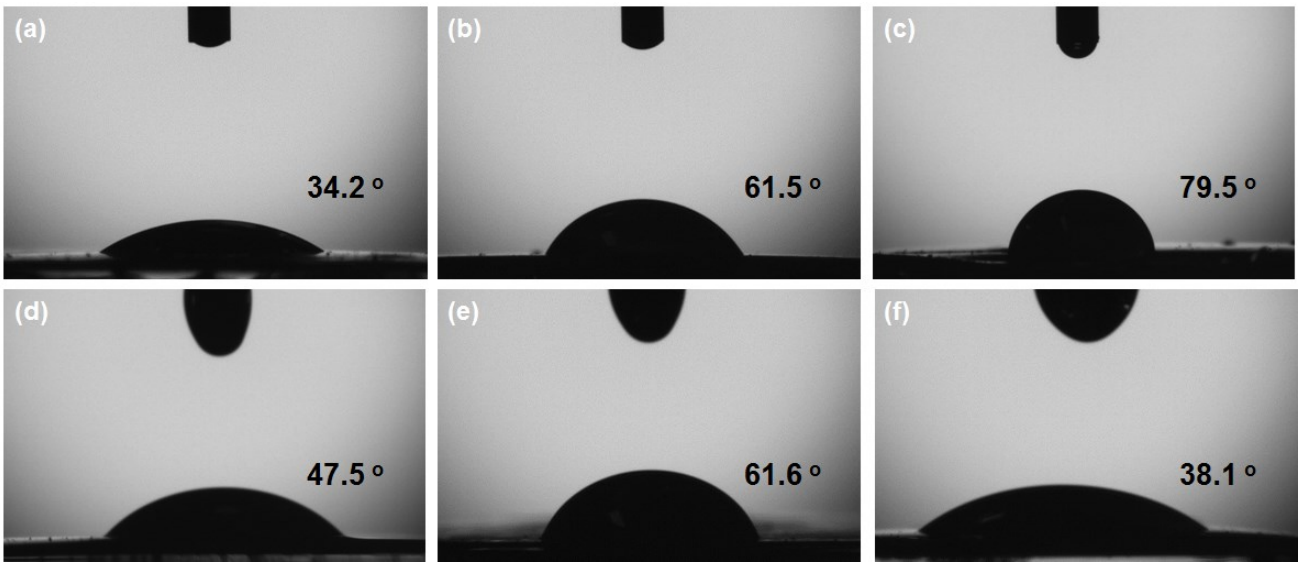


Figure S11. Resistance of PEGBEM-POEM (10:0), PEGBEM-POEM (7:3) and PEGBEM-POEM (5:5) when sputtered with (a) ITO, (b) aluminum, and (c) platinum. The polymers were prepared on a FTO glass substrate and the resistance was measured using a dynamic potential sweep method.

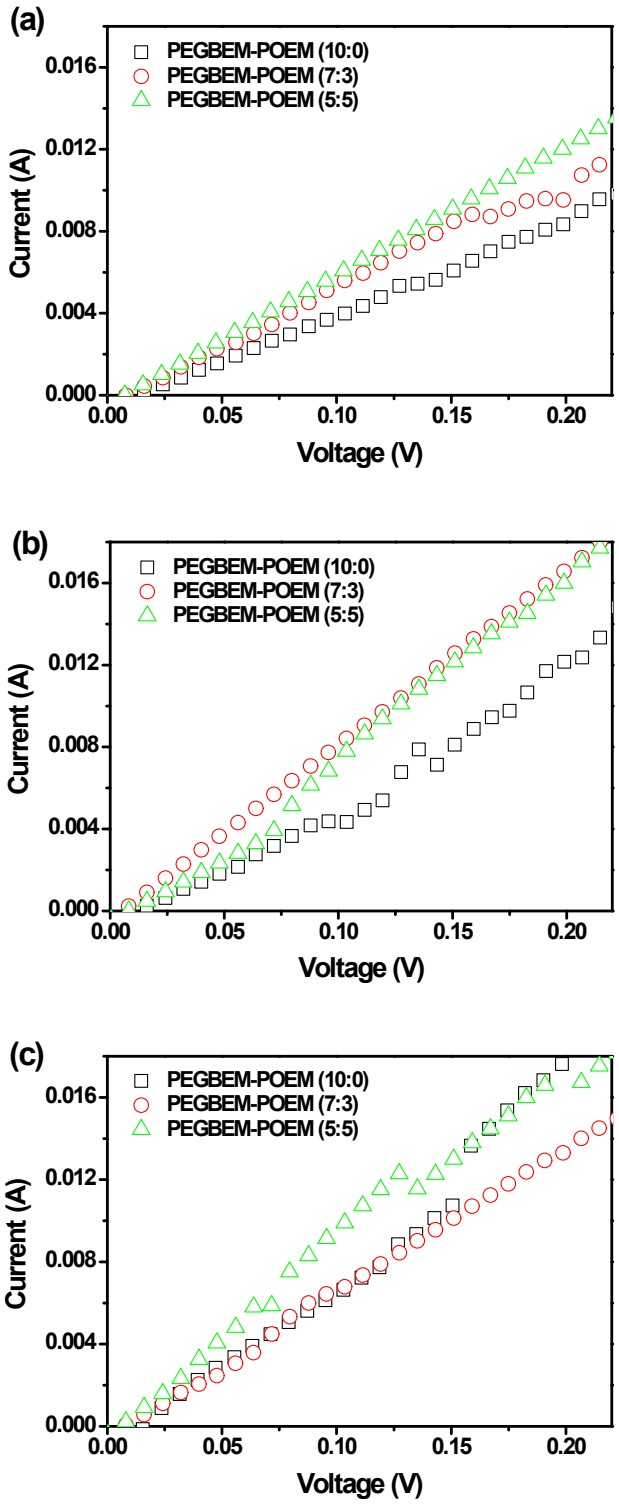


Table S1. Resistance of PEGBEM-POEM comb copolymer structures of various ratios prepared on a FTO glass substrate. The resistance was measured using a dynamic potential sweep method.

Sample	Polymer	Sputtered element	Resistance (ohm/cm)
#1	PEGBEM-POEM (10:0)		24.2
#2	PEGBEM-POEM (7:3)	ITO	18.4
#3	PEGBEM-POEM (5:5)		16.5
#4	PEGBEM-POEM (10:0)		17.6
#5	PEGBEM-POEM (7:3)	Al	12.1
#6	PEGBEM-POEM (5:5)		12.3
#7	PEGBEM-POEM (10:0)		12.4
#8	PEGBEM-POEM (7:3)	Pt	14.9
#9	PEGBEM-POEM (5:5)		11.4