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Supplementary Information

Free-Standing Film Electronics Using Photo-crosslinking Layer-by-Layer Assembly

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Experimental

Materials: Photo-crosslinkable polymers, PS-N_3 (M_n = 28.0 kg/mol) with UV-sensitive azide groups was synthesized via reversible addition fragmentation transfer (RAFT) polymerization. For PS-N_3, styrene (5.0 g, 0.048 mol), 4-vinyl-benzyl chloride (0.5 g, 3.33 mmol), 2,2'-azobis(2-methylpropionitrile) (AIBN) (2 mg, 0.014 mmol), and RAFT agent (27 mg, 0.09 mmol) were mixed and degassed. The reaction was carried out at 70 ^{o}C for 48 hours. The reaction mixture was then precipitated into methanol, resulting in the random copolymer as a pink powder. To avoid the coupling during the azidation, the dithioester end group was removed by the reaction with AIBN under nitrogen (80 ^{o}C for 12 hours). The solution was precipitated into methanol, obtaining the white powder. The change in color suggested that the dithioester group was removed. Then, the polymer was stirred with 3 equivalents of sodium azide in dimethylformamide at the ambient condition for 12 hours. The solution was filtered and precipitated into methanol to give a final product, PS-N_3, as a white powder. From the size exclusion chromatography (SEC), the M_n and PDI were 28.0 kg/mol and 1.1, respectively. The composition of the azide group in PS-N_3 was found to be 0.10 from proton NMR. UV irradiation of the azide groups in the polymer backbone leads to the formation of highly reactive nitrene radicals, which undergo facile crosslinking in the absence of additives.

(a)

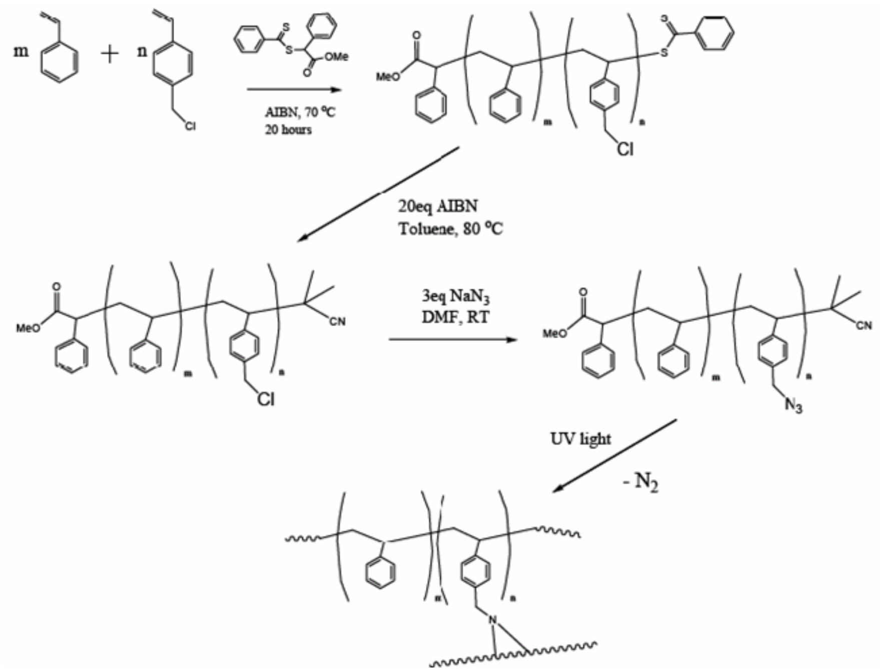


Figure S1. Schematics for the synthesis of PS-N_3.

PS-N_3 Multilayers: PS-N_3 was synthesized using via reversible addition fragmentation transfer (RAFT) polymerization.[18] For the build-up of multilayer films, PS-N_3 solution was completely wetted on the quartz, silicon or NaCl substrates. The substrate was then rotated with a spinner at 3000 rpm for 20 s and the resulting films were photo-crosslinked under UV irradiation (λ = 254 nm) for 60 s. The next layers were also sequentially deposited onto the previous films using the same procedure. In the case of free-standing films, the multilayers were sequentially deposited onto NaCl substrates with repetitive thermal cross-linking and then dipped into the water bath to dissolve the substrates. The thicknesses of multilayers deposited onto Si wafer and free-standing multilayer films were measured using ellipsometry (Gaertner Scientific Corp., L2W15S830) with 632.8 nm He-Ne laser light and digimatic micrometer (model:series 293, Mitutoyo), respectively.

OTFTs Based on Free-Standing multilayers: PS-N_3 multilayer-coated onto NaCl substrates with diameter of 2.54 cm were used for preparation of free-standing electronics. Patterned Al was deposited by evaporation for the formation of gate electrodes. Cross-linked PVP was deposited onto the gate patterns by spin-coating. A 470 nm PVP layer was prepared from a solution of PVP and poly(melamine-co-formal-dehyde) as a crosslinking agent, in propylene glycol monomethyl ether acetate (PEGMEA), deposited by spin-coating, and cured at 170 ^{o}C in vaccum oven. A pentacene thin film of about 50 nm thickness was deposited onto the multilayer-coated substrate by organic vapor phase deposition. After deposition of pentacene, Au electrodes were sputtered onto the films. OTFT film devices formed onto NaCl substrates were detached by water treatment. The current-voltage characteristics were measured using a HP 4284A.

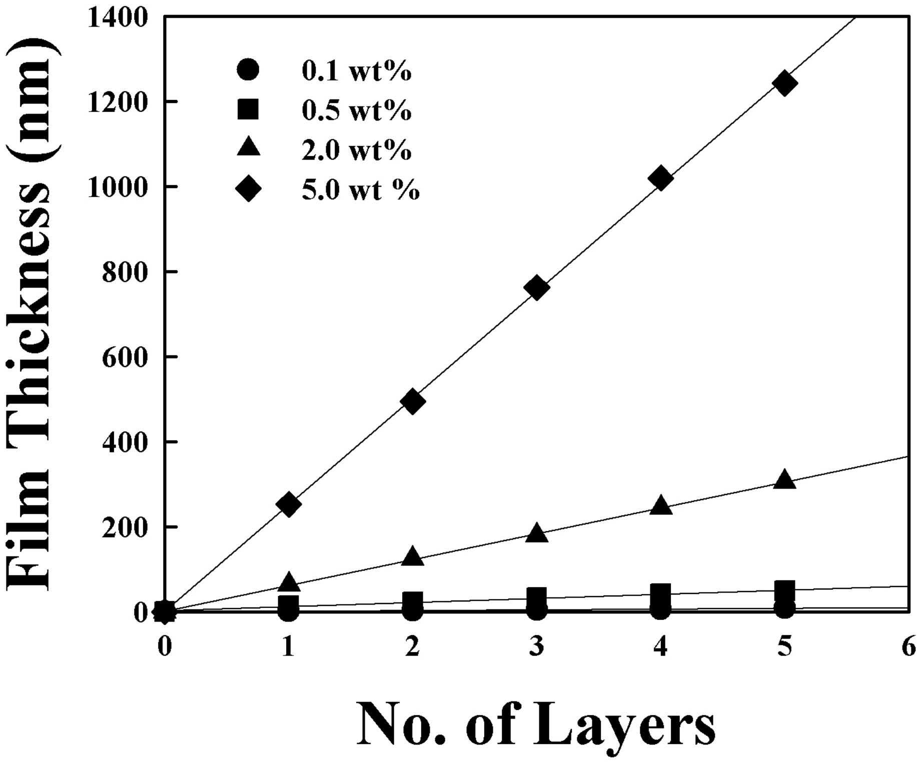
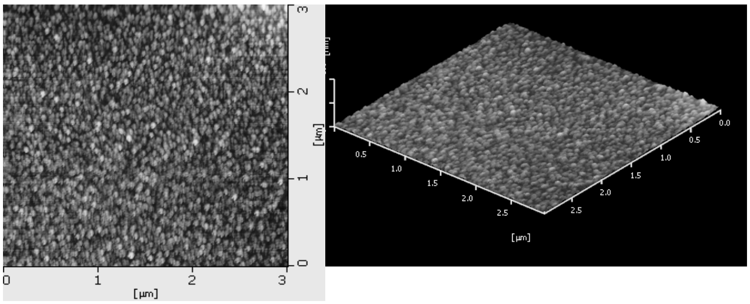
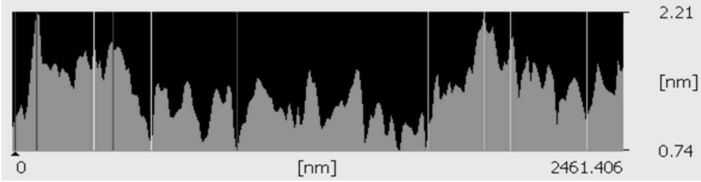


Figure S2. Change in the thickness of $(PS\text{-}N_3)_n$ multilayers prepared from different solution concentrations as a function of layer number (n).

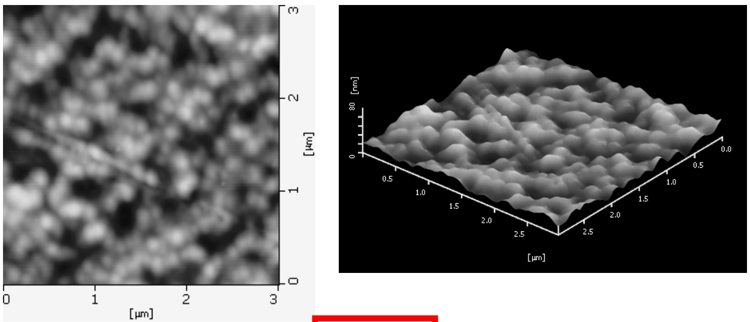
(a)



	Z1[nm]	Z2[nm]	[nm] ΔZ [nm]	Distance [nm]	Φ[°]
■	1.092064	2.205445	1.113381	86.55494	0.736971
	1.881249	0.888729	0.992520	230.8132	0.246376
	1.913584	1.106023	0.807561	307.7509	0.150348
	0.969716	2.181742	1.212026	226.0046	0.307265
■	1.862728	0.759414	1.103315	500.0952	0.126406



(b)



	Z1[nm]	Z2[nm]	[nm] ΔZ [nm]	Distance [nm]	Φ[°]
■	39.75805	9.030879	30.72717	298.2318	5.882494
	34.09758	11.47265	22.62493	764.6970	1.694704
	9.434884	35.59937	26.16448	948.2243	1.580569
	30.61390	10.99502	19.61888	252.3500	4.445502
■	34.26047	13.64473	20.61575	1368.808	0.862872

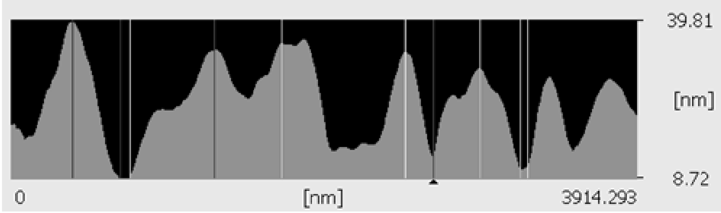


Figure S3. AFM images of (a) $(PS\text{-}N_3)_{30}$ and (b) commercializd PET film. In this case, the average peak to valley distance of $(PS\text{-}N_3)_{30}$ multilayers and PET films are about 1 and 25 nm, respectively.