Supporting Information

Effects of the Density of Chemical Cross-links and Physical Entanglements of Ultraviolet-Irradiated Polystyrene Chains on Domain Orientation and Spatial Order of Polystyrene-

block-

Poly(methyl methacrylate) Nano-domains.

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Figure S1. (a) Photos of UVIN set-up and dosages measured at the sample-to-lamp distance of 2.2 cm, and (b) photos of UVIAT set-up and dosages measured at the sample-to-lamp distance of 3.5 cm. Note that the photos in (a) were taken for the UVIN set-up at a table out of the glove box.

Figure S2. Photos of the sample chamber for swelling experiments of a film during solvent annealing (SA) in toluene vapor by recording variations in film thickness during SA. The swelling experiments were conducted at 25 °C at which the saturated pressure of toluene was 0.03762181 bar\(^1\).

Characterization of UVIAT-Treated Polystyrenes.

The UVIAT-treated PS layers were characterized by XPS and AFM. For brevity, we only discuss the surface characterization of the PS\(_{290}\) layers since the variations in surface property exhibit a similar trend regardless of MW for the UVIAT-treated PS layers. Figure S3 shows XPS C\(_{1s}\) spectra of the PS\(_{290}\) layers with UVIAT of various time intervals. As Figure S3 shows, before the UVIAT treatment, the PS\(_{290}\) layers show an
intense peak centered at 286.5 eV and a small hump centered at 291 eV. The peak is associated with the C-C/C-H species while the small hump corresponds to a satellite line of benzene rings. After the UVIA treatment, several additional peaks appear in the region of 285-294 eV. The emerging peaks are associated with oxidized carbon species, such as hydroxyl groups at 285.4 eV, carbonyl groups at 287.6 eV and carboxyl groups at 288.9 eV. The XPS result indicates that the UVIA treatment caused oxidation of the PS$_{290}$ layers and that the extent of oxidization increased with time. The surface observations and height profiles measured by an AFM indicate that the oxidation induced by brief UVIA only increased the surface roughness slightly and had little influence on the height (Figures S4&S5). Before UVIA the root-mean-square (RMS) surface roughness of the pristine PS$_{290}$ was 0.28 nm. After UVIA of 60 min, the RMS surface roughness increased twofold.

Figure S6 shows static angle, advancing angle, receding angle and the contact angle hysteresis for water droplet on a PS$_{290}$ layer with UVIA of various time intervals. The reported contact angle values represent an average over at least five measurements on different areas of each sample. As Figure S6 shows, with no or brief UVIA (<20 min), the contact angle hysteresis values measured for the PS$_{290}$ layer are of the same magnitude. The increased hysteresis should be due to the surface roughening. Nevertheless, the extent of the surface roughening was extremely small (less than 0.6 nm). This result indicates that the surface roughness would not be significantly increased by mild oxidation with UVIA. To estimate the surface energy, we undertook measurements of the static contact angles of water and diiodomethane on the UVIA-treated PS layers. According to the Owens-Wendt-Rabel-Kaelble (OWRK) method, the surface energy of UVIA-treated PS layers can be calculated from the contact angle of liquids of the two types. As Figure S7 shows, UVIA treatment of varied duration and dosage changed the surface property of the PS layers from hydrophobic to hydrophilic,
evident from a continuously decreasing contact angle of water. In contrast, the contact angle of liquid diiodomethane on the UVIA-treated PS layers revealed no such decreasing trend with increasing duration and dosage of UVIA. The OWRK analysis indicates that the surface energy increased from $45.5\pm1.4$ to $67.2\pm3.0$ mJ/m$^2$ (Figure S7) when oxidation with UVIA took from 1 to 60 min. The increment of the surface energy depends strongly on the dosage of light to which the surface of PS is exposed. Exposing PS layers to a high dosage of UV light increases their surface energy.

Figure S3. XPS C1s spectra of the PS$_{290}$ layer (a) before and (b-c) after UVIA of various time periods: (b)10 and (c) 30 min.

Figure S4. AFM topographic images of the PS$_{290}$ layer (initial thickness: 27.3 nm) before (a) and (b-d) after UVIA of various time periods: (b) 5, (c) 10 and (d) 60 min. The values denote RMS surface roughness. Scale bar: 500 nm.
Figure S5. Height profiles of the PS$_{290}$ layer before (a) and (b-d) after UVIA of various time periods: (b) 5, (c) 10 and (d) 60 min. The inset in (d) shows 10 $\times$10 $\mu$m$^2$ topographic image of a scratched region. The border between the film and the substrate was slightly deformed by scratching. The height values represent an average over at least five measurements on different positions (except for the border region) of each sample.

Figure S6. Static contact angle (green triangles), advancing (black squares) as well as receding angles (red diamonds), and hysteresis (blue circles) of water on a PS layer treated with UVIA for varied duration.
**Figure S7.** Contact angle of water (solid symbols) and diiodomethane (half open symbols) on the surface of PS layers with UVIA of varied duration, and variation of surface energy (open symbols) for UVIA-treated PS layers. The intensity of UVIA was between 0.2 Jcm$^{-2}$ and 12.4 Jcm$^{-2}$. PS$_6$: black symbols, PS$_{45}$: red symbols; PS$_{100}$: blue symbols and PS$_{290}$: green symbols.

**Figure S8.** XPS C1s spectra of the PS$_{290}$ layers after UVIN of (a) 0, (b) 2.5 and (b) 6 h.
Figure S9. AFM topographic images (a-c) and height profiles (d-g) of the PS\textsubscript{290} layer after UVIN of (a) 0, (b, d-e) 2.5 and (c, f-g) 6 h. The height values represent an average over at least five measurements on different positions (except for the border region) of each sample.

Figure S10. Immobilized layer thickness as a function of (a) time of UVIN, and (b) molecular weight of the polymer with UVIN of 2.5 (solid symbols) and 6 h (open symbols). Polystyrene of average molecular weight 290 kg/mol was used in (a). The dash line in (a) is plotted as a visual guide.

Figure S11. 2×2μm\textsuperscript{2} AFM topographic images of cylindrical nano-domains of PS\textsubscript{57-}b-PMMA\textsubscript{25} on a neutralized PS layer with brief UVIN of 1h (a) before and (b) after selective removal of the PMMA block. The film was isothermally annealed at 230 °C.
for 24h before selective removal of the PMMA block with UV irradiation followed by acetic acid rinsing. Scale bar: 500 nm

![Figure S12](image)

**Figure S12.** (a-e) 2×2μm² AFM topographic images of cylindrical nano-domains of PS₅₇-b-PMMA₂₅ (ca. 75 nm) on a neutralized PS₂₉₀-6 layer (22.8 nm) after O₂ plasma etching was carried out for varied duration: (a) 0, (b) 60, (c) 300, (d) 420, and (e) 540 sec. Scale bar: 500 nm. SEM images of (f) top-view and (g) side-view of sample (a). Scale bar in the SEM images: 200 nm. To increase the contrast between the PS and PMMA domains, the PMMA domains were degraded to form pores via UV exposure.

An O₂ plasma etching approach was further imposed on the standing cylindrical nanodomains with hexagonal packing to identify whether the perpendicular orientation could grow and propagate through the entire film thickness. With vertical etching followed by AFM characterization, the internal nanodomains buried within the specimen could be probed without difficulty. As Figure S12 shows, regardless of etching time, the specimen displays a morphology of dot-like nanodomains with hexagonal order, indicative of the propagation of perpendicular nano-cylinders throughout the thickness of the PS₅₇-b-PMMA₂₅ film on PS₂₉₀-6.
Figure S13. Concentration-depth profile of the neutralized PS$_{290}$ layer. The sputter intervals used were 5 sec in the early stage (0-20 sec) of sputter or 30 sec in the late stage (20-470 sec) of sputter.

An ion gun with argon ions was used to sputter out sample elements to reveal a concentration-depth profile. Argon ion of 3keV energy at a scan size of 1mm×1mm and a 5sec or 30 sec sputter intervals were used. As Figure S13 shows, only the most top surface of the PS layer formed oxygenated species. The Si$_{2p}$ and O$_{1s}$ signals did not emerge until the sputter interval reached 260 sec. These signals are associated with a thin layer of SiO$_x$ of the substrate.

Figure S14. (a) 1D in-plane SAXS profiles of nano-lamellae in PS-b-PMMA films of varied MWs on PS$_{290}$-2.5. (b) A plot of D spacing vs N. The dashed line is power law
fits of D vs N with the best fit exponents. The solid symbols denote $d$ spacing values for the specimens with acetic acid rinsing while the open symbols denote those for the specimens without acetic acid rinsing.

References: