Supporting Information

Fabrication and Characterization of Silica Nanotubes with Controlled Dimension

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Synthesis of PDMAEMA-DBT with Various Chain Lengths

*Synthesis of PDMAEMA*₂₂-*DBT*: CPDB (237 mg, 0.85 mmol) and AIBN (20 mg, 0.12 mmol) were mixed with DMAEMA (4.0 g, 25.5 mmol) and THF (4 mL) in a glass tube, and then the tube was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then the sealed tube was placed in an oil bath at 70 °C while stirring for 8 h. After cooling to room temperature, the polymer solution was diluted with THF and then poured into excess petroleum ether while stirring. The precipitate was collected and then dried in a vacuum oven at room temperature. The red solid was dissolved in THF, and the precipitation procedure was repeated three times. The resulting product was dried under vacuum at room temperature overnight. ¹H NMR spectrum and GPC were used to characterize the resultant polymers.

*Synthesis of PDMAEMA*₃₆-*DBT*: CPDB (142 mg, 0.51 mmol) and AIBN (12 mg, 0.073 mmol) were mixed with DMAEMA (4.0 g, 25.5 mmol) and THF (4 mL) in a glass tube, and then the tube was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then the sealed tube was placed in an oil bath at 70 °C while stirring for 8 h. The product was treated with the same procedure mentioned above. ¹H NMR spectrum and GPC were used to characterize the resultant polymers.

*Synthesis of PDMAEMA*₆₀-*DBT*: CPDB (89 mg, 0.32 mmol) and AIBN (7 mg, 0.043 mmol) were mixed with DMAEMA (4.0 g, 25.5 mmol) and THF (4 mL) in a glass tube, and then

the tube was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then the sealed tube was placed in an oil bath at 70 °C while stirring for 8 h. The product was treated with the same procedure mentioned above. ¹H NMR spectrum and GPC were used to characterize the resultant polymers.

*Synthesis of PDMAEMA*₁₁₃-*DBT*: CPDB (47 mg, 0.17 mmol) and AIBN (4 mg, 0.024 mmol) were mixed with DMAEMA (4.0 g, 25.5 mmol) and THF (4 mL) in a glass tube, and then the tube was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then the sealed tube was placed in an oil bath at 70 °C while stirring for 8 h. The product was treated with the same procedure mentioned above. ¹H NMR spectrum and GPC were used to characterize the resultant polymers.

*Synthesis of PDMAEMA*₁₄₇-*DBT*: CPDB (36 mg, 0.13 mmol) and AIBN (3 mg, 0.018 mmol) were mixed with DMAEMA (4.0 g, 25.5 mmol) and THF (4 mL) in a glass tube, and then the tube was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then the sealed tube was placed in an oil bath at 70 °C while stirring for 8 h. The product was treated with the same procedure mentioned above. ¹H NMR spectrum and GPC were used to characterize the resultant polymers.

Preparation of Polymeric Nanowires with different length and diameters

When PDMAEMA₂₂-DBT was used as Macro-RAFT agent, a typical polymerization procedure is as follows. PDMAEMA₂₂-DBT (37 mg, 10⁻² mmol), St (1.04 g, 10 mmol), AIBN (0.16 mg, 10⁻³ mmol) and methanol (1.50 g) were added in a glass tube with a magnetic bar, and then the system was degassed by three freeze-pump-thaw cycles. The tube was sealed by flame under vacuum, and then the sealed tube was placed in an oil bath at 80 °C while stirring. After 24 h of polymerization, the reaction mixture was cooled to room temperature, and then diluted with methanol. Most of the residual styrene was removed by three centrifugation-redispersion cycles. The mixture was dried naturally. To prepare the sample for TEM observation, a small portion of the solid was dispersed in methanol. For ¹H NMR and GPC measurements, other small portion of the dried polymer

nanomaterial was dissolved in THF, and then the block copolymers were obtained by pouring the solution into excess petroleum ether while stirring. The resultant powder was filtrated and dissolved in THF, and then precipitated in petroleum ether again. The polymer obtained by filtration was dried in a vacuum oven at room temperature overnight. Most of the nanowires were used as template for fabrication of silica nanotubes.

When the PDMAEMA₃₆-DBT was used as Macro-RAFT agent, the polymerization procedure is as follows. PDMAEMA₃₆-DBT (48 mg, 8×10^{-3} mmol), St (2.08 g, 20 mmol), AIBN (0.13 mg, 8×10^{-4} mmol) and methanol (1.60 g) were added in a glass tube with a magnetic bar, and then the system was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then the sealed tube was placed in an oil bath at 80 °C while stirring. After 24 h of polymerization, the reaction mixture was cooled to room temperature, and the product was treated with the same procedure mentioned above. TEM, ¹H NMR and GPC were used to characterize the resultant product.

When the PDMAEMA₆₀-DBT was used as Macro-RAFT agent, the polymerization procedure is as follows. PDMAEMA₆₀-DBT (39 mg, 4×10^{-3} mmol), St (2.08 g, 20 mmol), AIBN (0.066 mg, 4×10^{-4} mmol) and methanol (1.4 g) were added in a glass tube with a magnetic bar, and then the system was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then the sealed tube was placed in an oil bath at 80 °C while stirring. After 44 h of polymerization, the reaction mixture was cooled to room temperature, and the product was treated with the same procedure mentioned above. TEM, ¹H NMR and GPC were used to characterize the resultant product.

When the PDMAEMA₁₁₃-DBT was used as Macro-RAFT agent, the polymerization procedure is as follows. PDMAEMA₁₁₃-DBT (18 mg, 10^{-3} mmol), St (2.08 g, 20 mmol), AIBN (0.033 mg, 2× 10⁻⁴ mmol) and methanol (1.4 g) were added in a glass tube with a magnetic bar, and then the system was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then the sealed tube was placed in an oil bath at 80 °C while stirring. After 36 h of polymerization, the reaction mixture was cooled to room

temperature, and the product was treated with the same procedure mentioned above. TEM, ¹H NMR and GPC were used to characterize the resultant product.

When the PDMAEMA₁₄₇-DBT was used as Macro-RAFT agent, the polymerization procedure is as follows. PDMAEMA₁₄₇-DBT (19 mg, 8×10^{-4} mmol), St (2.08 g, 20 mmol), AIBN (0.026 mg, 1.6×10^{-3} mmol) and methanol (1.2 g) were added in a glass tube with a magnetic bar, and then the system was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then the sealed tube was placed in an oil bath at 80 °C while stirring. After 60 h of polymerization, the reaction mixture was cooled to room temperature, and the product was treated with the same procedure mentioned above. TEM, ¹H NMR and GPC were used to characterize the resultant product.

Sample	$D_{\rm PDMAEMA}{}^a$	$M_{\rm n}({\rm NMR})^b$	$M_{\rm n}({\rm GPC})^c$	$M_{\rm w}/M_{\rm n}({\rm GPC})^c$
1	22	3700	1800	1.27
2	36	5900	3600	1.13
3	60	9700	5500	1.16
4	98	15700	9000	1.08
5	113	18000	11400	1.07
6	147	23400	14500	1.19

Table S1. Degrees of polymerization, molecular weights and molecular weightdistributions of the PDMAEMA-DBTs.

^{*a*}D_{PDMAEMA} means degree of polymerization of PDMAEMA; ^{*b*}Calculated according to ¹H NMR data. ^{*c*}The molecular weights and molecular weight distributions of the PDMAEMA-DBTs were obtained by GPC measurements.



Figure S1. TEM images of various polymeric nanowires prepared by RAFT dispersion polymerization of St using PDMAEMA_x-DBTs (x=22, 36, 60, 98, 113 and 147). (A) PDMAEMA₂₂-PS₁₅₀ nanowires; (B) PDMAEMA₃₆-PS₂₅₈ nanowires; (C) PDMAEMA₆₀-PS₆₅₄ nanowires, (D) PDMAEMA₉₈-PS₁₂₅₇ nanowires, (E) PDMAEMA₁₁₃-PS₁₉₃₅ nanowires, (F) PDMAEMA₁₄₇-PS₃₂₈₅ nanowires.



Fig. S2 ¹³C NMR spectra of (A) PDMAEMA₉₈-DBT and (B) PDMAEMA₉₈-PS₁₂₅₇ in CDCl₃.

Sample ^{<i>a</i>}	$S_{BET}/m^2g^{-1}b$	$V_{p}/cm^{3}g^{-1}c$	$S_{mp}/m^2g^{-1}d$	V _{mp} /cm ³ g ⁻¹ ^e
1	120.8	0.52	88.8	0.042
2	306.2	0.63	131.3	0.059
3	431.6	1.20	223.4	0.102
4	401.0	0.82	109.7	0.049
5	270.3	0.73	128.2	0.061
6	265.1	0.99	145.1	0.066

 Table S2. Mesopore parameters of the silica nanotubes

^{*a*} Sample 1-6 represent the silica nanotubes fabricated from the polymeric nanowires of PDMAEMA₂₂-PS₁₅₀, PDMAEMA₃₆-PS₂₅₈, PDMAEMA₆₀-PS₆₅₄, PDMAEMA₉₈-PS₁₂₅₇, PDMAEMA₁₁₃-PS₁₉₃₅ and PDMAEMA₁₄₇-PS₃₂₈₅ as templates respectively. ^{*b*} Surface area. ^{*c*} Pore volume. ^{*d*} the surface area of micropore. ^{*e*} the micropore volume.