Supporting Information for:

Optical Alignment of Si-Containing Nanodomains Formed by Photo-Responsive Amorphous Block Copolymer Thin Films

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Figure S1. ¹H-NMR spectrum of mono-hydride PDMS in CDCl₃.



Figure S2. ¹H-NMR spectrum of mono-carbinol PDMS (P1) in CDCl₃.



Figure S3. ¹H-NMR spectrum of the dithiobenzoate-type macro-CTA PDMS (P2) in CD₂Cl₂.



Figure S4. SEC traces of the dithiobenzoate-type macro-CTA PDMS (P2) (a) in toluene (40°C, PDMS standards calibration) and (b) in THF (40°C, PS standards calibration).



Figure S5. SEC traces of the macro-CTA PDMS (P2) and several PDMS-*b*-P(DR1MA-*co*-RMA) BCPs (M1 to M4) in THF at 40°C (UV-detection at 254 nm).



Figure S6. ¹H-NMR spectrum of PDMS₁₃₅-*b*-PMMA₄₇₆ (M1) in CD₂Cl₂.



Figure S7. ¹H-NMR spectrum of PDMS₁₃₅-*b*-P(DR1MA₁₀-*co*-MMA₂₃₆) (M2) in CD₂Cl₂.



Figure S8. ¹H-NMR spectrum of PDMS₁₃₅-*b*-P(DR1MA₁₉-*co*-MMA₁₆₅) (M3) in CD₂Cl₂.



Figure S9. ¹H-NMR spectrum of PDMS₁₃₅-*b*-P(DR1MA₂₇-*co*-MMA₅₇) (M4) in CD₂Cl₂.



Figure S10. ¹H-NMR spectrum of PDMS₁₃₅-*b*-P(DR1MA₃₀-*co*-nBMA₇₀) (B4) in CD₂Cl₂.



Figure S11. ¹H-NMR spectrum of PDMS₁₃₅-*b*-P(DR1MA₂₉-*co*-nHMA₆₃) (H4) in CD₂Cl₂.

The equations used to determine the M_n of the BCPs by ¹H-NMR are given below:

$$Mn_{M1} = Mn_{PDMS} + \frac{H_b}{3} \times MW_{MMA}$$
 (see Figure S6)

 $Mn_{M4} = Mn_{PDMS} + \frac{H_l}{2} \times MW_{DR1MA} + \frac{H_{i+j+h} - 4 \times \frac{H_l}{2}}{3} \times MW_{MMA} \text{ (see Figure S7 to S9)}$

 $Mn_{B4} = Mn_{PDMS} + \frac{H_l}{2} \times MW_{DR1MA} + \frac{H_{f+g+i+j} - 6 \times \frac{H_l}{2}}{2} \times MW_{nBMA}$ (see Figure S10)

 $Mn_{H4} = Mn_{PDMS} + \frac{H_l}{2} \times MW_{DR1MA} + \frac{H_{f+g+i+j} - 6 \times \frac{H_l}{2}}{2} \times MW_{nHMA}$ (see Figure S11)

where the MW is the molecular weight of the corresponding repeating unit;

 M_{nPDMS} (10 kg/mol) was used as reference ($\frac{H_d}{6} \times MW_{DMS}$, Figure S2);

H_b is the resulted integration value for the –COOCH₃ protons from the MMA units at 3.6 ppm;

 H_1 is the integration value for the aromatic protons of the DR1MA units at 6.88 ppm or H_p at 8.28 ppm;

 H_{i+j+h} is the integration value for the protons overlapped at 3.4 – 3.75 ppm, namely H_i and H_j are the –CH₂–N(–azo)–CH₂– protons from the DR1MA units and H_h are –COOCH₃ protons from the MMA units;

 $H_{f+g+i+j}$ is the integration value for the protons overlapped at 3.4 – 4.2 ppm, namely H_f , H_j and H_i are the –COO–CH₂–CH₂–N(–azo)–CH₂– protons from the DR1MA units and H_g are –COO CH₂– protons from the *n*BMA units;

 $H_{f+g+i+j}$ is the integration value for the protons overlapped at 3.4 – 4.2 ppm, namely H_f , H_j and H_i are the –COO–CH₂–CH₂–CH₂–N(–azo)–CH₂– protons from the DR1MA units and H_g are –COO CH₂– protons from the *n*HMA units.



Figure S12. DSC traces of various BCPs acquired at a heating rate of 10°C/min. (A) Traces of the PDMS-*b*-P(DR1MA-*co*-MMA) series. (B) Traces of the PDMS₁₃₅-*b*-P(DR1MA₂₇-*co*-MMA₅₇) (M4), PDMS₁₃₅-*b*-P(DR1MA₃₀-*co*-nBMA₇₀) (B4) and PDMS₁₃₅-*b*-P(DR1MA₂₉-*co*-nHMA₆₃) (H4) samples.



Figure S13. Typical UV-Vis absorption spectrum for the synthesized BCPs (here M4) in THF $(3.7 \cdot 10^{-5} \text{ M})$ at 25°C.

GISAXS pattern of the nanostructured M4 BCP thin film:

The GISAXS pattern presented in Figure S14 evidences the formation of hexagonally-structured BCPs domains as demonstrated by the two Bragg spots (denoted as T(10) and R(10), respectively) along the q_z direction related to the Bragg diffraction of the transmitted and reflected beams. The absence of Debye-Scherrer rings highlights the unperturbed in-plane orientation of the cylindrical structure over the whole film thickness. Besides, the appearance of these Bragg spots, above the Yoneda band, further confirms the parallel orientation of the {10} planes of the cylindrical structure as regards to the substrate.



Figure S14. 2D GISAXS pattern of the nanostructured M4 BCP thin film obtained at an incident angle of 0.2° . The observed diffraction features are consistent with hexagonally-structured domains aligned with their {10} planes parallel to the film surface.



Figure S15. a) (1 x 1 μ m) AFM topographic view of a disordered M4 layer deposited by spincoating and b) its associated 2D-FFT dominated by noise.



Figure S16. a) (1 x 1 μ m) 3D-AFM topographic view of an as-cast (disordered) M4 layer exposed to a *p*-polarized beam laser ($\lambda_w = 532 \text{ nm}$, P = 30 mW.cm⁻²) beam during 30 min. b) The AFM topographic profile reveals that the SRG pattern adopts a sinusoidal shape with a period of ~357 nm and a SMA > 100 nm.