

Supporting Information:

Fabrication of Sub-3 nm Feature Size based on Block Copolymer Self-Assembly for Next Generation Nanolithography

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S1. Synthetic route and molecular characterization of PDHS-*b*-PS.

Synthetic routes of PDHS-*b*-PS *via* the combination of RAFT polymerization and hydrolysis reaction are shown in **Scheme S1**. First, a target molecular weight of PDMOS was synthesized by RAFT polymerization of DMOS in 1,4-dioxane at 68 °C using cyanomethyl dodecyl trithiocarbonate RAFT agent. The monomer conversion was ~ 95 % in 24h. Synthesized PDMOS homopolymer RAFT agents were prepared by four different DMOS/CMDTTC feed ratios. Degree of polymerization (*N*) of PDMOS homopolymer was determined from ¹H-NMR in CDCl₃ by comparing the peak area of methoxy protons (3.48-3.93 ppm) of the PDMOS to that of the -CH₂CN protons (3.2-3.4 ppm) at the chain end of PDMOS. The calculated *N* was 6, 7, 7.8 and 8.4, respectively, which depended on the feed ratio of DMOS/CMDTTC, as expected. SEC trace showed unimodal and narrow PDI (1.06) for 8.4 *N* of PDMOS in **Figure S1a** (black).

Then, PDMOS was used as a macro-chain transfer agent for the RAFT polymerization of styrene in 1,4-dioxane using [PDMOS] : [AIBN] = 1 : 0.25 at 68 °C for 24 h. *N* of PS in corresponding block copolymers was determined from ¹H-NMR in CDCl₃ by comparing the peak area of methoxy protons “b” (3.48-3.93 ppm) of PDMOS and aromatic protons “a” (5.75-5-7.22 ppm) of PDMOS and PS to that of -CH₂CN protons “c” (3.2-3.4 ppm) at the chain end of PDMOS (**Figure S1b**). *N* and M_n (NMR) of PS correspond to styrene monomer loading with respect to corresponding PDMOS RAFT macro-chain transfer agent. Monomer conversion of the resulting block copolymers was ~ 70 %. SEC trace of PDMOS-*b*-PS block copolymer from corresponding PDMOS homopolymer showed unimodal and narrow PDI (1.05) in **Figure S1a** (red).

PDMOS-*b*-PS were then reacted with BBr₃ to convert PDMOS methoxy group into the corresponding PDHS hydroxyl group (Scheme S1). The characterization of PDHS-*b*-PS and

PDMOS-*b*-PS are included in Table 1 in the main text. The typical $^1\text{H-NMR}$ spectra of PDHS-*b*-PS obtained from sample DHS8.4-S10 are shown in **Figure S1c**. The conversion of methoxy group in PDMOS into the corresponding hydroxyl group in PDHS was confirmed by the disappearance of the old characteristic peak attributed to the methoxy proton “b” at 3.48-3.93 ppm and appearance of the new characteristic peak attributed to the hydroxyl proton “c” at 7.8 ppm (Figure S1c). The calculated conversion (%) of methoxy group into hydroxyl group obtained by complete disappearance peak area of methoxy group “b” of PDMOS was $\sim 100\%$ (Figure S1c). The M_n (NMR) of PDHS-*b*-PS was calculated from M_n (NMR) of PDMOS-*b*-PS by subtraction of molecular weight of methoxy group of PDMOS and molecular weight of end group. SEC trace of PDHS-*b*-PS from corresponding PDMOS-*b*-PS showed unimodal and narrow PDI (1.05) in Figure S1a (blue).

Typical Synthesis of Poly(dimethoxystyrene) (PDMOS) (1)

In a dried and argon purged polymerization tube, 2 mL (1.35×10^{-2} mol) of DMOS, 0.43 mg (1.35×10^{-3} mol) of CMDTTC, and 44.36 mg (2.70×10^{-4} mol) of AIBN were added in 2 mL 1,4-dioxane. The homogeneous solution was degassed under argon for 45 min. The polymerization tube was immersed in a preheated oil bath at 68 °C for 24 h. The reaction was stopped by freezing the reaction mixture in liquid nitrogen. A tiny portion of the polymerization mixture was used to determine the monomer conversion by $^1\text{H-NMR}$. The rest of the crude mixture was dissolved in 5 mL 1,4-dioxane, precipitated from 400 mL hexane and dried under vacuum at room temperature for 24 h. Monomer conversion was 95% determined by $^1\text{H-NMR}$.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ [ppm]: 1.10-2.23 (broad, PDMOS polymer backbone), 3.2-3.4 (broad, $-\text{CH}_2\text{CN}$ end-group), 3.48-3.93 (broad, methoxy group), 5.75-5-6.7 (broad, aromatic

group).

Typical Synthesis of Poly(dimethoxystyrene)-*b*-polystyrene (PDMOS-*b*-PS) (2)

In a dried and argon purged polymerization tube, 0.4 mL (3.52×10^{-3} mol) of styrene, 0.4 g (2.35×10^{-4} mol) of PDMOS macro-RAFT agent (1), and 9.6 mg (5.88×10^{-5} mol) of AIBN were added in 3 mL 1,4-dioxane. The homogeneous solution was degassed under argon for 45 min. The polymerization tube was immersed in a preheated oil bath at 68 °C for 24 h. The reaction was stopped by freezing the reaction mixture in liquid nitrogen. A tiny portion of the polymerization mixture was used to determine the monomer conversion by $^1\text{H-NMR}$. The rest of the crude mixture was dissolved in 5 mL 1,4-dioxane, precipitated from 400 mL methanol and dried under vacuum at room temperature for 24 h. Monomer conversion was 70% determined by $^1\text{H-NMR}$.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ [ppm] (Figure S1b): 1.04-2.3 (broad, PDMOS and PS backbone), 3.2-3.4 (broad, $-\text{CH}_2\text{CN}$ end group), 3.48-3.93 (broad, methoxy group), 5.75-5-7.22 (broad, aromatic group of PDMOS and PS).

Typical Synthesis of Poly(dihydroxystyrene)-*b*-polystyrene (PDHS-*b*-PS) (3)

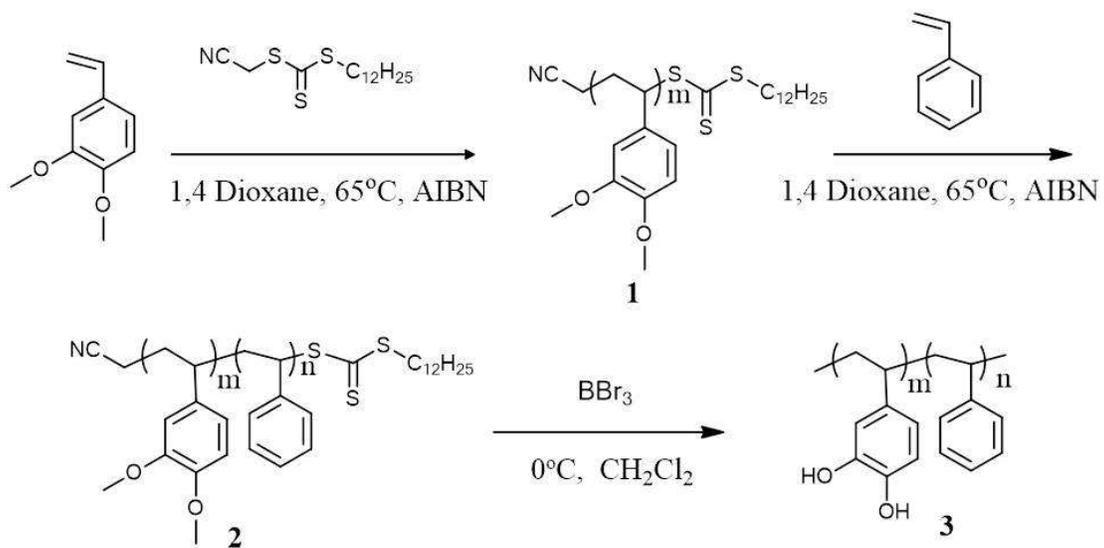
The synthesized PDMOS-*b*-PS (2) was further reacted with BBr_3 to convert the methoxy groups to corresponding hydroxyl groups. In a dried 100 mL round bottle flask, PDMOS-*b*-PS diblock copolymer (300 mg, 1.09×10^{-4} mol) and anhydrous dichloromethane (15 mL) were added. After that, 1.5 ml (1.00 M) of anhydrous dichloromethane solution containing BBr_3 was added dropwise to the above solution under ice cooled condition. The solution was stirred at room temperature for 12 h. The mixed solution was added dropwise to a 200 mL of aqueous 1 M HCl. After stirring for 10 h, the precipitate was collected by filtration and dried

under vacuum. Collected crude product was further dissolved in 2 mL of THF and precipitated from 200 mL of hexane to remove residual end group, then filtered. Finally, solid product was vacuum dried at room temperature for 24h.

$^1\text{H-NMR}$ (300 MHz, $(\text{CD}_3)_2\text{CO}$, δ [ppm] (Figure 1c): 1.04-2.5 (broad, PDMOS and PS backbone), 5.75-5-7.8 (broad, Hydroxyl and aromatic group of PDHS and aromatic group of PS).

Molecular Characterization

The number average molecular weight (M_n) and volume fraction of PS (f_{PS}) were determined by ^1H nuclear magnetic resonance spectra ($^1\text{H-NMR}$: Bruker Avance III 400) with a solvent of chloroform-d (CDCl_3) for poly(3,4-dimethoxystyrene)-*block*-polystyrene (PDMOS-*b*-PS) and acetone-d ($(\text{CD}_3)_2\text{CO}$) for PDHS-*b*-PS (Figure S1 and S3). Polydispersity index (PDI) of PDHS-*b*-PS was measured by size exclusion chromatography (SEC: Waters 2414 refractive index detector) based on PS standards (Figure S2). Two 300 mm (length) \times 7.5 mm (inner diameter) columns including particle size of 5 μm (PLgel 5 μm MIXED-C: Polymer Laboratories) were used with THF as an eluent, and a flow rate of 1 mL/min at 30 $^\circ\text{C}$. The microdomains of all block copolymers were investigated by SAXS and TEM. The molecular characteristics of all samples are summarized in Table 1 in the main text.



Scheme S1. Synthetic routes for PDHS-*b*-PS by RAFT polymerization and hydrolysis reaction.

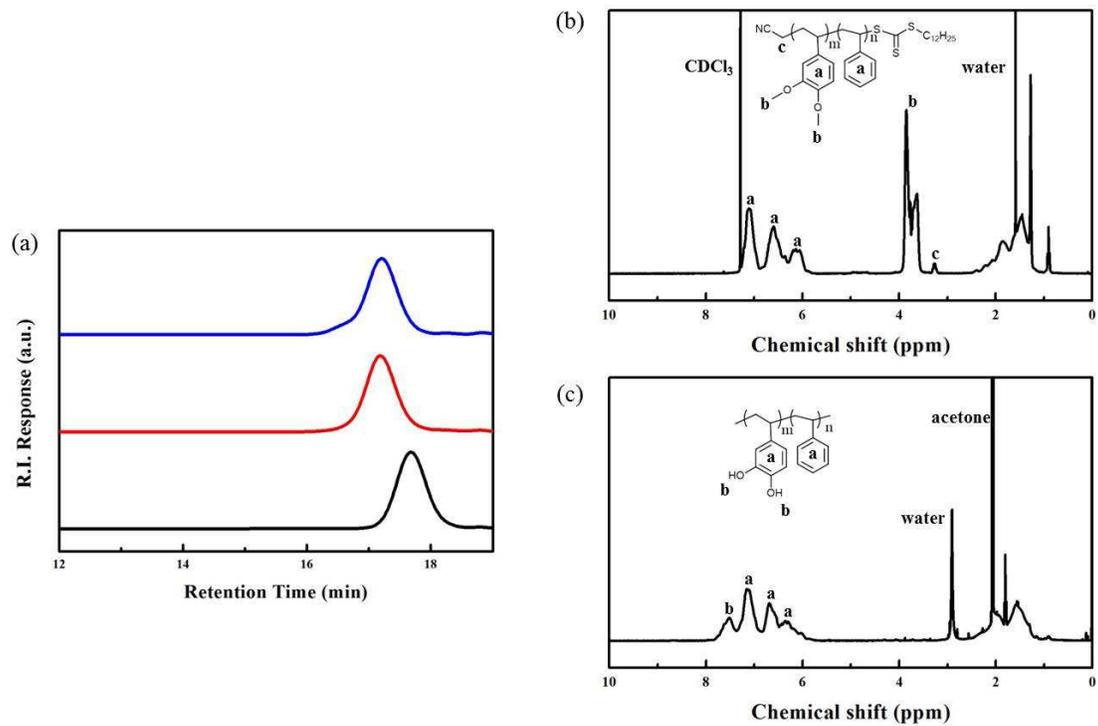


Figure S1. (a) SEC traces for DHS8.4-S10 sample showing PDMOS (black), PDMOS-*b*-PS (red) and PDHS-*b*-PS (blue), (b) ¹H-NMR spectra of PDMOS-*b*-PS before hydrolysis reaction and (c) ¹H-NMR spectra of PDHS-*b*-PS after hydrolysis reaction.

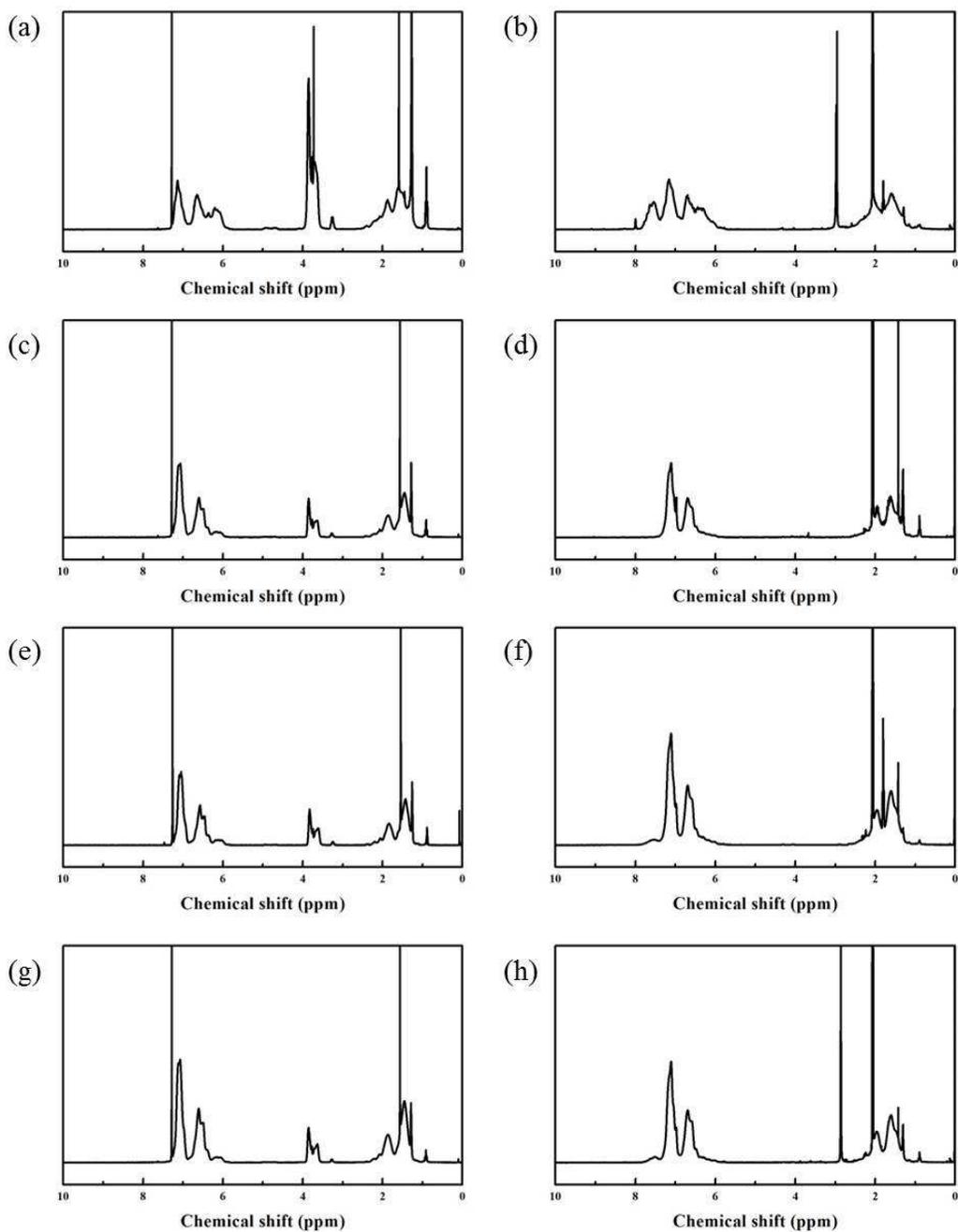


Figure S2. ^1H -NMR spectra before and after hydrolysis reaction for DHS6-S7.6 (a and b), DHS7-S31 (c and d), DHS7.8-S38 (e and f) and DHS8.4-S54 (g and h).

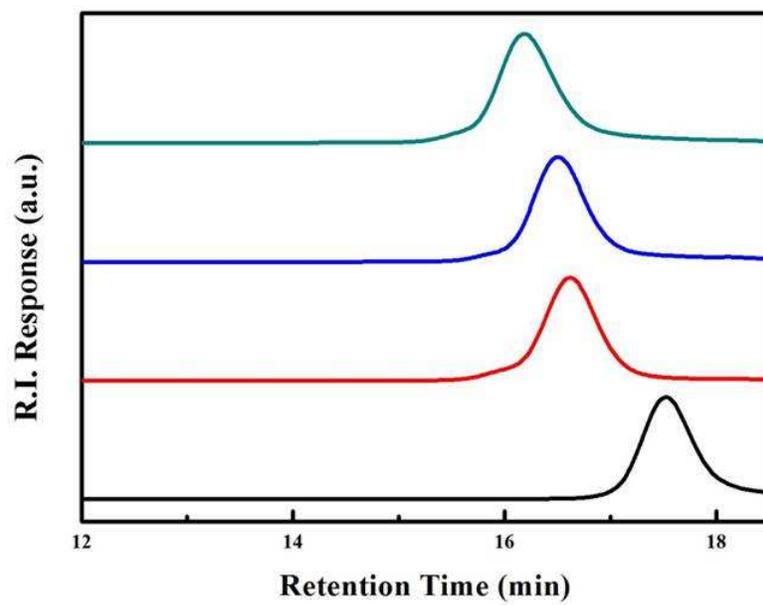


Figure S3. SEC traces for DHS6-S7.8 (black), DHS7-S31 (red), DHS7.8-S38 (blue) and DHS8.4-S54 (green).

S2. Uniformity of ZnO₂ nanowires.

Figure S4 shows AFM height image and height profile of ZrO₂ nanowires on a silicon substrate prepared by DHS8.4-S54 followed by O₂ plasma treatment. It is seen that ZrO₂ nanowires are uniformly formed through the entire substrate. The height, diameter, and center-to-center spacing of ZrO₂ nanowire measured at various positions are 0.97 ± 0.16 nm, 5.8 ± 1.0 nm, and 10.6 ± 1.5 nm, respectively.

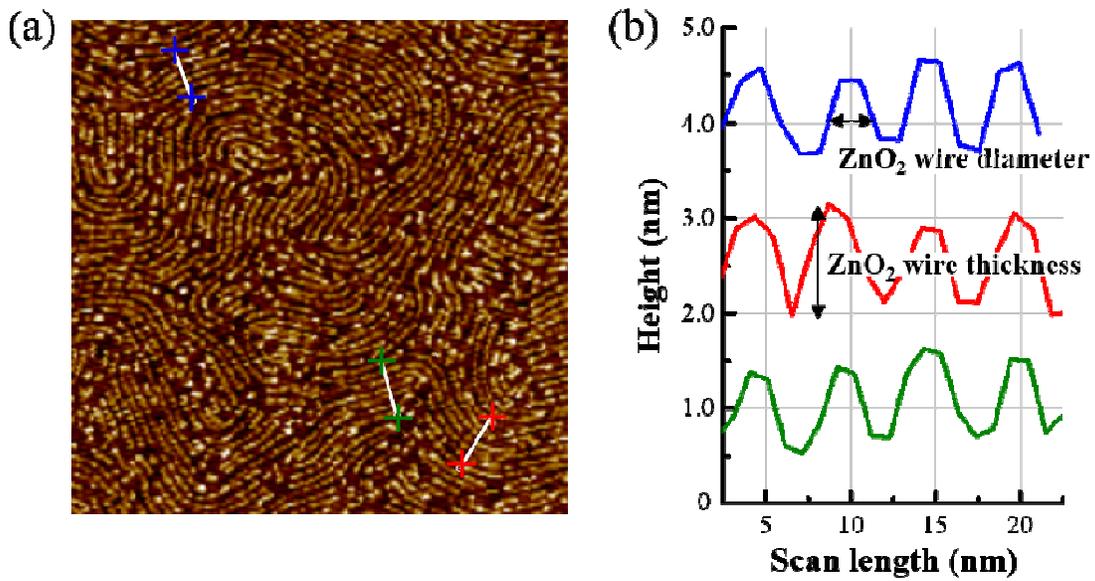


Figure S4. (a) AFM height image and (b) height profiles measured at three different positions in AFM height images for ZrO₂ nanowire on a silicon substrate prepared by DHS8.4-S54 followed by O₂ plasma treatment.

S3. Glass transition temperature (T_g) of PDHS-*b*-PS.

Figure S5 shows the second heating run of differential scanning calorimetry (DSC) trace for DHS8.4-S54 sample. Glass transition temperatures of PS and PDHS blocks in DHS8.4-S54 are ~ 63 °C and ~ 98 °C, respectively. Because DHS8.4-S54 has the largest degree of polymerization among all PDHS-*b*-PS samples, the equilibrium microdomain was obtained by thermal annealing of the samples at 170 °C.

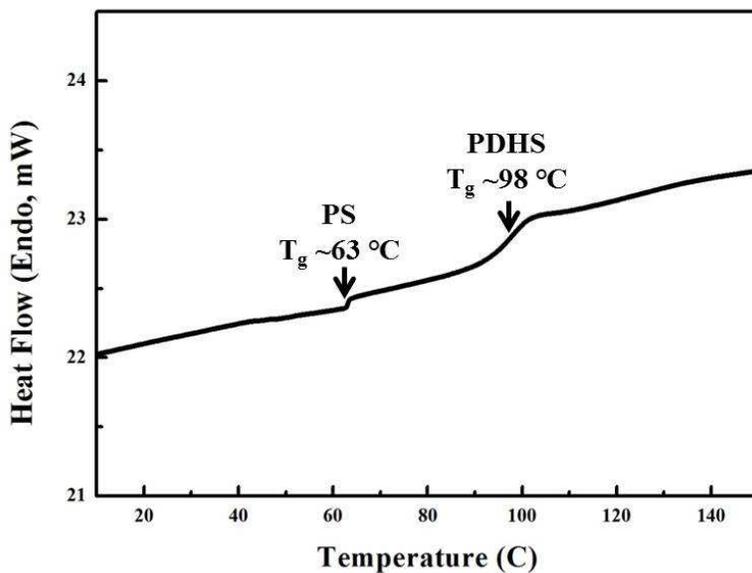


Figure S5. DSC trace obtained during the second heating run of DHS8.4-S54. A heating/cooling rate of 10 °C/min was used.

S4. The Ordered-to-disordered transition temperature (T_{ODT}) of PDHS-*b*-PS.

Figure 6a gives SAXS profiles for DHS8.4-S10 at various temperatures. The first order peak of DHS8.4-S10 suddenly changed into a broad peak at 230 °C, which is referred to the order to disorder transition (T_{ODT}). **Figure 6b** shows plots of $1/I(q^*)$ and full width at half maximum (FWHM) versus $1/T$ for DHS8.4-S10, from which the T_{ODT} was determined to be 230 °C.

Figure S7 gives temperature dependence of depolarized light scattering intensity of all the samples. T_{ODT} of DHS8.4-S710 was determined to be 230 °C, which is consistent with SAXS measurement. The values of T_{ODTs} for DHS7-S31, DHS7.8-S38 and DHS8.4-S54 are 280 °C, 300 °C and > 310 °C, respectively. On the other hand, DHS6-S7.8 becomes fully disordered over the entire experimental temperatures.

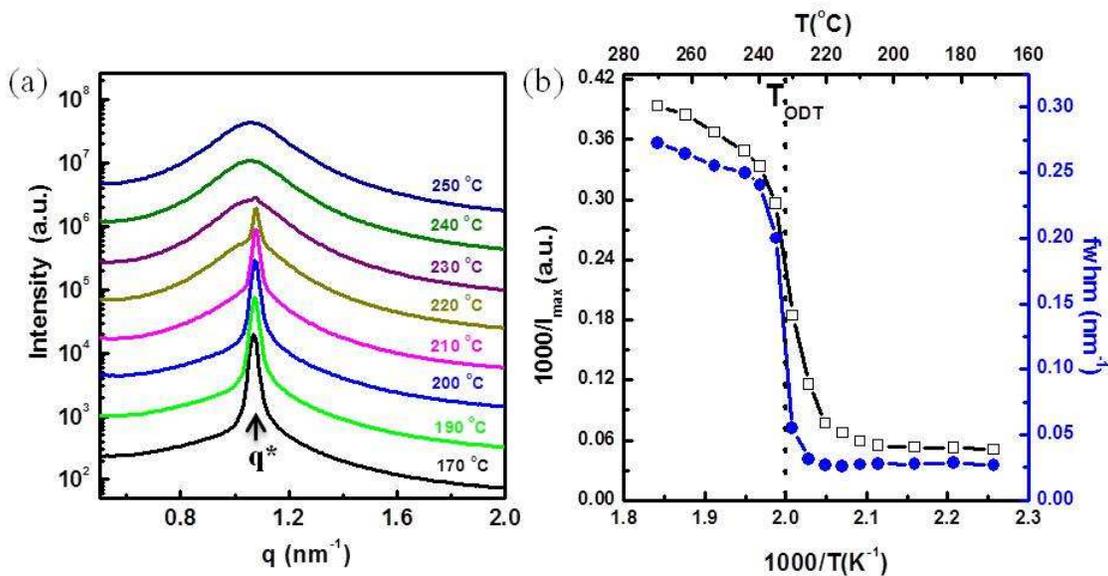


Figure S6. (a) SAXS profiles at various temperatures and (b) plots of $1/(q^*)$ and FWHM versus $1/T$ for DHS8.4-S10. SAXS profiles were shifted vertically to avoid overlap each other.

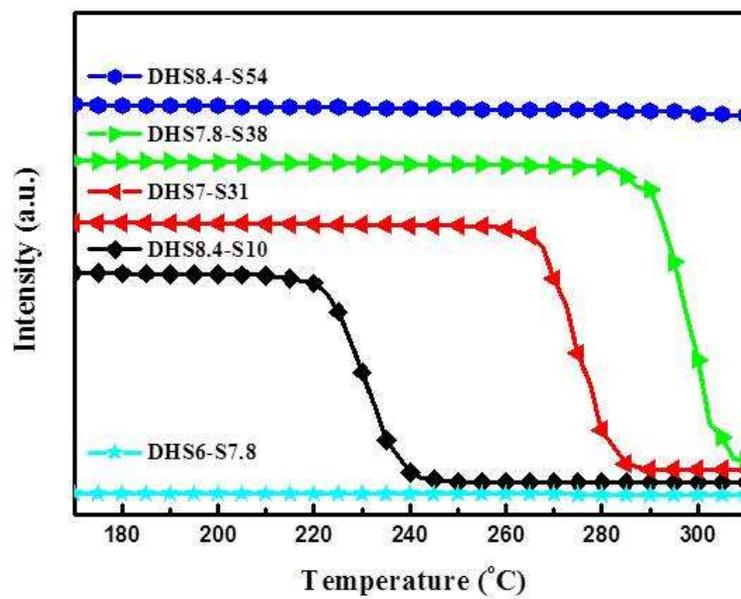


Figure S7. Temperature dependence of depolarized light scattering intensity for DHS6-S7.8, DHS8.4-S10, DHS7-S31, DHS7.8-S38 and DHS8.4-S54.