Supplementary Material for

ZnO vapor phase infiltration into photo-patternable polyacrylate networks for microfabrication of hybrid organic-inorganic structures

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1) Estimation of hydroxyl group densities

The molecular weight of PETA is 298.29 g/mol. The density of the liquid monomer at room temperature is given by the manufacturer as 1.18 g/cm^3. Since crosslinking involves shrinkage by approximately 10 %, the density of the crosslinked acrylate was estimated as 1 g/cm^3. With 1 hydroxyl group per monomer unit, the resulting hydroxyl density is:

$$\frac{1\ mol/mol \cdot 1 g/cm^3}{298.29\ g/mol} = 0.0033\ mol/cm^3$$

The density of the (PS-r-PHEMA) copolymer was assumed to follow a linear relation from the density of PS ($\rho = 1.05\ g/mol$) and PHEMA ($\rho = 1.15\ g/mol$). The molecular weight of styrene and HEMA is 104.15 g/mol and 130.16 g/mol respectively. With 1 hydroxyl group per HEMA unit, the estimated hydroxyl density is:

$$\frac{0.2 \cdot 1\ mol/mol \cdot (0.2 \cdot 1.15 + 0.8 \cdot 1.05) g/cm^3}{(0.2 \cdot 130.16 + 0.8 \cdot 104.15)\ g/mol} = 0.0019\ mol/cm^3$$

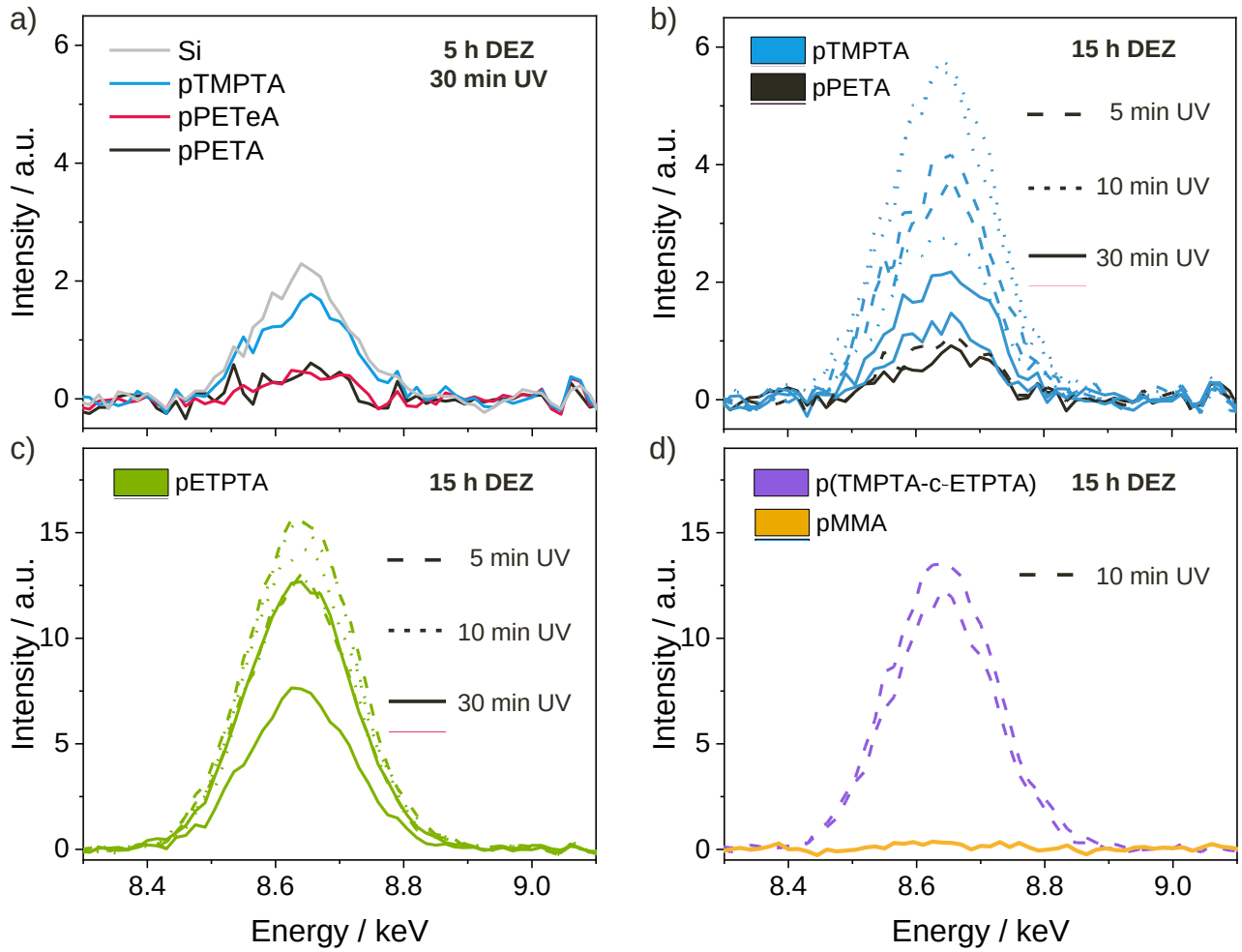

Figure S1: XRF spectra of polyacrylate films after different UV exposure times and DEZ hold times during VPI at 120 ° C. a) pPETA, pPETeA, pTMPTA after 30 minutes UV polymerization and a 5-hour DEZ hold. The spectrum for Si after subjection to the same VPI process is shown for comparison. b) pPETA and pTMPTA, c) pETPTA and d) p(TMPTA-c-ETPTA) and pMMA after a 15-hour DEZ hold. pMMA was not exposed to UV. All spectra were baseline-corrected with respect to a spectrum collected before VPI.

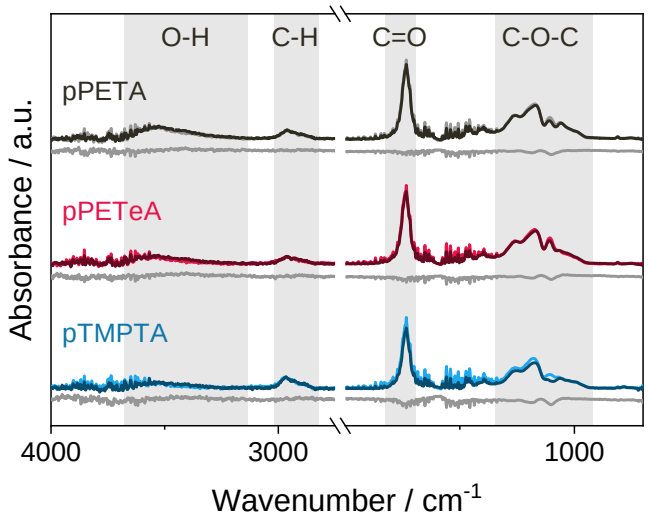

Figure S2: FTIR spectra of crosslinked acrylate films crosslinked under UV for 30 min before (light color) and after (dark color) VPI with a 5-hour DEZ hold at 120° C. The difference spectra are shown as gray lines. Relevant absorption bands are highlighted in gray.

Table S1: List of crosslinked acrylate films and reference silicon samples infiltrated with DEZ in the present study. The film thickness before and after VPI was measured by spectroscopic ellipsometry. No film thicknesses are given for the silicon wafers after exposure to 1 cycle of VPI because for such thin layers, the correlation between optical constants and thickness during fitting of the ellipsometer data were found to be too high to obtain meaningful results.

Sample ID	Material	UV exposure / min	DEZ hold / h	Thickness before VPI / nm	Δt / nm	Thickness after VPI / nm	Δt / nm	Thickness change / %	XRF Zn Kα peak area / a.u.	Δ / a.u.
D2-13	p(TMPTA-ETPTA)	10	15	186.6	0.8	212.7	1.8	12.3	2.41	0.02
D2-14	p(TMPTA-ETPTA)	10	15	188.2	0.9	220.2	1.5	14.5	2.47	0.01
D3-12	p(TMPTA-ETPTA)	10	15	205.7	0.3	226.0	0.7	9.0	2.84	0.02
C6-3	pETPTA	5	15	248.8	0.2	267.0	0.3	6.8	2.63	0.01
C7-5	pETPTA	5	15	248.2	0.6	290.0	0.9	14.4	3.31	0.02
D2-2	pETPTA	10	15	231.1	0.2	234.5	0.2	1.4	2.61	0.02
C7-7	pETPTA	10	15	248.7	0.6	289.7	1.1	14.1	3.16	0.02
D3-2	pETPTA	10	15	223.5	0.4	242.5	0.4	7.8	2.96	0.02
C6-4	pETPTA	30	15	225.1	0.2	240.9	0.4	6.6	2.61	0.01
C7-13	pETPTA	30	15	239.0	0.8	247.0	0.8	3.2	1.51	0.01
B6-4	pPETA	30	5	182.1	1.1	178.6	0.9	-2.0	0.06	0.01
C5-16	pPETA	5	15	252.8	0.2	252.0	0.4	-0.3	0.19	0.01
C5-13	pPETA	30	15	244.9	0.2	239.6	0.2	-2.2	0.14	0.01
B6-9	pPETeA	30	5	178.9	0.1	177.2	0.1	-0.9	0.07	0.01
B8-7	pTMPTA	30	5	139.1	0.1	139.9	0.1	0.6	0.30	0.01
C7-21	pTMPTA	5	15	178.4	0.1	183.8	0.1	3.0	0.69	0.01
C4-10	pTMPTA	5	15	109.5	0.1	114.5	0.1	4.4	0.81	0.01
D2-19	pTMPTA	10	15	153.1	0.2	161.1	0.2	5.0	1.09	0.01
D3-25	pTMPTA	10	15	171.6	0.1	183.7	0.2	6.6	1.18	0.01
C7-24	pTMPTA	10	15	176.2	0.1	183.8	0.2	4.1	0.57	0.01
C4-31	pTMPTA	30	15	150.8	0.1	153.6	0.1	1.8	0.23	0.01
C4-15	pTMPTA	30	15	101.8	0.1	104.7	0.1	2.7	0.42	0.01
C4-30	Silicon		15						0.35	0.01
C5-19	Silicon		15						0.23	0.01
C7-27	Silicon		15						0.03	0.01
C7-30	Silicon		15						0.03	0.01
C7-31	Silicon		15						0.18	0.01
D2-24	Silicon		15						0.14	0.01
D3-29	Silicon		15						0.40	0.01
D3-30	Silicon		15						0.32	0.01
D5-16	Silicon		15						0.65	0.01

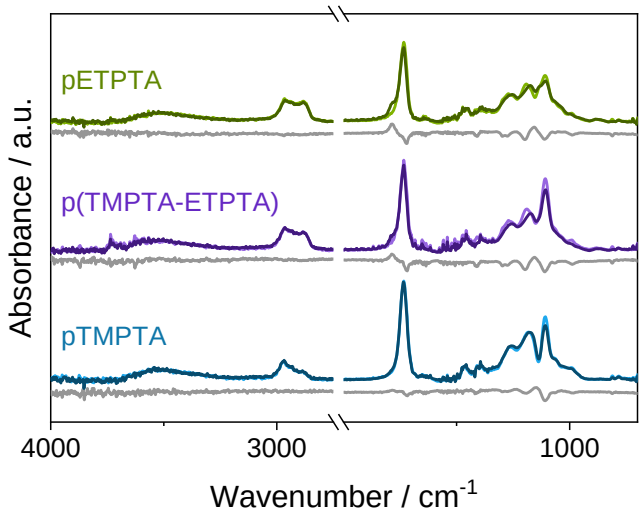

Figure S3: Thermal stability of crosslinked acrylate films: FTIR spectra before (light color) and after (dark color) 24 h at 120 ° C in vacuum. The difference spectra are shown in gray. All films were UV-polymerized for 10 min.

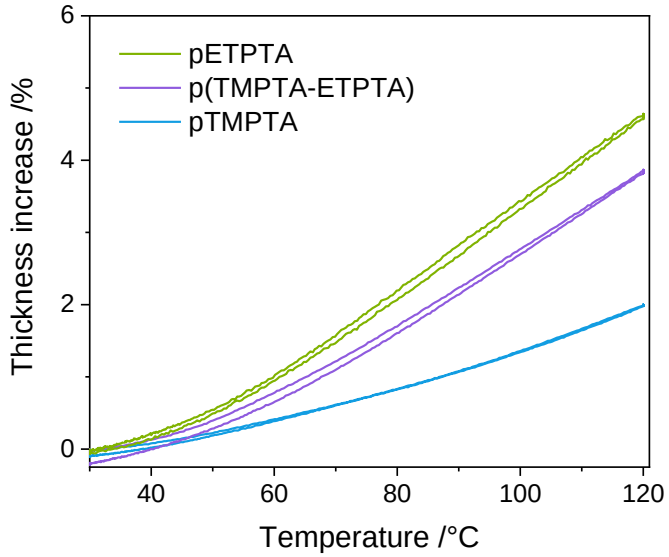

Figure S4: Thermal expansion of a pTMPTA, p(TMTPA-ETPTA) and pETPTA thin film measured by ellipsometry.

@Figure S4: For the thermal expansion measurements, a M-2000 V spectroscopic ellipsometer (J.A. Woollam) equipped with a THMS600 heating stage (Linkam) whose temperature was controlled by a T95 system controller (Linkam) was used. Before the measurement, the polymer films were equilibrated at 120° C on a hot plate for 1 h. Film thickness was monitored in a temperature range from 30° C to 120 ° C with a heating/cooling rate of 9° C/min and the samples were held at the maximum temperature for 5 min. Ellipsometry scans were taken continuously during heating, hold and cooling at an angle of incidence of 70° and in a wavelength range between 370 and 1000 nm. Fitting was performed with the CompleteEASE software (J. A. Woollam, Version 5.19) using a model consisting of a silicon substrate, a 1.7 nm native oxide layer, and a Cauchy layer.

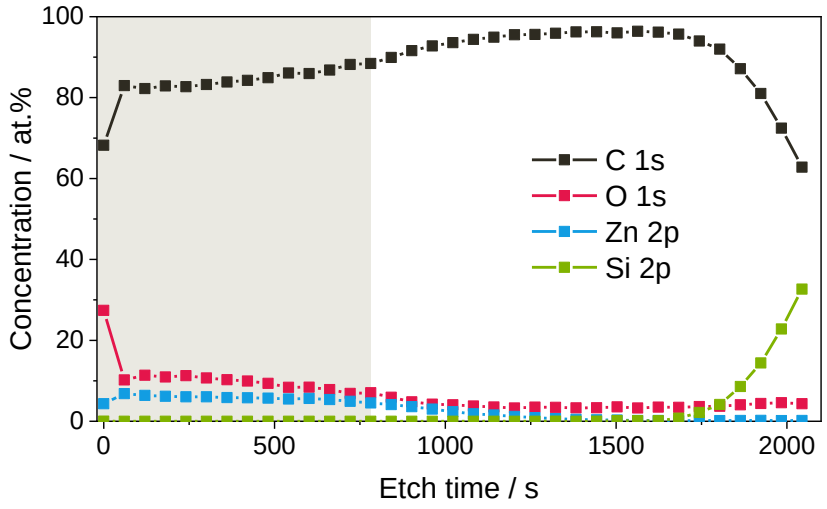

Figure S5: XPS depth profile of a lithographically patterned p(TMPTA-c-ETPTA) film on pMMA. The grey area indicates the thickness of the p(TMPTA-c-ETPTA) film.