Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Photo-Directing Chemoepitaxy: the Versatility of Poly(aryl methacrylate) Films in Tuning Block Copolymer Wetting

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Materials. Phenol (99%), 4-phenylphenol (97%), 2-naphthol (99%), dichloromethane (DCM; 99%), methacrylic anhydride (94%), 4-dimethylaminopyridine (DMAP; 98%), 1,4-dioxane (99.8%), 2-cyano-2-propyl benzodithioate (CPDB; 97%), glycidyl methacrylate (GMA; 97%), propylene glycol monomethyl ether acetate (PGMEA; 99.5%), anisole (99%) were purchased from Sigma-Aldrich and used as received. 1-naphthol (99%) and pyridine (99%) were purchased from Merck and Fluka respectively. 2,2-azobis(isobutyronitrile) (AIBN; 98%, Fluka) was recrystallized from methanol for purification. PS-*b*-PMMA (38k–37k) block copolymer with molar mass dispersity of 1.08 was purchased from Polymer Source Inc. and used without further purification.

Synthesis of acrylic methacrylate monomers. The synthesis of PMA, BPMA, 1-NMA and 2-NMA monomers were conducted in a similar manner. For instance, into an ice-cold solution of phenol (4.71g, 0.05 mol), 4-dimethylaminopyridine (1.22g, 0.01 mol) and pyridine (4.75g,

0.06 mol) in anhydrous DCM (300 mL), methacrylic anhydride (9.25g, 0.06 mol) was added in a dropwise manner. After stirring at room temperature for 48 h, the solution was poured into 300 mL ice-cold saturated $NaHCO_3$ and separated in a separation funnel. The aqueous layer was extracted with DCM thrice before combining and drying using anhydrous $MgSO_4$. The extraction was further concentrated under reduced pressure rotary evaporation. The product was further purified by flash column chromatography with hexane/ethyl acetate (3/1, v/v), yielding colorless liquid after removal of solvents.

Synthesis of poly(aryl methacrylate) via RAFT polymerization. The polymerization of PMA, BPMA, 1-NMA and 2-NMA monomers were conducted in a similar manner. For example, in a 5 mL glass tube equipped with rubber stopper, phenyl methacrylate (PMA) (486 mg, 3 mmol), GMA (8.52 mg, 6×10^{-2} mmol), CPDB (2.21 mg, 1×10^{-2} mmol) and AIBN (0.33 mg, 2×10^{-3} mmol) were dissolved in 2 mL 1,4-dioxane before deoxygenating with argon gas for 20 min. The polymerization was conducted at 70 ^{o}C for 24 h and terminated by inserting the tube into iced water for 10 min. The polymer solution was then precipitated by pouring into diethyl ether. The precipitate was re-dissolved in THF and reprecipitated in diethyl ether twice. The precipitate was dried under vacuum at 40 ^{o}C overnight and a pink powder was obtained.

Photo-Fries rearrangement reaction of monomers and polymers. UV irradiation studies were performed using an unfiltered high-pressure Xenon UV lamp. The light intensity (integrated power density) of 10 mW cm^{-2} at 254 nm was measured by a Hamamatsu spectroradiometer. Monomers (PMA, BPMA, 1-NMA and 2-NMA) were dissolved separately in DMSO-d_6 with a concentration of 0.1 mol L^{-1} and transferred to an NMR tube for UV irradiation. Similarly, poly(PMA), poly(1-NMA) and poly(2-NMA) were dissolved in DMSO-d_6 with a concentration of 40 mg mL^{-1} and transferred to NMR tubes for UV irradiation. Poly(BPMA) was not used for UV irradiation experiments due to its poor solubility in DMSO-d_6. The integrated power density at 254 nm was measured to be 10 mW cm^{-2}.

Preparation of substrate films. The original silicon wafers were cleaned *via* washing with methanol (3 min), acetone (3 min) and deionised water (3 min) sequentially under sonication before drying in a vacuum oven. The obtained wafers were then treated with O_2 plasma in an Oxford instruments PlasmaPro80 reactive ion etcher with a 10 sccm gas flow rate, 50 mTorr chamber pressure, 150 W radio frequency power and 60 s etch time. Thin films were prepared by spin coating a 10 mg mL^{-1} polymer solution in anisole at 5000 rpm (30 s) onto wafer surface and baked under vacuum at 160 ^{o}C for 48 hours for crosslinking. Uncrosslinked polymers were removed by immersing the film in anisole for 5 mins. After removal of solvent on the surface and drying under vacuum at 120 ^{o}C for 24 hours, films with a thickness of ~20 nm (measured by ellipsometry) were obtained.

Solvent Strip Test of Films. Three wafers (wafer A, B and C) with crosslinked polymers were prepared for each solvent strip test. The thickness of crosslinked films was measured in multiple locations and average/std dev of films was recorded before testing. Wafer A was baked at 150 ^{o}C for 90 s and the thickness was measured. This wafer is used as a reference for thickness change resulting from thermal annealing. On wafer B PGMEA was puddled for 90 s before spinning off the solvent. The film was then baked at 150 ^{o}C for 90 s and the thickness change of the film was measured. on wafer C PGMEA was puddled for 5 s and then the solvent was spun off until removed. The thickness of the film was measured and the delta-film thickness was calculated.

Self-assembly of PS-b-PMMA films. PS-*b*-PMMA (38k–37k) block copolymers were dissolved in PGMEA with a concentration of 18 mg mL^{-1} before passing through a PTFE syringe filter (0.22 μm pore size). The filtered polymer solution was spin coated on the surface of crosslinked photoactive films at 5000 rpm (30 s) and baked at 220 °C on a hotplate for 300 s. The obtained films were further annealed at 190 °C for 24 h under nitrogen atmosphere.

Nuclear magnetic resonance (NMR). NMR spectra were collected on a Bruker Avance 400 MHz spectrometer at 298 K using DMSO-d_6 as solvents. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS).

Ellipsometry. The film thicknesses were obtained via ellipsometric analysis on a J.A Woollam M-2000 spectroscopic ellipsometer. Measurements were taken at five angles (55, 60, 65, 70, 75°) at wavelengths between 450 and 1000 nm. The thickness was calculated by fitting the Cauchy model on a silicon wafer with an oxide layer to the obtained data.

Thermogravimetric analysis (TGA). The decomposition temperature (T_d) was obtained from TGA using the STARe TGA/DSC system. Under N_2 flow (10 cm^3 min^{-1}), the samples were heated from 25 to 380 °C at 10 °C min^{-1}.

Grazing angle attenuated total reflectance - Fourier transform infrared spectroscopy (GATR-FTIR). FTIR spectra of the thin films on silicon wafers were obtained using a Nicolet Nexus 5700 FTIR spectrometer (Thermo Electron Corp., Waltham, MA) equipped with a Harrick grazing angle attenuated total reflectance (GATR) accessory (Harrick Scientific Products, Pleasantville, NY) fitted with a KRS-5 MIR polarizer (Harrick Scientific Products, Pleasantville, NY).

X-ray photoelectron spectroscopy (XPS). XPS measurements were performed using a Kratos Axis ULTRA spectrometer (Kratos Analytical, Manchester, U.K.) with a 165 mm hemispherical electron-energy analyser and monochromatic AlKα X-ray source (1486.6 eV) operating at 300 W (15 kV, 20 mA).

Contact angle measurements. Static contact angles were measured using a Data Physics Instruments Optical Contact Angle Series 5 (OCA 5) goniometer. The contact angles reported here were measured by the addition of a 5 μL drop of either water or diiodomethane at five different locations on each thin film. Surface energies were calculated using the method reported in the literature.[1]

Atomic force microscopy (AFM). Topography characterization was conducted via AFM on an Asylum Research Cypher Scanning Probe Microscope operating in tapping mode in air, with the instrument being mounted on an anti-vibration table (Table Stable Ltd.). Height and phase images were captured at 512 points per line at 1 Hz using Etalon cantilevers (resonant frequency 140 kHz, spring constant 3.5 N m^{-1}, radius of curvature < 10 nm).

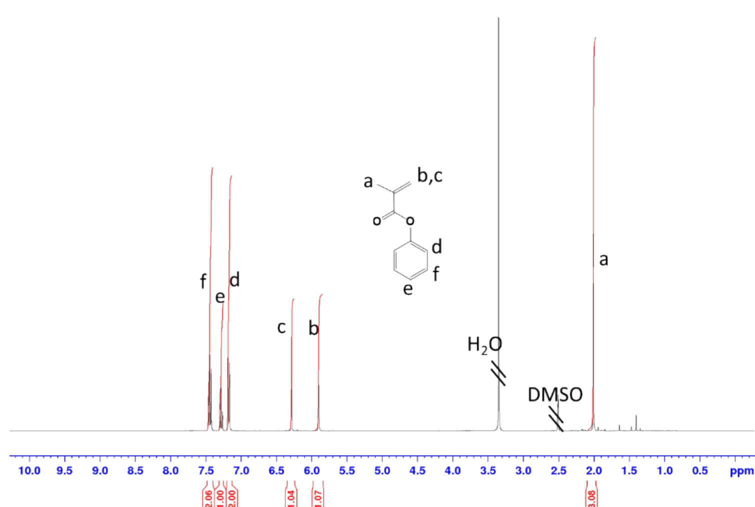


Figure S1. ^{1}H NMR spectrum (DMSO-d_6) of phenyl methacrylate.

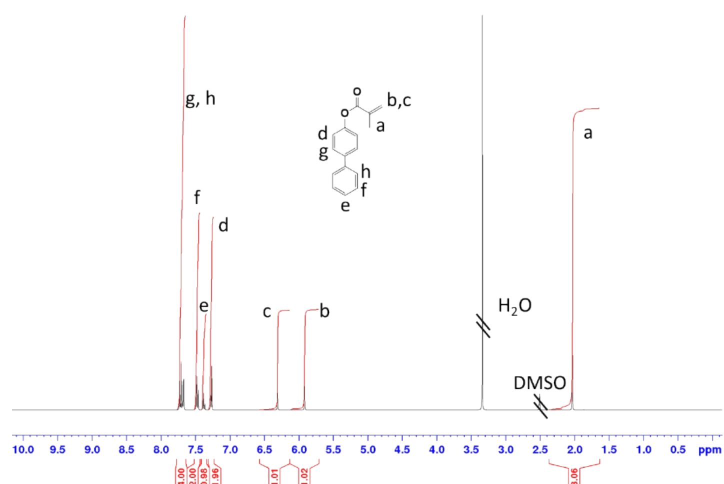


Figure S2. ^{1}H NMR spectrum (DMSO-d_6) of 4-biphenyl methacrylate.

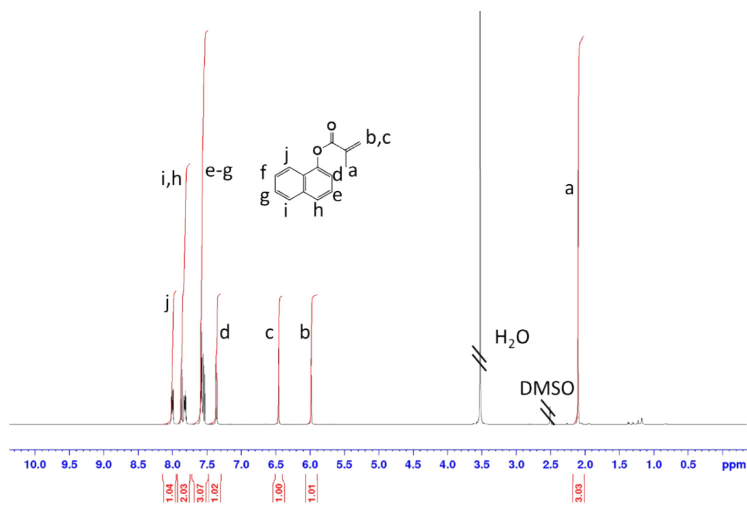


Figure S3. ^{1}H NMR spectrum (DMSO-d_6) of 1-naphthyl methacrylate.

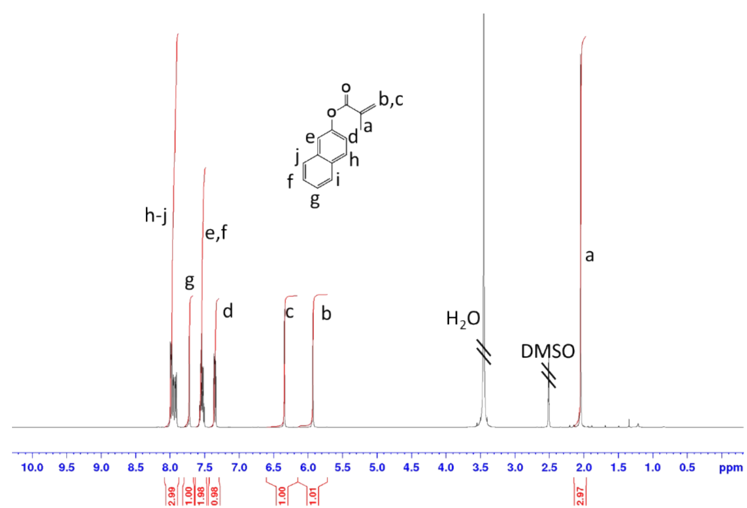


Figure S4. ^{1}H NMR spectrum (DMSO-d_6) of 2-naphthyl methacrylate.

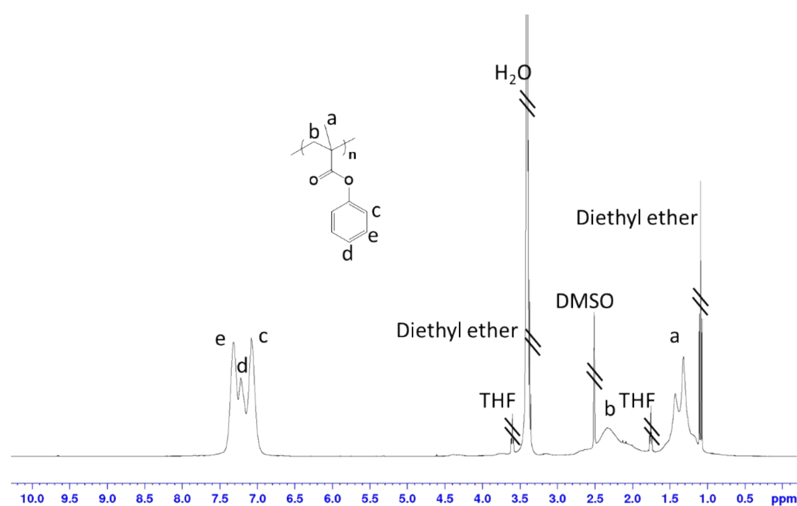


Figure S5. ^{1}H NMR spectrum (DMSO-d_6) of poly(PMA).

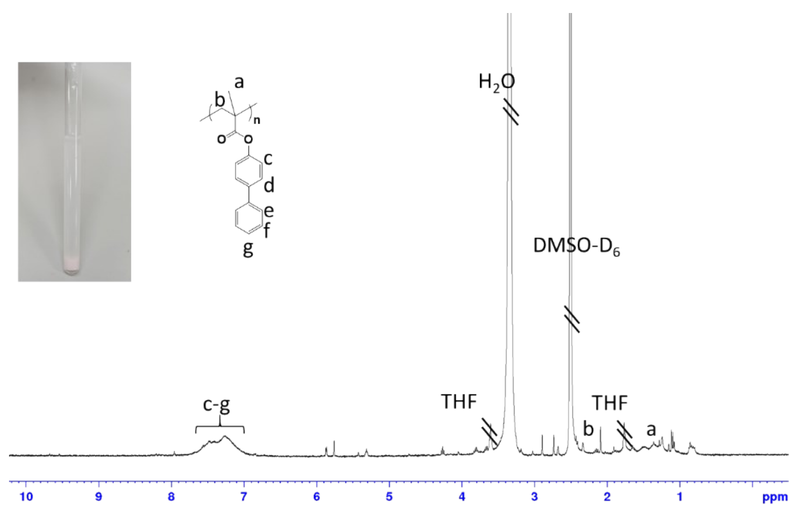


Figure S6. ^{1}H NMR spectrum (DMSO-d_6) of poly(BPMA).

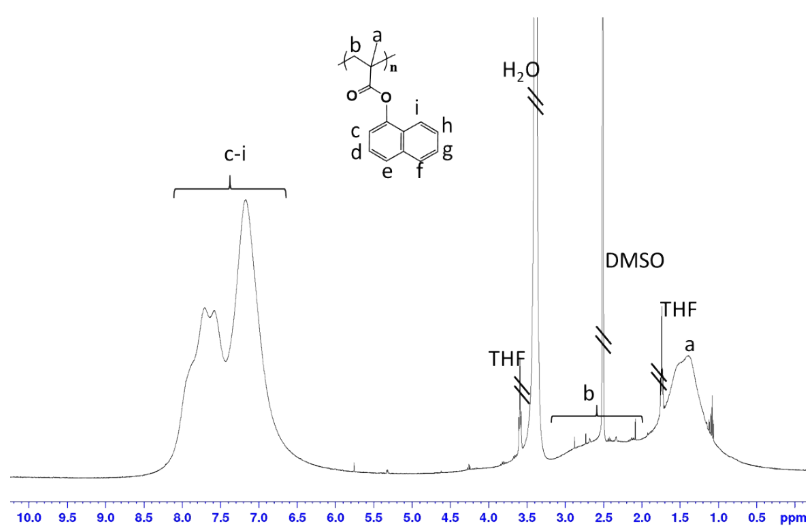


Figure S7. ^{1}H NMR spectrum (DMSO-d_6) of poly(1-NMA).

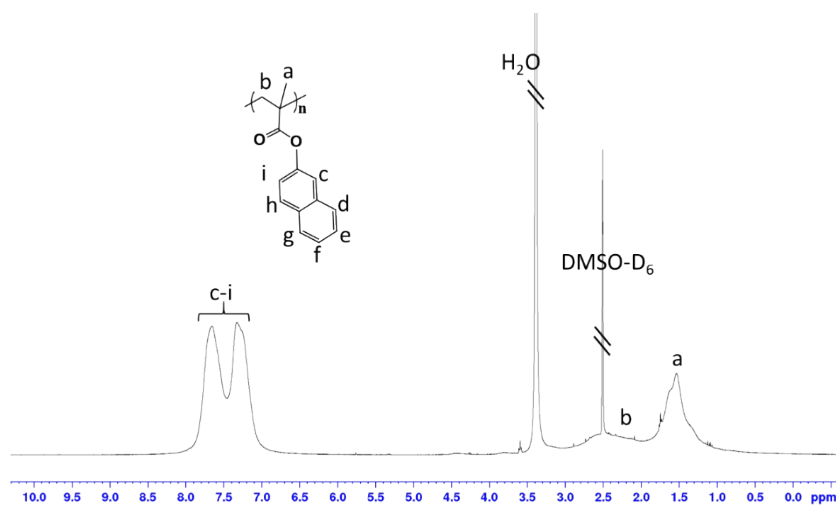


Figure S8. ^{1}H NMR spectrum (DMSO-d_6) of poly(2-NMA).

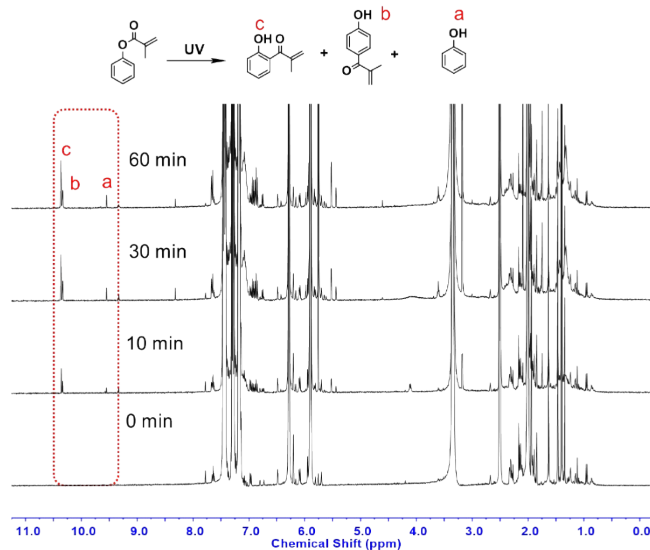


Figure S9. ^{1}H NMR spectra (DMSO-d_6) of PMA after exposure to UV light for varying times.

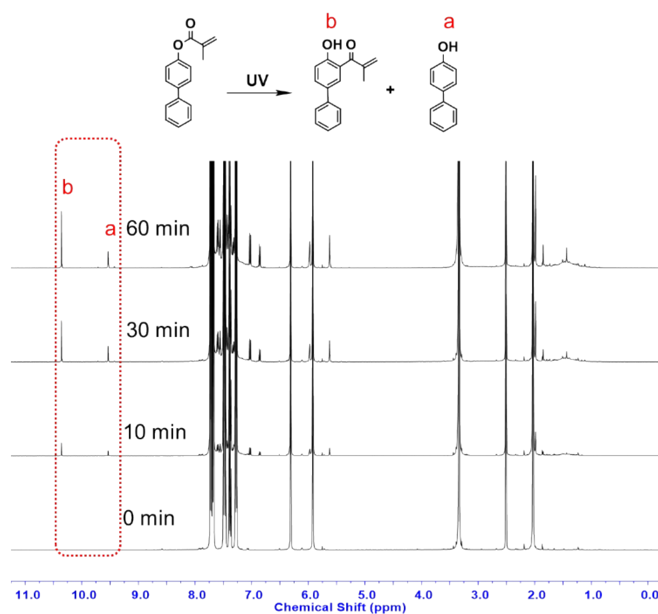


Figure S10. ^{1}H NMR spectra (DMSO-d_6) of BPMA after exposure to UV light for varying times.

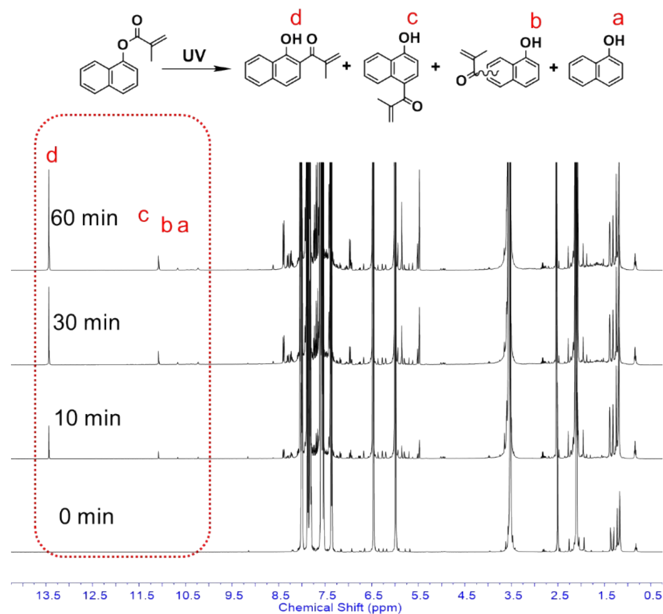


Figure S11. ^{1}H NMR spectra (DMSO-d_6) of 1-NMA after exposure to UV light for varying times.

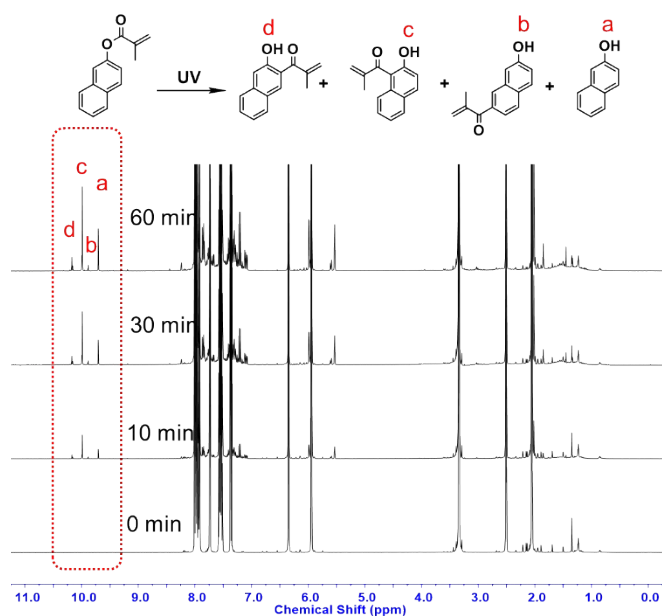
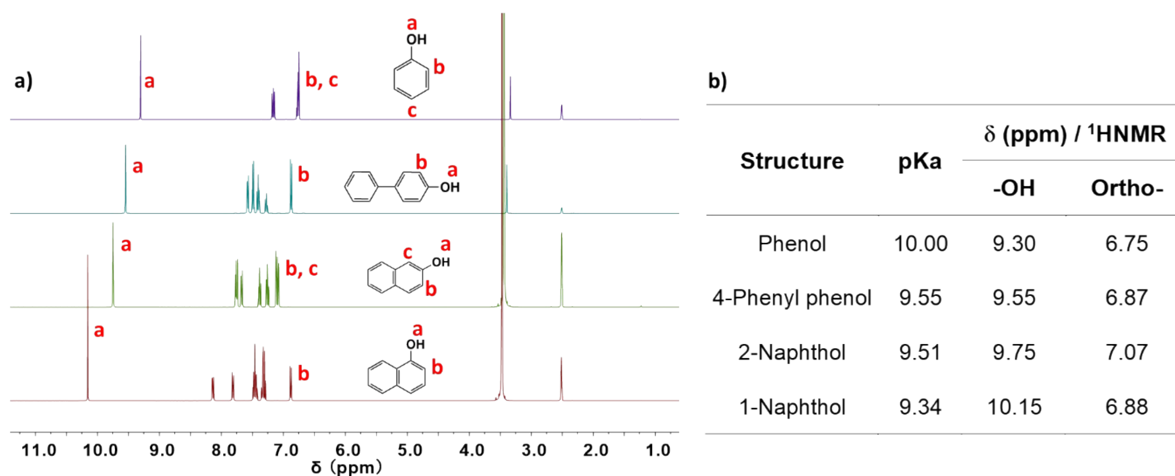


Figure S12. ^{1}H NMR spectra (DMSO-d_6) of 2-NMA after exposure to UV light for varying times.



Structure	pKa	δ (ppm) / ^{1}HNMR	
		-OH	Ortho-
Phenol	10.00	9.30	6.75
4-Phenyl phenol	9.55	9.55	6.87
2-Naphthol	9.51	9.75	7.07
1-Naphthol	9.34	10.15	6.88

Figure S13. a) ^{1}H NMR spectra (DMSO-d_6) of phenol, 4-phenylphenol, 2-naphthol and 1-naphthol; b) chemical shifts and pKa values of phenol, 4-phenylphenol, 2-naphthol and 1-naphthol.

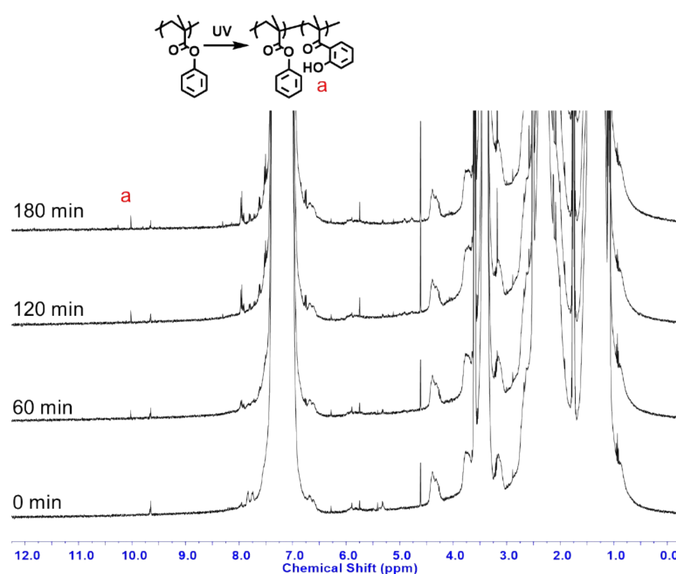


Figure S14. ^{1}H NMR spectra (DMSO-d_6) of poly(PMA) after exposure to UV light for varying times.

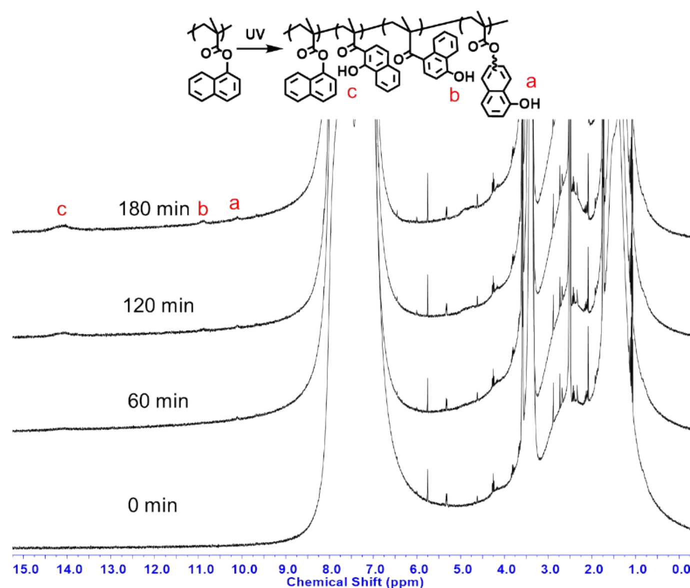


Figure S15. ¹H NMR spectra (DMSO-d_6) of poly(1-NMA) after exposure to UV light for varying times.

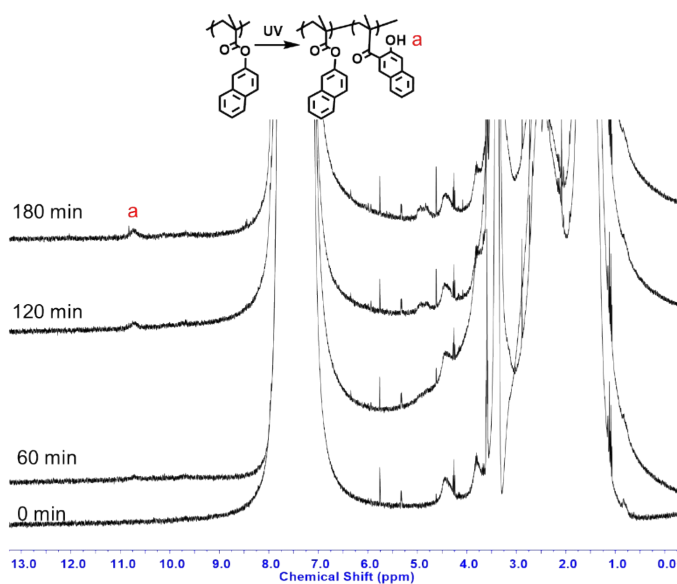


Figure S16. ¹H NMR spectra (DMSO-d_6) of poly(2-NMA) after exposure to UV light for varying times.

Table S1. Solvent resistance to PGMEA of uncrosslinked substrate films.

Sample	Test	Wafer A (nm)	Wafer B (nm)	Wafer C (nm)
Poly(PMA)	**Before**	20.7 ± 0.8	21.1 ± 0.4	22.2 ± 0.4
	After	20.8 ± 0.7	0	0

	$\Delta_{thickness}$	0.1	-21.1	-22.2
Poly(1-NMA)	**Before**	21.6 ± 0.1	21.1 ± 0.2	22.1 ± 0.2
	After	21.4 ± 0.1	0.4 ± 0.3	1.7 ± 0.3
	$\Delta_{thickness}$	-0.2	-20.7	-20.4
Poly(2-NMA)	**Before**	20.4 ± 0.1	20.4 ± 0.3	20.6 ± 0.6
	After	20.3 ± 0.1	0	0
	$\Delta_{thickness}$	-0.1	-20.4	-20.6

Table S2. Contact angle and surface free energy of films.

Sample	Contact Angle / °		Surface Free Energy / mJ/m^2		
	Water	Diiodomethane	γ_s^d	γ_s^p	γ_s
PS	93 ± 1	24 ± 1	46.5 ± 0.4	0.2 ± 0.1	46.6 ± 0.4
PMMA	74 ± 1	40 ± 2	39 ± 1	5.8 ± 0.2	45 ± 1
Poly(PMA)	89 ± 3	30.9 ± 0.9	43.8 ± 0.1	0.8 ± 0.4	44.6 ± 0.5
Poly(1-NMA)	86 ± 2	35 ± 4	42 ± 2	1.6 ± 0.2	44 ± 2
Poly(2-NMA)	89.8 ± 1.9	32.7 ± 2.3	43.0 ± 1.0	0.7 ± 0.3	43.8 ± 1.1

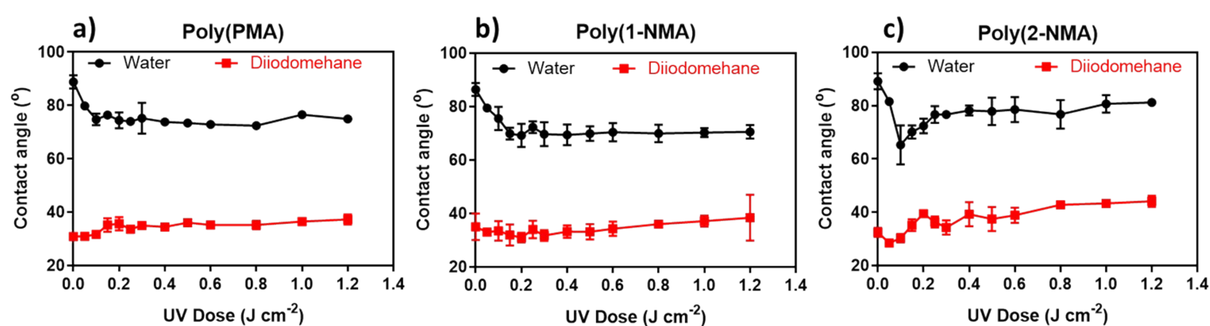


Figure S17. Water contact angle (blue) and diiodomethane (red) contact angle measured from the surfaces of (a) Poly(PMA), (b) Poly(1-NMA) and (c) Poly(2-NMA) thin films.

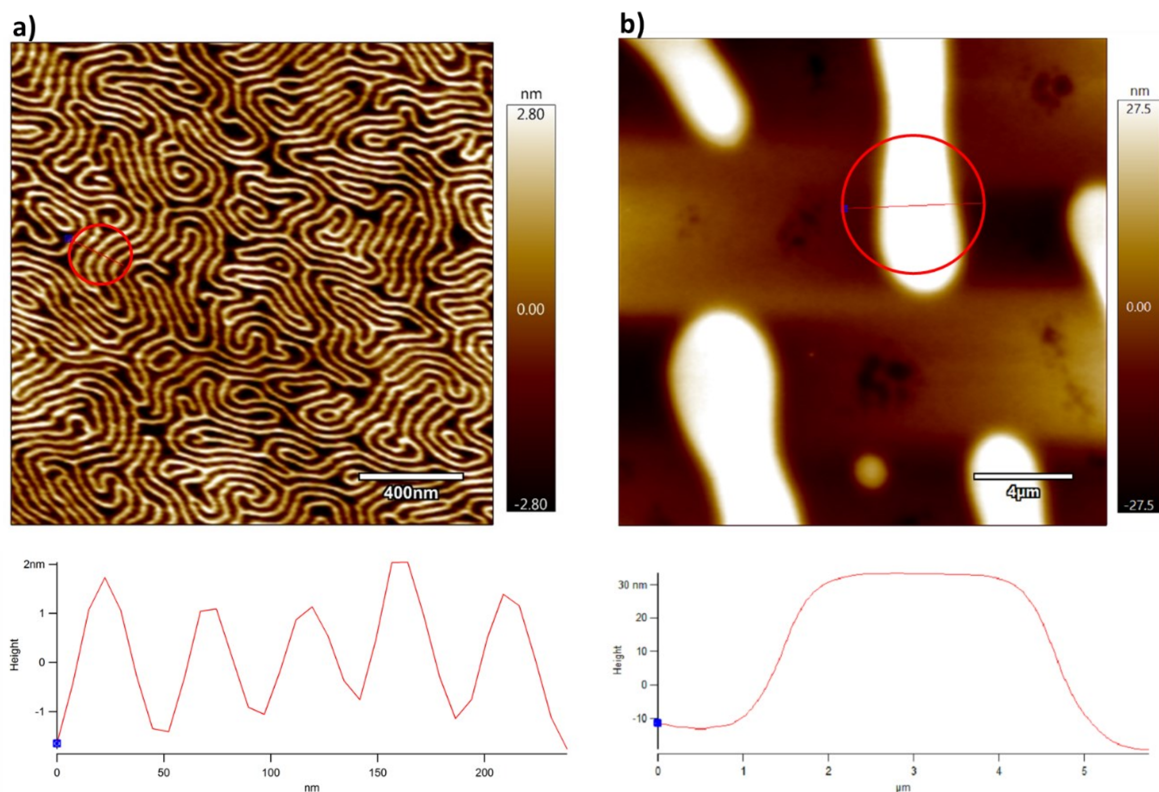


Figure S18. AFM height images of symmetric PS-*b*-MMA (38k-*b*-36.8k, Lo = 39 nm) thin films assembled on a) Poly(PMA) (UV dose = 0 J cm^{-2}) and b) Poly(2-NMA) (UV dose = 0.1 J cm^{-2}) surfaces.

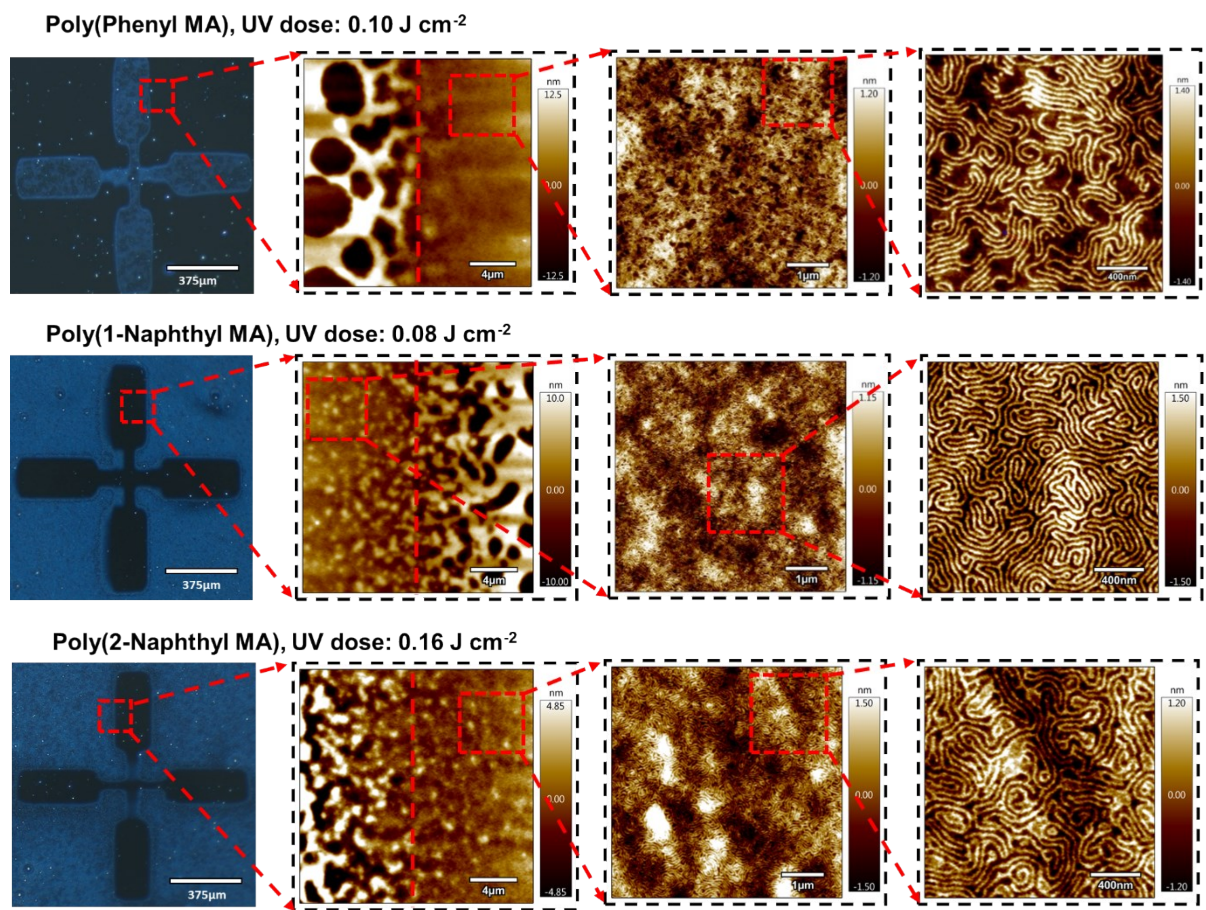


Figure S19. Optical microscopy and AFM (height) images of the interface of PS-*b*-PMMA film patterns on the surface of different substrate films after thermal annealing.

Reference

1. Owens, D. K.; Wendt, R. C., Estimation of the surface free energy of polymers. *J. Appl. Polym. Sci.* **1969,** *13* (8), 1741-1747.