Electronic Supplementary Information (ESI) for

UV light-initiated RAFT polymerization induced self-assembly

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EXPERIMENTAL

Materials: All reagents were purchased from either Sigma-Aldrich or Aladdin. 4-Vinylpyridine (4VP) was distilled under vacuum after dried with CaH₂. Styrene was passed through a basic alumina column to remove inhibitor. 2,2'-azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and stored at 0 °C before use. S-1-dodecyl-S-(α,α '-dimethyl- α ''-acetic acid) trithiocarbonate (DDMAT) was synthesized according to the method of Lai *et al.*¹ Methanol was distilled before use. All other reagents and solvents were analytically pure and used as received without further purification.

Light Source: The UV light source is a UV nail gel curing lamp ($\lambda_{max} = 365$ nm) equipped with 4× 9 W bulbs. The intensity of the light was measured as 2.50 mW cm⁻² by a UV radiometer covering broad UV range.

Experimental of photolysis of AIBN.^{2, 3}: The photolysis of AIBN was monitored both by UV-vis spectra and ¹H NMR spectroscopy in our experiments. The UV-vis absorption spectra of AIBN (3.0 $\times 10^{-2}$ mol/L) in methanol were recorded after the solution had been exposed to the UV light at different time intervals. For ¹H NMR analysis, a solution of AIBN (1.0 $\times 10^{-1}$ mol/L) in *d*₄-methanol (0.6 mL) was introduced into a NMR tube and irradiated with the UV light at timed intervals (time = 15 min) at room temperature. The photolysis half-life (*t*_{1/2}) of AIBN was determined by the plot of the relative concentration of AIBN at $\delta = 1.70$ ppm to time.

Synthesis of P4VP macro-CTA⁴ : The P4VP macro-CTA was prepared by thermal initiated RAFT solution polymerization in isopropanol at 80° C. A typical polymerization procedure is described as

follows: 4VP (4.24 g, 40 mmol), DDMAT (72 mg, 0.2 mmol) and AIBN (6.40 mg, 0.04 mmol) were dissolved in 10 mL isopropanol. The solution was degassed by bubbling with nitrogen for 30 min, and then placed in a preheated oil bath at 80 °C. The polymerization was stopped after 6 h by immersing in liquid nitrogen and exposing to air. The resulting polymer was purified by precipitation into excess n-hexane for three times and dried under vacuum at 40 °C overnight. The M_n calculated by ¹H NMR was 4500g/mol. Its ¹H NMR spectrum is shown in Figure S4b. The M_n and polydispersity index obtained by GPC were $M_n = 6500$ g/mol, PDI = 1.09, respectively.

UV light-initiated RAFT PISA of Styrene with P4VP macro-CTA: In UV light-initiated RAFT polymerization experiments, the glass bottle charged with the reaction mixture was placed in the centre of a UV curing lamp, which was equipped with a magnetic stirring apparatus and a blowing air device for keeping constant temperature. The reaction mixture was deoxygenated by three freeze-pump-thaw cycles and backfilled with nitrogen gas. Then the mixture was irradiated under UV light (36 W, $I_{365} = 2.50 \text{ mW cm}^{-2}$) at room temperature. A typical experiment with molar ratio of P4VP/St/AIBN = 5:16800:1 was conducted as follows: P4VP (17 mg, 2.62 × 10⁻³ mmol), styrene (0.91 g, 8.6 mmol) and AIBN (0.08 mg, 4.87×10^{-4} mmol) were dissolved in 1 mL methanol in a 10 mL glass bottle. The polymerization was conducted in the UV curing lamp at room temperature for a fixed time and then stopped by turning off the UV light and exposing to air. The polymer was purified by precipitation in excess diethyl ether and collected by centrifugation. After drying in a vacuum oven at 40 °C overnight, the block copolymer was characterized by ¹H NMR and GPC.

For the kinetics study of the UV light-initiated RAFT polymerization by GPC, the same recipe mentioned above with molar ratio of P4VP/St/AIBN = 5:16800:1 was added into methanol in a Schlenk flask (25 mL) equipped with a magnetic bar. The polymerization was conducted in the UV curing lamp while stirring. During the polymerization, samples were taken periodically from the flask with a degassed syringe and quenched in air. After purification with the same procedure mentioned above, the block copolymers were measured by GPC analysis.

For the kinetics study of the UV light-initiated RAFT polymerization by *in situ* ¹H NMR spectroscopy, the same recipe mentioned above with the molar ratio of P4VP/St/AIBN = 5:16800:1 was thoroughly dissolved in d_4 -methanol (1.0 mL) in a NMR tube. The ¹H NMR spectra were

recorded immediately after the exposure of the NMR tube to the UV light at timed intervals (time = 0 h, 1 h, 3 h, 5 h, 7 h and 9 h) at room temperature.

Characterizations.

Nuclear Magnetic Resonance (NMR): The ¹H NMR spectra were recorded in CDCl₃ or d_4 -methanol using teramethylsilance as an internal reference at room temperature on a Bruker AVANCE III 400 MHz NMR spectrometer in 5 mm diameter tubes.

Ultraviolet–Visible (UV–vis) Spectroscopy: All the UV-Vis absorption spectra were conducted on a Perkin Elmer Lambda 950 UV-Vis-NIR spectrometer. Spectra were recorded in methanol in a 10 mm path length cell. Samples were baseline corrected with the pure solvent. Spectra were collected between 200 and 400 nm.

Gel Permeation Chromatography (GPC): The number average molecular weight (M_n) and molecular weight distributions (M_w/M_n) were assessed by Waters 1515 GPC equipped with refractive index detector at 40 °C. THF was used as eluent at a flow rate of 1.0 mL/min. A series of monodisperse polystyrene standards ranging from 800 to 113000 g/mol were used for calibration.

Transmission Electronic Microscopy (TEM): TEM images were performed with a JEOL JEM-2100F microscope at an accelerating voltage of 200 kV. TEM samples were prepared by dropping a diluted methanol dispersion solution on a carbon-coated copper grid, and dried under ambient temperature before testing.

Dynamic Light Scattering (DLS): DLS measurements were conducted at 25 °C using a scattering angle of 173° with a Malvern Zetasizer Nanoseries (Nano-ZS90) instruments equipped with a 4 mW He–Ne laser operating at 633 nm. The samples were diluted and dispersed in methanol. The intensity-average diameter and polydispersity of the copolymer micelles were calculated by cumulants analysis of the experimental correlation function using Dispersion Technology Software version 6.20.

Results and Discussion:

The typical absorption peak at 345nm associated with the functional -N=N- group of AIBN was decreased gradually under the UV light irradiation. The absorbs at 290 nm was belong to the product of dimethyl-*N*-(2-cyano-2-propyl)-ketenimine (DKI).⁵ The photolysis rate was very fast and most AIBN decomposed within 3.5 h.



Figure S1. UV-vis spectroscopic evolution of AIBN (3.0×10^{-2} mol/L) upon UV irradiation in methanol at different time intervals. Experimental condition: UV light intensity: $I_{365} = 2.50$ mW cm⁻², 25 °C.

At 1h, the signal at $\delta = 1.70$ ppm of AIBN decreased, and there was a new signal formed at $\delta = 1.50$ ppm, which is the signal of the more thermodynamical decomposition product tetramethylsuccinonitrile (TMSN).² The new signals formed at $\delta = 1.72$ ppm and 1.56 ppm were assigned to the characteristic signals of dimethyl-*N*-(2-cyano-2-propyl)-ketenimine (DKI).^{3, 5} After 3 h irradiation, the signal at $\delta = 1.70$ ppm was remained very small.



Figure S2. Typical ¹H NMR spectra changes of AIBN upon UV irradiation at (a) 0 h, (b) 1.0 h, (c) 2.0 h, (d) 3.0 h in d_4 -methanol. Experimental condition: UV light intensity: $I_{365} = 2.50$ mW cm⁻², 25 °C.

The photolysis half-life ($t_{1/2}$) of AIBN was determined by the time for the concentration of AIBN at $\delta = 1.70$ ppm to decrease to one half its original value.



Figure S3. Plot of $[I]/[I]_0$ as a function of time (h) for AIBN in d_4 -methanol (time intervals:15 min). $[I]_0$: the initial concentration of AIBN, [I]: the residual concentration of AIBN.

The M_n of P4VP-*b*-PS was 7600 g/mol and the mean DP of PS block was about 30 which was calculated based on the integral values of the signals at $\delta = 8.31$ ppm (pyridine ring) and $\delta = 6.57$ and 7.09 ppm (phenyl rings).



Figure S4. ¹H NMR spectra of (a) S-1-dodecyl-S-(a,a'-dimethyl-a''-acetic acid) trithiocarbonate (DDMAT) RAFT agent, (b) P4VP macro-CTA, and (c) P4VP-*b*-PS block copolymer prepared by UV light-initiated RAFT polymerization with a feed molar ratio of P4VP/St/AIBN = 5:16800:1 in methanol (0.8 g) for 3 h.

The mean DP of PS was calculated based on the integration ratio of the signals at $\delta = 8.31$ and $2.62 \sim 0.76$ ppm, which were 19, 38 and 70 for 1 h, 3 h and 5 h, respectively. After that, the mean DP of PS was kept apparently unchanged at 70. This may be attributed to the partial detecting of the soluble part of the P4VP-*b*-PS micelles in *d*₄-methanol.⁶



Figure S5. In situ ¹H NMR spectra for the UV light-initiated RAFT polymerization with molar ratio of P4VP/St/AIBN = 5:16800:1 at different polymerization times: (a) 0 h, (b) 1 h, (c) 3 h, (d) 5 h, (e) 7 h and (f) 9 h in d_4 -methanol.

Table S1. Experimental results of UV-light initiated RAFT polymerization at different styrene content

No. ^{<i>a</i>}	P4VP ₄₀ -b-P S _m ^b	M_n^b (g/mol)	$M_{\rm n}^{\ c}$ (g/mol)	$M_{ m w}^{\ c}$ (g/mol)	$M_{ m w}/M_{ m n}^{\ c}$	$D_h^d(\mathrm{nm})$	PDI^d
1	m=37	8300	12600	17400	1.39	56	0.020
2	m=71	11200	15800	20500	1.30	73	0.006
3	m=85	13400	18800	24000	1.28	92	0.016

^{*a*} The experiments were conducted at different amounts of styrene: (1) 0.46 g (P4VP/St/AIBN = 5:8400:1), (2) 0.91g (P4VP/St/AIBN = 5:16800:1) and (3) 1.82 g (P4VP/St/AIBN = 5: 23600:1). Experimental condition: UV light intentsity: $I_{365} = 2.50$ mW cm⁻², irradiation time: 9 h, 25 °C. ^{*b*} Determined by ¹H NMR. ^{*c*} Determined by GPC using polystyrene standards in THF. ^{*d*} Hydrodynamic diameters and polydispersity index determined by DLS measurement.



Figure S6. ¹H NMR spectra of P4VP-*b*-PS block copolymers (a) prepared by UV light-initiated RAFT polymerization for 9 h, (b) prepared by the secondary polymerization at 80 $^{\circ}$ C for 24 h after UV light irradiation for 9 h. Experimental condition: the molar ratio of P4VP/St/AIBN = 5:16800:1 in methanol (0.8 g).

References

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