# Electronic Supplementary Information (ESI) for

# RAFT dispersion polymerization induced self-assembly (PISA) of boronic acid-substituted acrylamides

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# Experimental Section

## Materials

2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DMP; TCI, >98%), 2,2′-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044; Wako, 97%), and 2,2′-azobis(2-methylpropionitrile) (AIBN; Sigma Aldrich, 98%) were used as received. Milli-Q water, ethanol (EtOH; VWR, ≥99%), ethyl acetate (EtOAc; VWR, ≥99%), diethyl ether ($Et_2O$; Fisher, >99.5%), dioxane (Fluorochem >99%), anisole (TCI, >99%), and *N*,*N*-dimethylformamide (DMF; VWF, HPLC-grade ≥99.9%) were used directly as solvents. *N,N*-Dimethylacrylamide (DMA; TCI, 98%) was passed through a column of basic alumina (Acros Organics 40 – 300 µm, 60 Å) to remove the inhibitor prior to use.[1] 3-(Acrylamidophenyl)boronic acid (3-BAPhA) was prepared according to the literature,[2] from 3-aminophenylboronic acid (Fluorochem, 97%), acryloyl chloride (Alfa Aesar, 96%), and anhydrous sodium carbonate (Alfa Aesar 99.5%) in 1:1 tetrahydrofuran (THF; Fisher, >99.8%):water. 3-BAPhA (mp 146 - 148 °C, mp[3] 148 °C) was recrystallized twice from hot water and dried under vacuum before use. *N*-[3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]prop-2-enamide (3-BAEPhA) was prepared according to the literature,[4] from 3-acrylamidophenylboronic acid pinacol ester (Fluorochem, 99%), acryloyl chloride, and anhydrous sodium carbonate in $CH_2Cl_2$ (VWR, ≥99.8%, distilled over $CaH_2$, Alfa Aesar, 90-95%). 3-BAEPhA (mp = 166 – 168 °C) was recrystallized twice from EtOAc and dried under vacuum before use. 3-BAPhA and 3-BAEPhA were prepared in high purity, as indicated by the $^1H$ NMR spectra in $D_6$-DMSO (Goss Scientific, 99.9%) (Fig. S17). $^{13}C$ NMR spectra confirmed the absence of impurities (Fig. S17). Volumetric flasks were used for serial dilutions and to make standardized solutions.

## Instruments and Measurements

**General.** Melting points were measured on a Stuart Scientific melting point apparatus SMP1.

**Nuclear Magnetic Resonance (NMR) Spectroscopy.** NMR spectra were recorded using a Bruker Avance II 400 MHz spectrometer. The chemical shifts are in ppm relative to tetramethylsilane. $^{13}C$ NMR spectra at 100 MHz are with complete proton decoupling. NMR assignments are supported by distortionless enhancement by polarization transfer (DEPT). Conversion was estimated using $^1H$ NMR spectroscopy by comparing the monomer content at 2 h to the monomer content before polymerization (Fig S18). An accurately weighed amount of anisole (~0.350 g) is dissolved in EtOH (for dispersion polymerizations) or in DMF (for solution polymerizations) (10 mL) to make standardized solution. A polymerization sample (20 µl), external standard (anisole standardized, 20 µl), and $D_6$-DMSO (460 µl) are mixed in the NMR tube for conversion analysis. Conversion is calculated by comparing the anisole peak integral (representing the standardized solution) at 3.75 ppm (OMe, 3H) to the integral for the monomer (*cis*-vinyl, 1H) at 5.74 (3-BAPhA) or 5.76 (3-BAEPhA) ppm (Fig. S18).

**Gel Permeation Chromatography (GPC).** Molar mass distributions were measured using Agilent Technologies 1260 Infinity liquid chromatography system with Agilent GPC/SEC Software for Windows (version 1.2; Build 3182.29519) using a Polar Gel-M guard column (50 × 7.5 mm) and two Polar Gel-M columns (300 × 7.5 mm). DMF containing LiBr (0.01 $\text{molL}^{-1}$) was used as eluent at 1.0 $\text{mL}\cdot\text{min}^{-1}$ at 60 °C. Twelve narrow polydispersity poly(styrene, St) standards (Agilent, 580-301,600 $\text{gmol}^{-1}$, $Đ$ = 1.05) were used to calibrate the GPC system. Samples were dissolved in the eluent and filtered through a PTFE membrane with 0.22 µm pore size before injection (100 µL). Number average molecular weight ($M_n$) values are not absolute, but relative to linear poly(St) standards (as above).

Poly(3-BAPhA) could not be directly characterised by GPC because of its limited solubility and high affinity for the GPC stationary phase.[5]

**Preparation of GPC sample.** Molecular sieves (MS, Alfa Aesar, 3 Å, 0.800 g) were activated three times by microwave (Toshiba ER-7620 650 W) for 2 min periods at medium power, with 30 s swirling aeration intervals.[6] Pinacol (TCI, >98%, 0.148 g, 1.250 mmol) in $CHCl_3$ (Fisher, >99.8%, 5.00 mL) and the polymerization sample (20 µl) were added to the activated MS, and stirred for 24 h, at room temperature. MS were removed using gravity filtration, and the solution evaporated to a residue, which was dissolved in 1 mL of the GPC eluent.

**Transmission Electron Microscopy (TEM).** Micrographs were obtained at an accelerating voltage of 100 keV (JEOL-1400). Neat samples were deposited onto carbon-coated copper grids (Ted Pella, Redding CA). Excess solvent was drained using filter paper. The samples were subsequently stained with uranyl acetate for 2 min at room temperature. Images were recorded digitally using a Phurona CCD Camera (Emsis) and radius imaging software (Emsis).

## Polymerizations

### General procedure.

All polymerization solutions were added to borosilicate glass tubes sealed with septa and flushed with $N_2$ for 30 min. The solutions were heated at 70 °C in an aluminum-heating block for 2 h with stirring using a magnetic stirrer bar. Polymerizations were stopped by placing glass tubes in an ice-water bath.

**Preparation of poly(3-BAPhA) homopolymer for solubility studies.**

The initiator serial dilution used VA-044 (39 mg, 0.12 mmol) diluted 100 times with 20% aq. DMF. 3-BAPhA (0.573 g, 3.000 mmol), DMP (21.86 mg, 0.060 mmol), and VA-044 ($1.19 \times 10^{-3}$ $molL^{-1}$ from serial dilution) in 20% aq. DMF (1.00 mL) were heated at 70 °C for 2 h. The polymer was precipitated in $Et_2O$, filtered, and dried at room temperature under vacuum for 24 h to give poly(3-BAPhA), $M_n$ = 9,400 $g.mol^{-1}$, $Đ$ = 1.16 (after pinacol protection), Isolated = 0.395 g, Yield = 66% (Fig. S19(a)).

**Preparation of poly(3-BAEPhA) homopolymer for solubility studies.**

The initiator serial dilution used AIBN (61 mg, 0.37 mmol) diluted 250 times with DMF. 3-BAEPhA (0.683 g, 2.497 mmol), DMP (17.87 mg, 0.049 mmol), and AIBN ($1.48 \times 10^{-3}$ $molL^{-1}$ from serial dilution) in DMF (1.00 mL) were heated at 70 °C for 2 h. The polymer was precipitated in $Et_2O$, filtered, and dried at room temperature under vacuum for 24 h to give poly(3-BAEPhA), $M_n$ = 8,700 $g.mol^{-1}$, $Đ$ = 1.31, Isolated = 0.264 g, Yield = 38% (Fig. S19(b)).

**Solution homopolymerizations of 3-BAPhA.**

The serial dilution used AIBN (61 mg, 0.37 mmol) dissolved in 5% aq. DMF (25 mL), from which 1 mL is taken and added to DMP (37 mg, 0.1 mmol) to make a 5% aq. DMF solution (10 mL). A solution polymerization of 3-BAPhA (0.191 g, 1.00 mmol), DMP (0.01 $molL^{-1}$ from serial dilution), AIBN ($1.48 \times 10^{-3}$ $molL^{-1}$ from serial dilution) in 5% aq. DMF (1.00 mL) was heated at 70 °C for specific times (Fig. S6). Conversion was determined by $^1H$ NMR and GPC required pinacol protection, as described above.

**Solution homopolymerizations of 3-BAEPhA.**

The serial dilution used AIBN (61 mg, 0.37 mmol) dissolved in DMF (25 mL), from which 1 mL is taken and added to DMP (37 mg, 0.1 mmol) to make a DMF solution (10 mL). A solution polymerization of 3-BAEPhA (0.273 g, 1.00 mmol), DMP (0.01 $molL^{-1}$ from serial dilution), AIBN ($1.48 \times 10^{-3}$ $molL^{-1}$ from serial dilution) in DMF (1.00 mL) were heated at 70 °C for specific times (Fig. S6). Conversion was determined by $^1H$ NMR and GPC are as described above.

**Preparation of Poly(DMA) stabilizers.**

**General procedure: poly(DMA)$_{28}$.**

The initiator serial dilution used VA-044 (36 mg, 0.11 mmol) diluted 250 times with 20% aq. dioxane. DMP (0.163 g, 0.45 mmol), DMA (2.212 g, 22.32 mmol) and VA-044 ($4.50 \times 10^{-4}$ $molL^{-1}$ from serial dilution) in 20% aq. dioxane (5 mL) were heated at 70 °C for 2 h. The polymer was precipitated in $Et_2O$, filtered, and dried at room temperature under vacuum for 24 h to give poly(DMA)$_{28}$ macroRAFT, $M_n$ = 3,100 g.mol$^{-1}$, $Đ$ = 1.12, isolated = 1.951 g, Yield = 82%.

**Poly(DMA)$_{36}$** was prepared as above using DMP (0.163 g, 0.45 mmol), DMA (2.212 g, 22.32 mmol) and VA-044 ($4.50 \times 10^{-4}$ $molL^{-1}$ from serial dilution) in 20% aq. dioxane (5.00 mL): $M_n$ = 3,900 g.mol$^{-1}$, $Đ$ = 1.10, isolated = 2.114 g, Yield = 89%.

**Poly(DMA)$_{39}$** was prepared as above using DMP (0.163 g, 0.45 mmol), DMA (2.212 g, 22.32 mmol) and VA-044 ($4.50 \times 10^{-4}$ $molL^{-1}$ from serial dilution) in 20% aq. dioxane (5.00 mL): $M_n$ = 4,200 g.mol$^{-1}$, $Đ$ = 1.10, isolated = 2.004 g, Yield = 84%.

**Preparation of poly(DMA)$_{96}$.**

The initiator serial dilution used VA-044 (25 mg, 0.08 mmol) diluted 250 times with 20% aq. dioxane. Poly(DMA)$_{39}$ (1.284 g, 0.30 mmol), DMA (1.501 g, 15.14 mmol) and VA-044 ($3.20 \times 10^{-4}$ $molL^{-1}$ from serial dilution) in 20% aq. dioxane (5.00 mL) were heated at 70 °C for 2 h. The polymer was precipitated in $Et_2O$, filtered, and dried at room temperature under vacuum for 24 h to give poly(DMA)$_{96}$ macroRAFT, $M_n$ = 9,900 g.mol$^{-1}$, $Đ$ = 1.17, isolated = 2.088 g, Yield = 75% (Fig. S10).

**Attempted preparation of the longer stabilizer block by single RAFT polymerization.**

The initiator serial dilution used VA-044 (45 mg, 0.14 mmol) diluted 625 times with 20% aq. dioxane. DMP (81.5 mg, 0.22 mmol), DMA (2.212 g, 22.32 mmol) and VA-044 ($2.23 \times 10^{-4}$ $molL^{-1}$ from serial dilution) in 20% aq. dioxane (5 mL) were heated at 70 °C for 2 h. $M_n$ = 6,800 g.mol$^{-1}$, $Đ$ = 1.15; Conv. = 72% (measured by NMR, see above) (Fig S11).

**Representative RAFT dispersion polymerizations.**

**For 3-BAPhA.** The initiator serial dilution used VA-044 (42 mg, 0.13 mmol) diluted 250 times with 3:1 Water/EtOH. 3-BAPhA (0.400 g, 2.094 mmol), poly(DMA)$_{96}$ (0.416 g, 0.042 mmol), and VA-044 ($5.20 \times 10^{-4}$ $molL^{-1}$ from serial dilution) in 3:1 Water/EtOH (2.00 mL) were heated at 70 °C, while stirring at 1000 rpm with a magnetic stirrer bar for 2 h. The visual appearance at the end of the polymerizations is in Fig. 2. The upper free-flowing white suspension was separated upon cooling and manipulated as described in Fig 2. Conversion was by $^1H$ NMR and GPC required pinacol protection, as described above.

**For 3-BAEPhA.** The initiator serial dilution used VA-044 (24 mg, 0.07 mmol) diluted 250 times with 1:2 Water/EtOH. 3-BAEPhA (0.400 g, 1.464 mmol), poly(DMA)$_{96}$ (0.291 g, 0.029 mmol), and VA-044 ($2.80 \times 10^{-4}$ molL$^{-1}$ from serial dilution) in 1:2 Water/EtOH (2.00 mL) were heated at 70 °C, while stirring at 1000 rpm with a magnetic stirrer bar for 2 h. The visual appearance at the end of the polymerizations is in Fig. 3. Conversion was by $^{1}$H NMR and GPC are as described above.

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5. J K. T. Kim, J. L. M. Cornelissen, R. J. M. Nolte and J. C. M. van Hest, *J. Am. Chem. Soc.*, 2009, **131**, 13908-13909.
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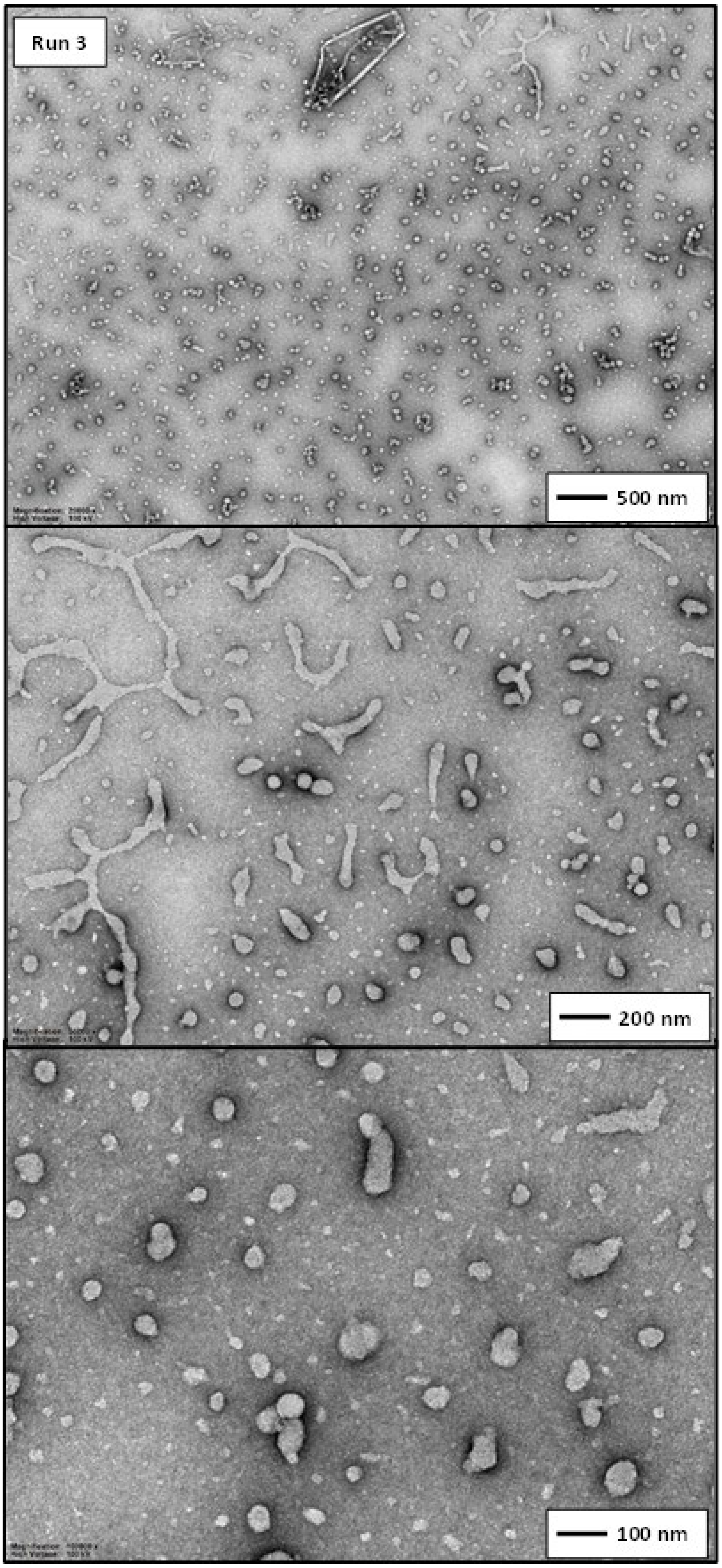
**Fig. S1** Additional TEM images for the dispersion polymerization in Fig. 1 (Run 3).



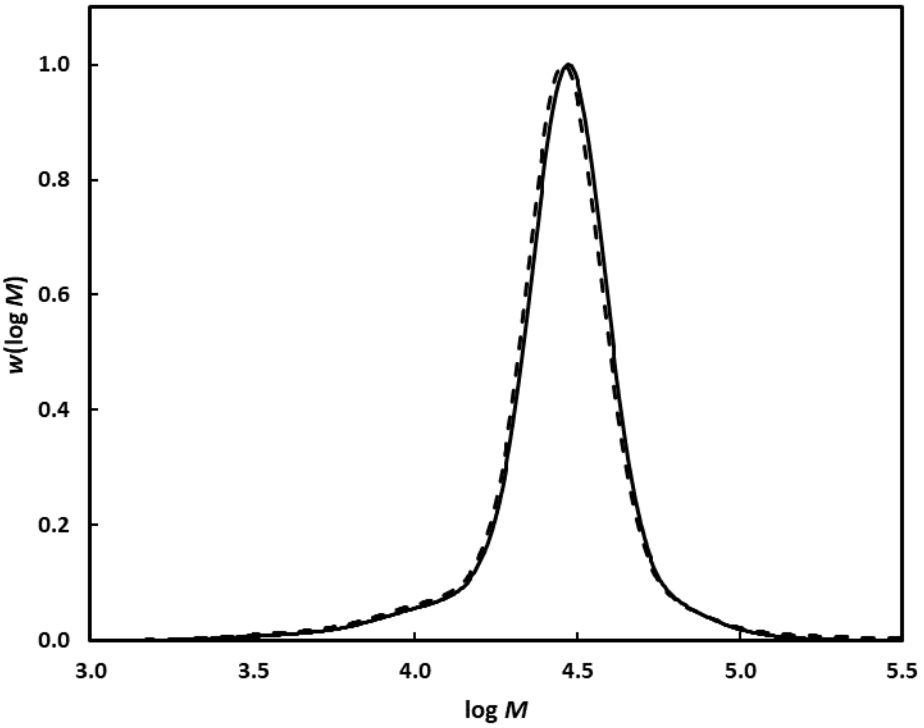


**Fig. S2** MWDs (using GPC) of the separate layers for the dispersion polymerization in Fig. 2, with the lower boroxine layer dashed (Run 4). $M_\text{n}$ = 24,500 gmol$^{-1}$, $Đ$ = 1.27 (continuous) and $M_\text{n}$ = 23,400 gmol$^{-1}$, $Đ$ = 1.37 (dashed).

**Fig. S3** Additional TEM images for the dispersion polymerization in Fig. 2 (Run 4).

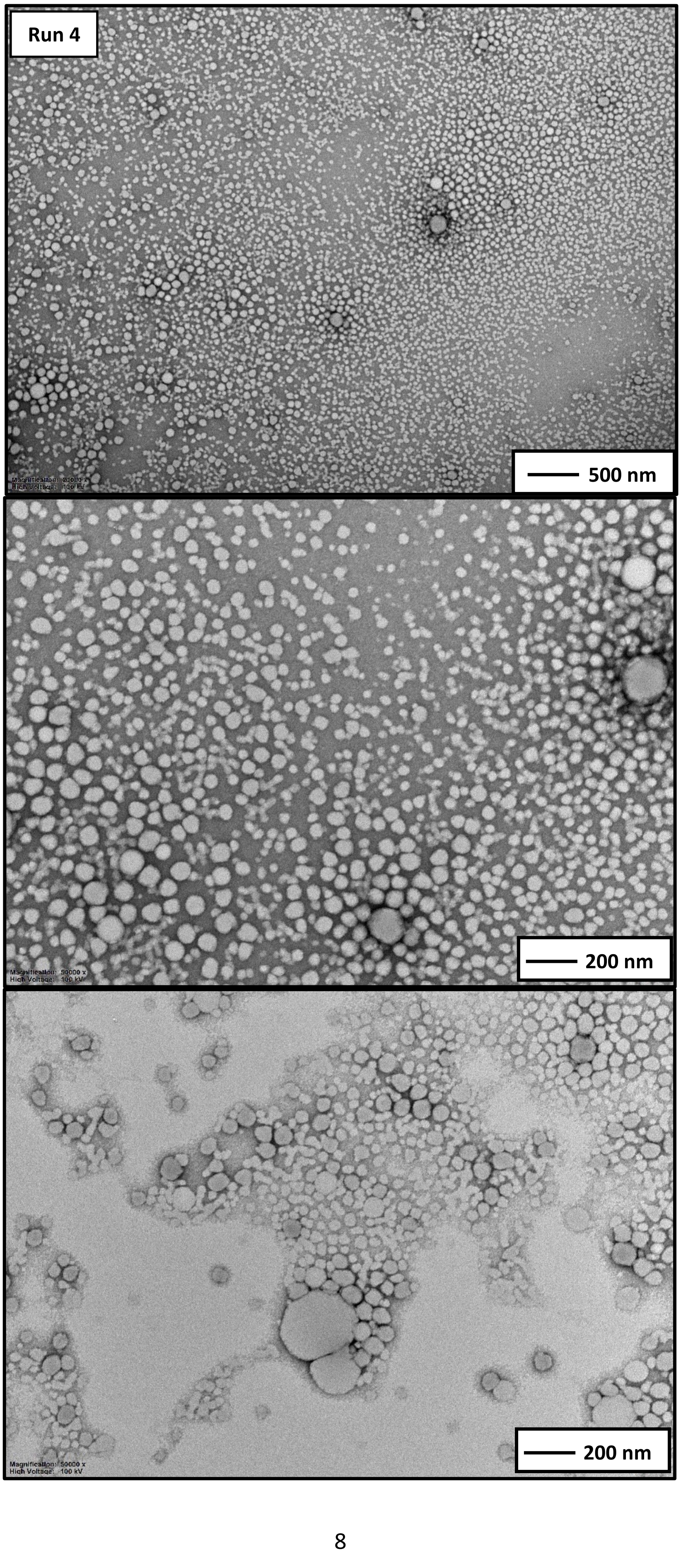


**Fig. S4** Additional TEM images for the room temperature 100-fold dilution (TEM after 24 h) in Fig. 2 (Run 4).

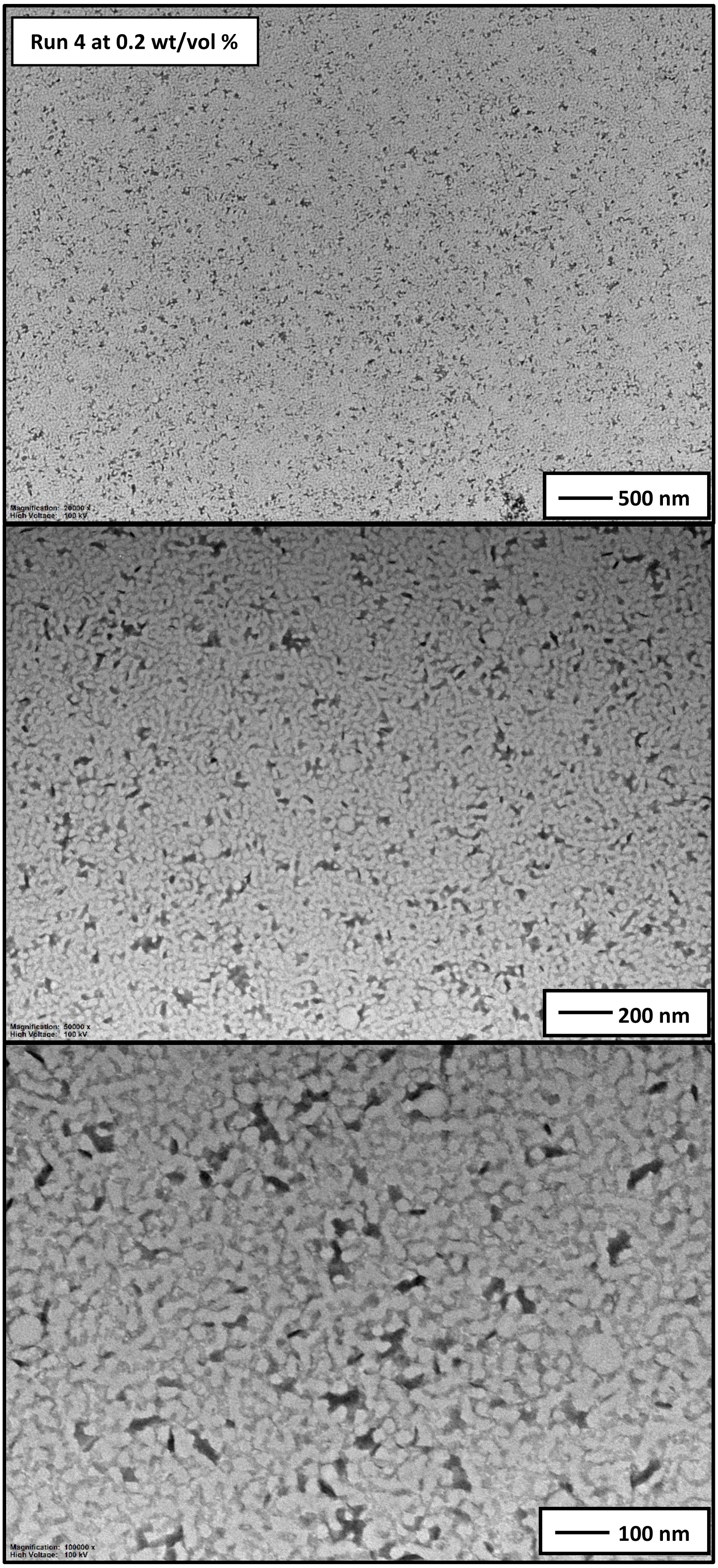
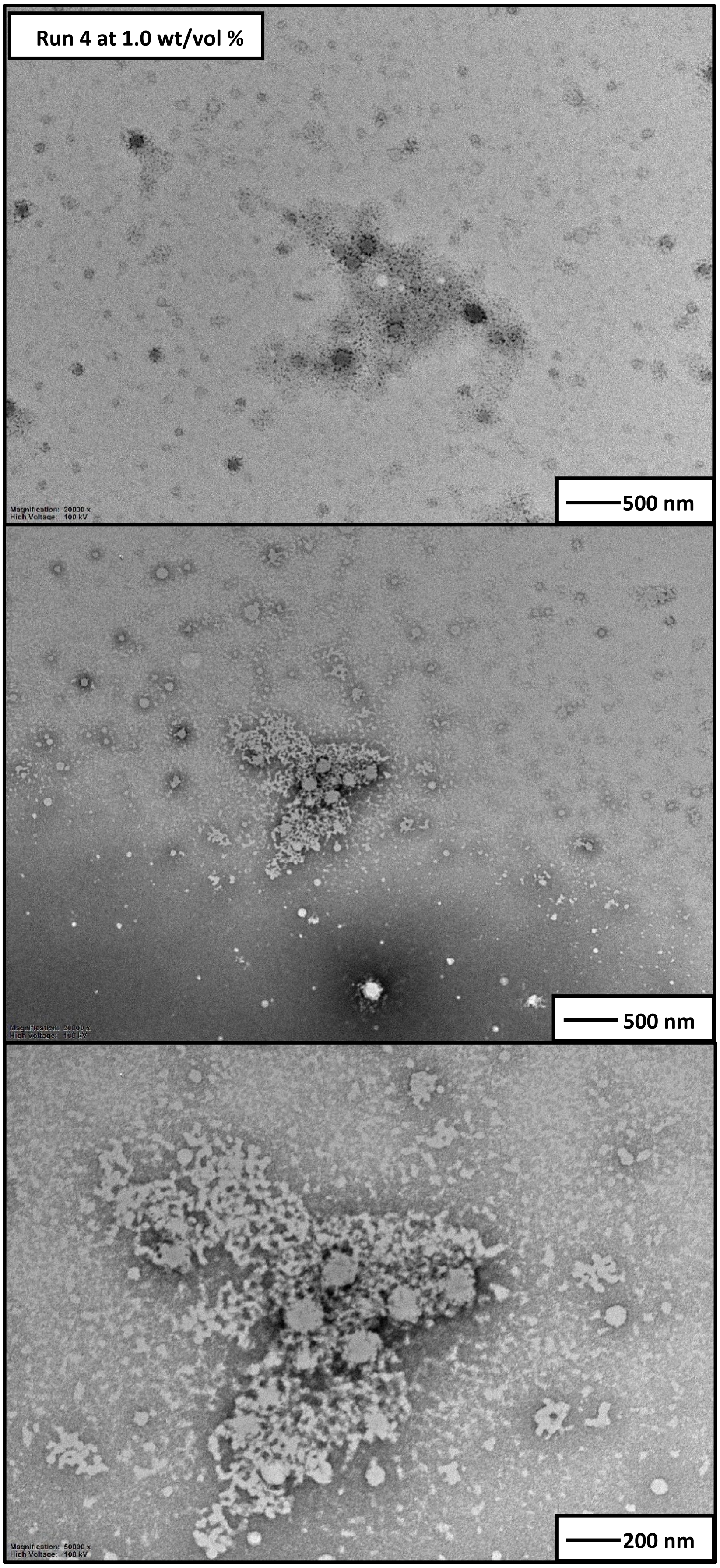


**Fig. S5** TEM images for the room temperature 20-fold dilution of the upper dispersion layer (TEM after 24 h) in Fig. 2 (Run 4).



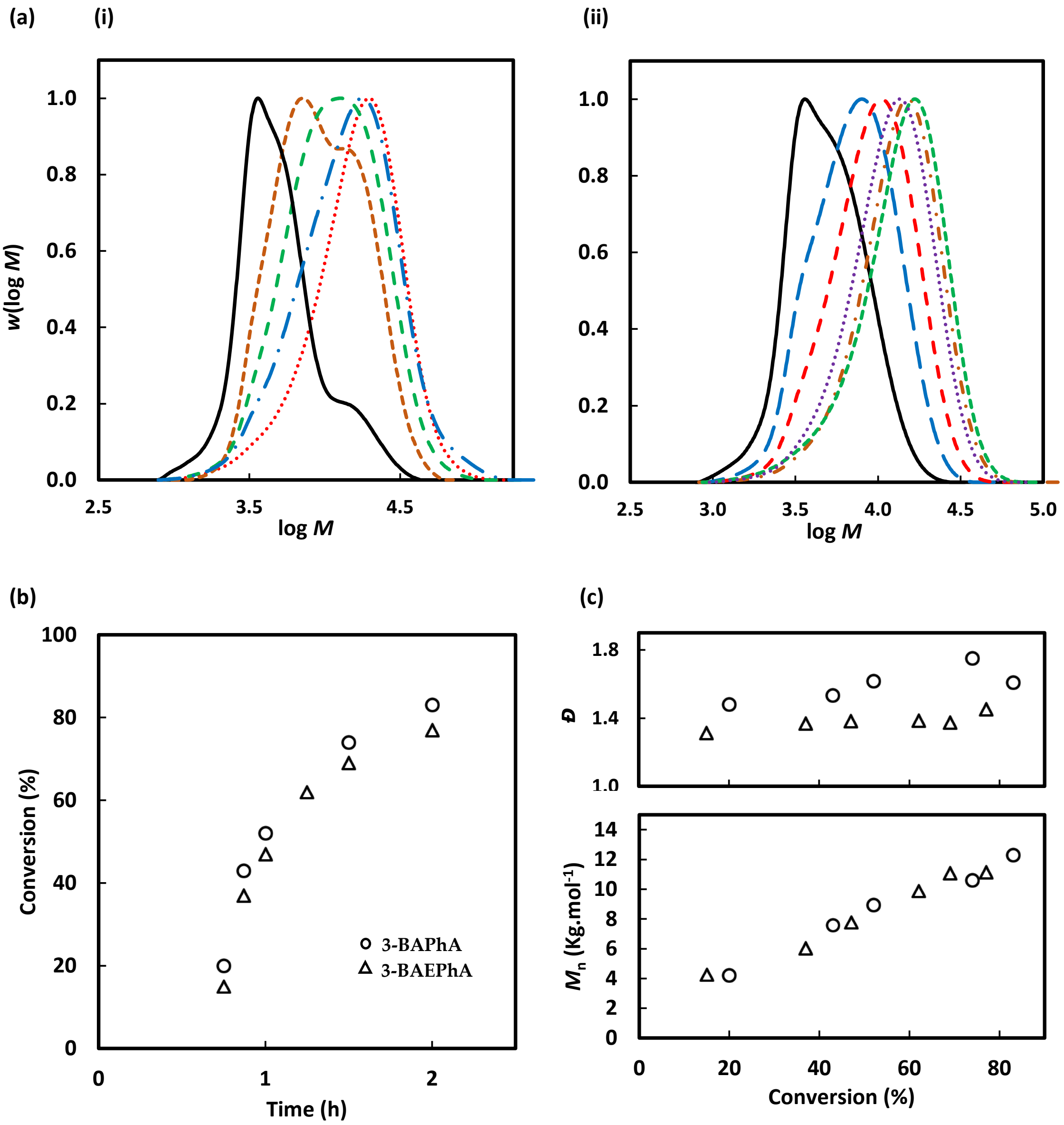


**Fig. S6** RAFT-mediated homogeneous polymerizations at 70 °C of 3-BAPhA and 3-BAEPhA (1 M) in 5% aqueous DMF and DMF, respectively, using [Monomer]$_0$/[DMP]$_0$/[AIBN]$_0$ = 101/1 /0.15. **(a)** MWDs correspond to conversions at **(i)** 3-BAPhA: 20% (0.75 h), 43% (0.87 h), 52% (1 h), 74% (1.5 h) and 83% (2 h), and **(ii)** 3-BAEPhA: 15% (0.75 h), 37% (0.87 h), 47% (1 h), 62% (1.25 h), 69% (1.5 h), and 77% (2 h). **(b)** Conversion versus time plot, and **(c)** $M_n$ and $Đ$ (after pinacol protection for 3-BAPhA) vs. conversion. Note that points represent individual experiments at different times (not sampling of polymerizations).

**Fig. S7** Additional TEM images for the dispersion polymerization in Fig. 3 (Run 5).

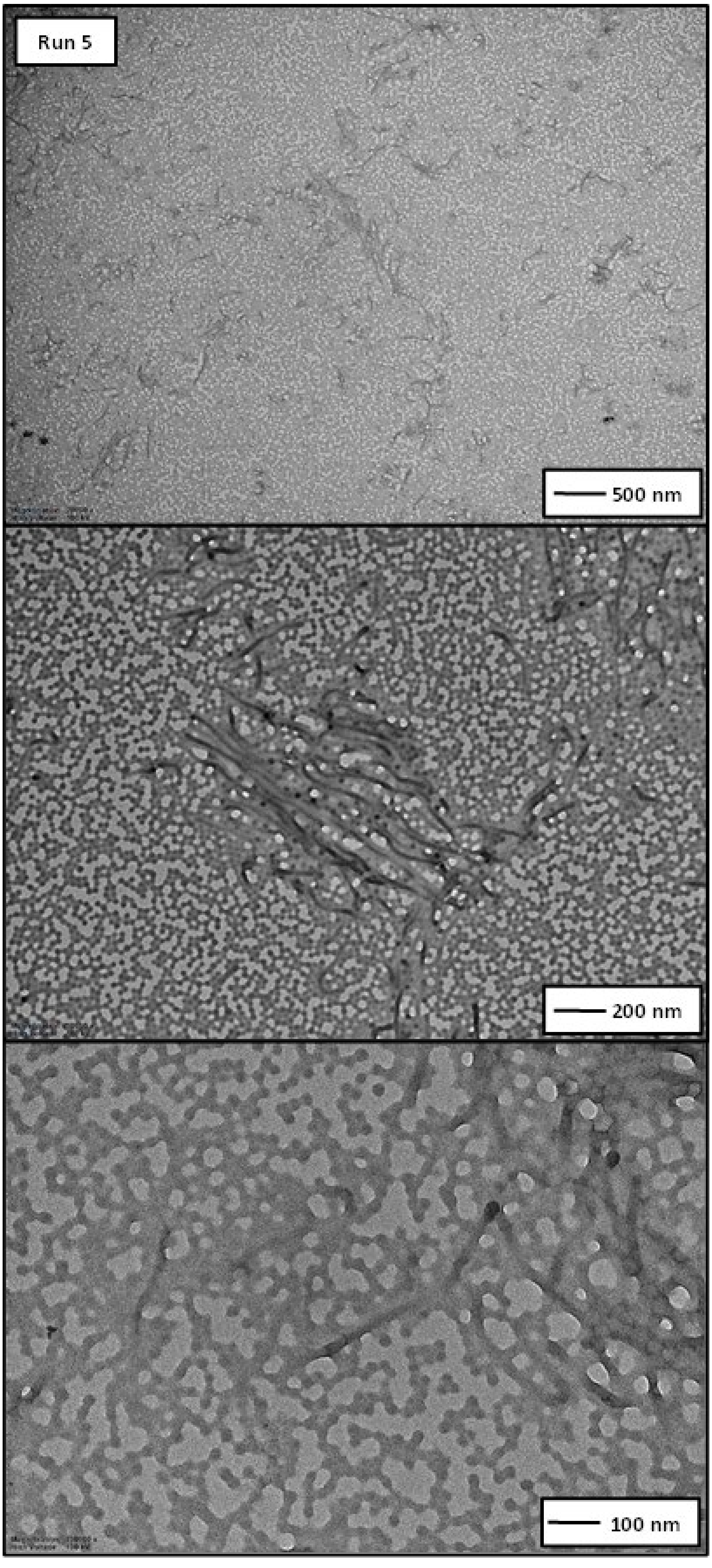


**Fig. S8** Additional TEM images for the dispersion polymerization in Fig. 3 (Run 6).

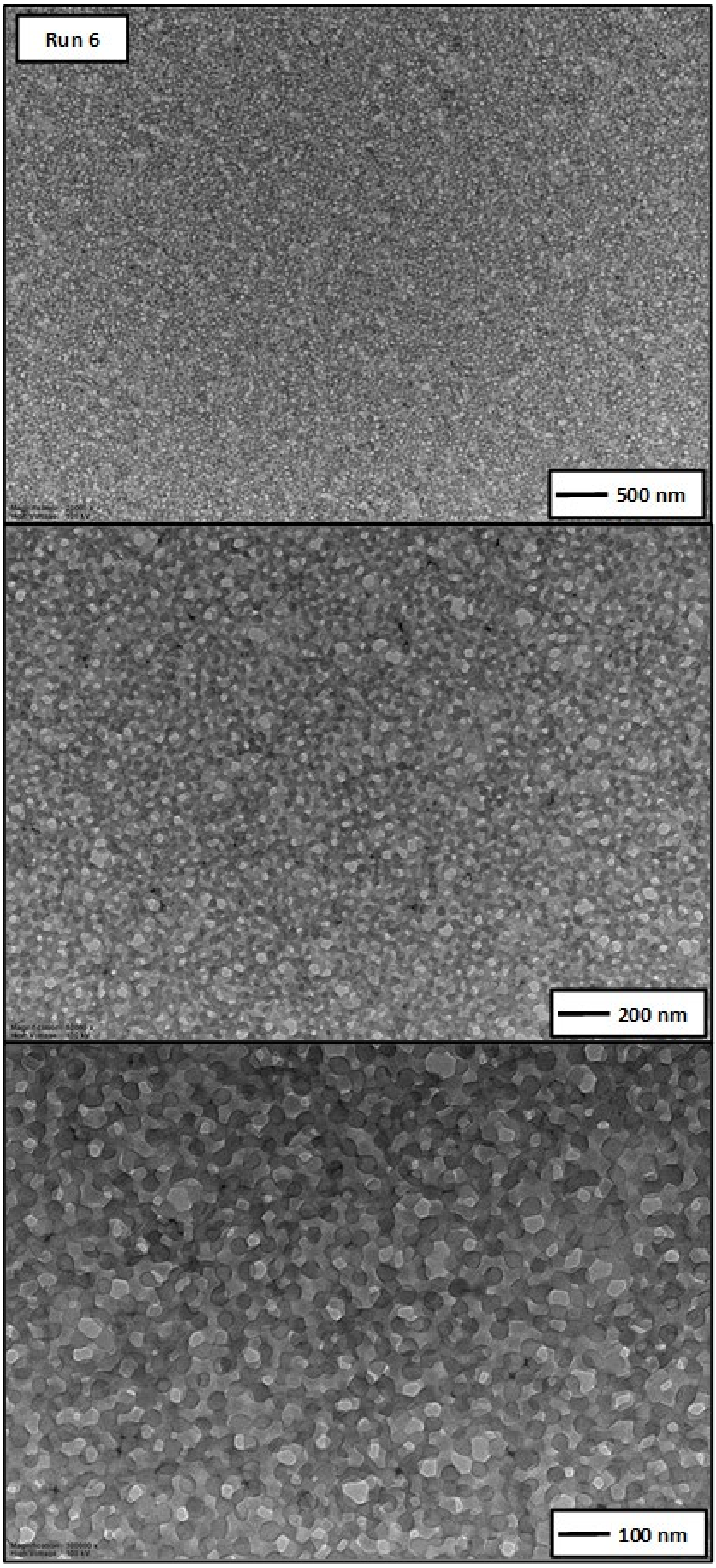
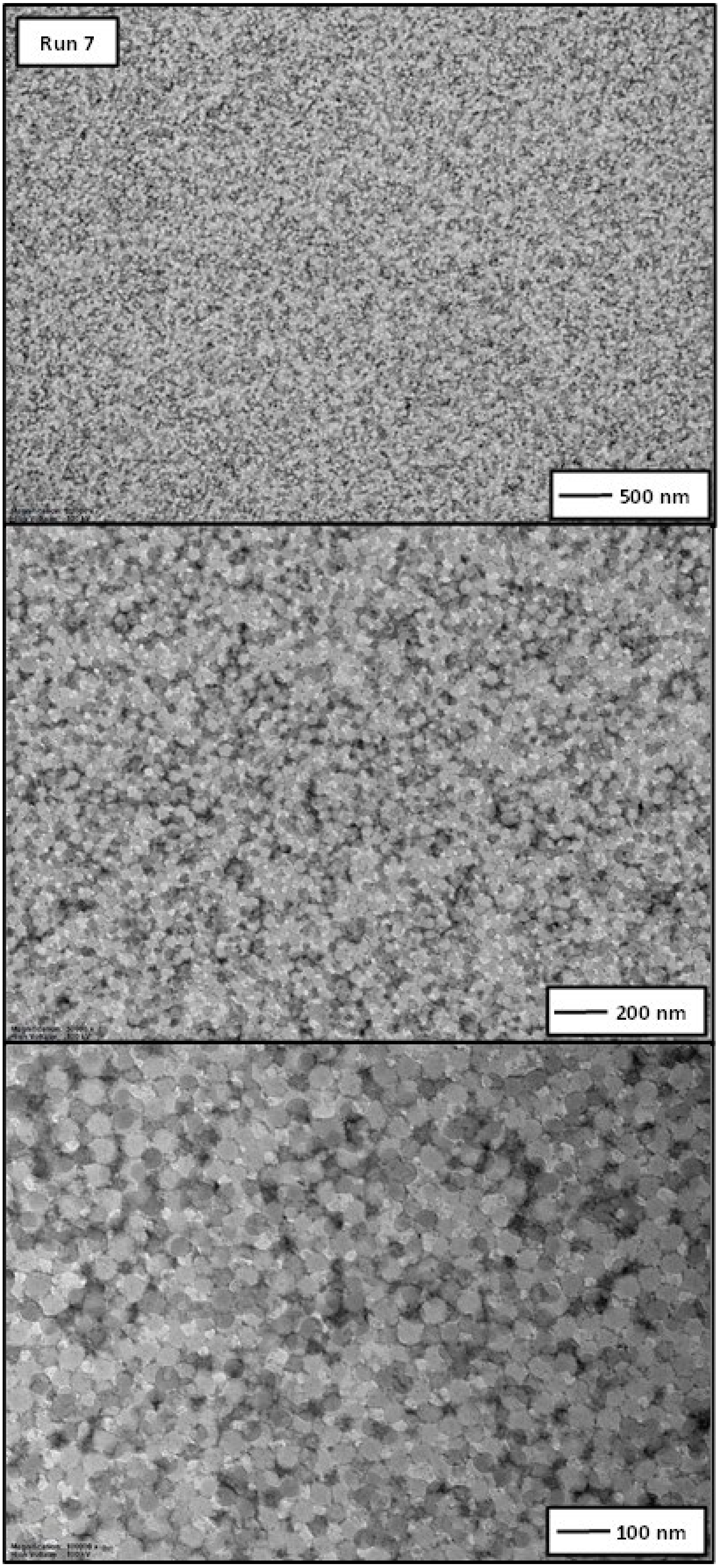


**Fig. S9** Additional TEM images for the dispersion polymerization in Fig. 3 (Run 7).



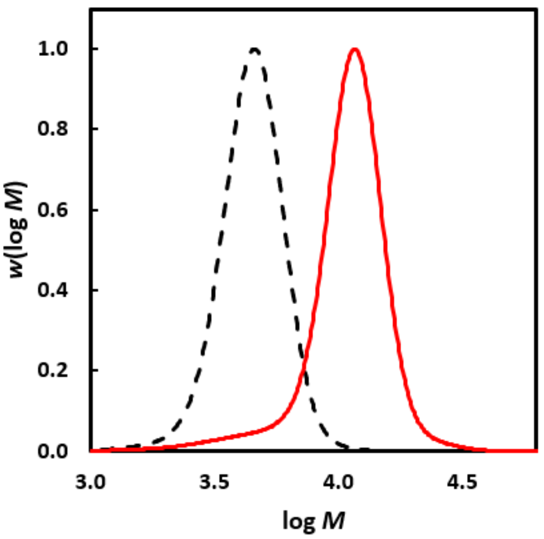


**Fig. S10** MWDs (from GPC) for the preparation of poly(DMA)$_{96}$ (solid red line) by chain extension of poly(DMA)$_{39}$ with DMA in 20% aq. dioxane at 70 °C. $M_n$ = 4,200 gmol$^{-1}$, $Đ$ = 1.11 (dashed) and $M_n$ = 9,900 gmol$^{-1}$, $Đ$ = 1.17 (continuous red).

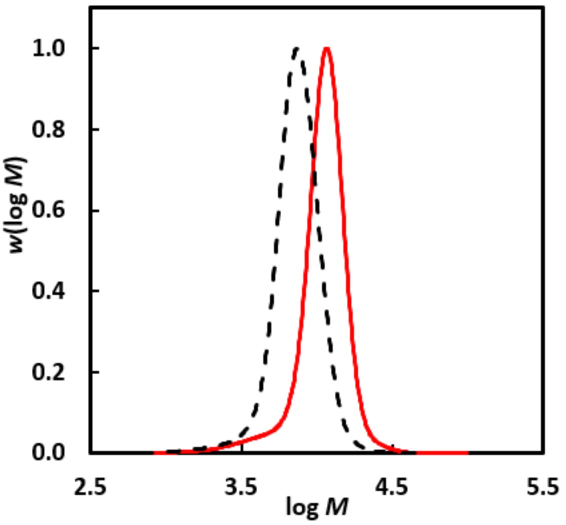


**Fig. S11** MWDs (from GPC) of poly(DMA)$_{96}$ ($M_n$ = 9,900 gmol$^{-1}$, $Đ$ = 1.17 , red line) prepared by chain extension of poly(DMA)$_{39}$ with [DMA]$_0$/[RAFT]$_0$ = 50, compared to poly(DMA) prepared under the same conditions (see Experimental), but using one RAFT polymerization of DMA, where [DMA]$_0$/[DMP]$_0$ = 100 ($M_n$ = 6,800 gmol$^{-1}$, $Đ$ = 1.15, dashed line).

**Fig. S12** Additional TEM images for the dispersion polymerization in Fig. 4 (Run 8).

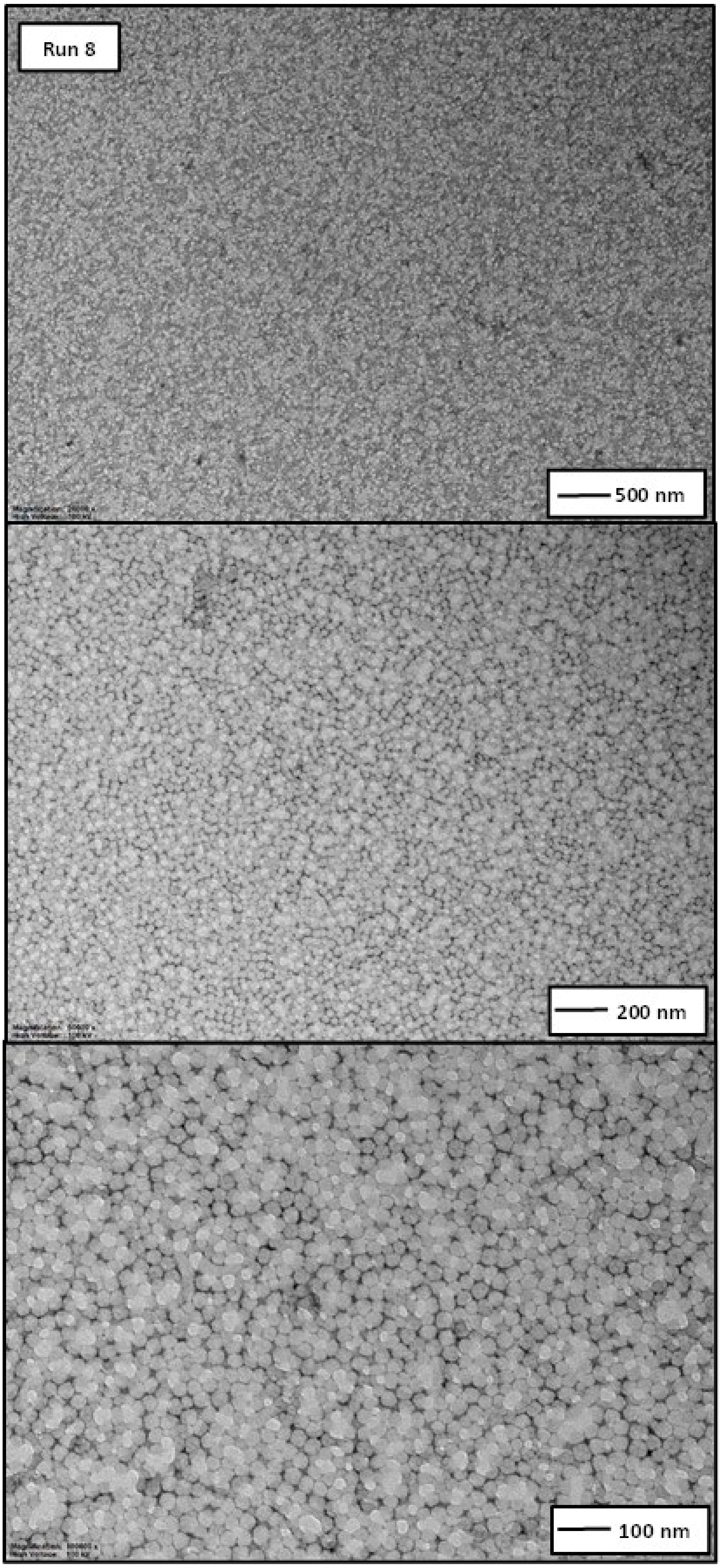


**Fig. S13** Additional TEM images for the dispersion polymerization in Fig. 4 (Run 9).

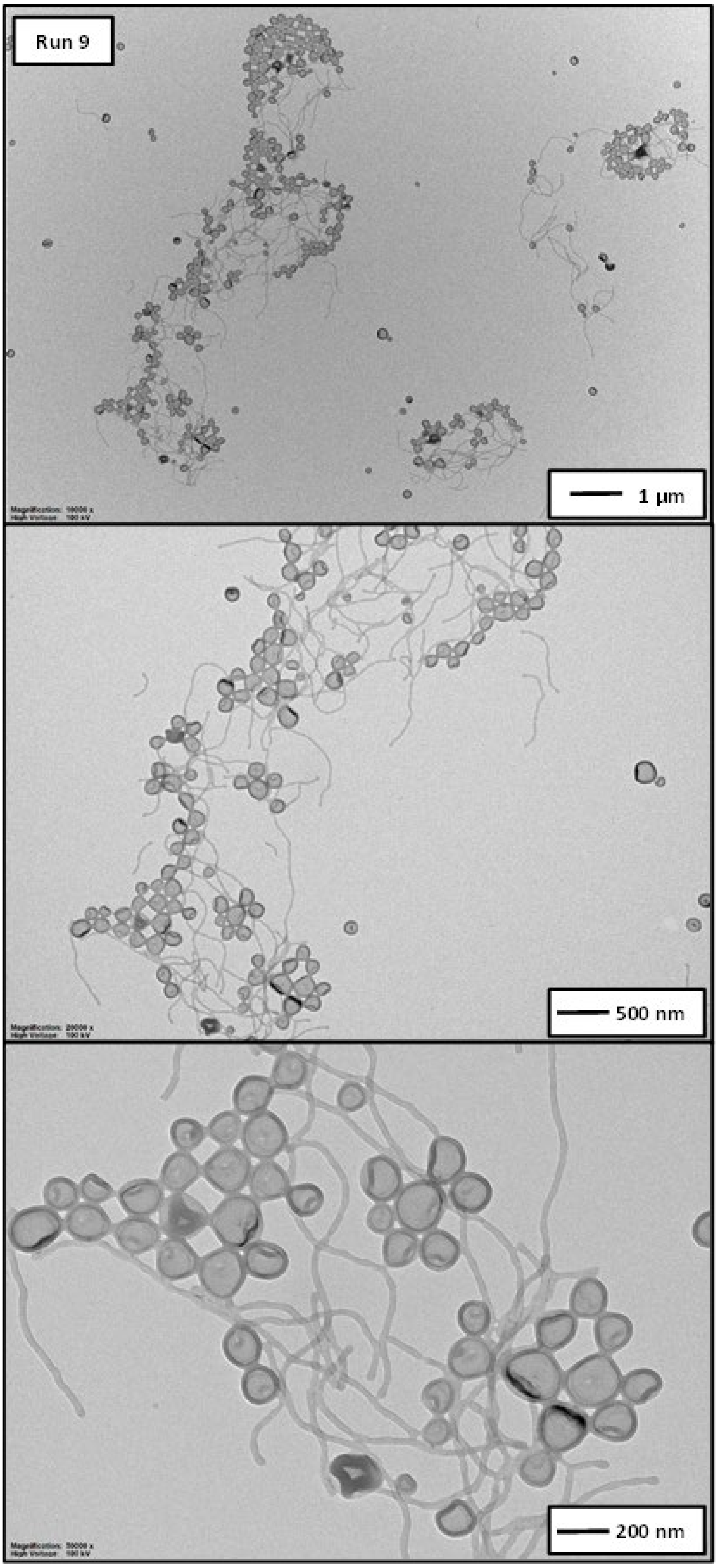


**Fig. S14** Additional TEM images for the dispersion polymerization in Fig. 4 (Run 10).

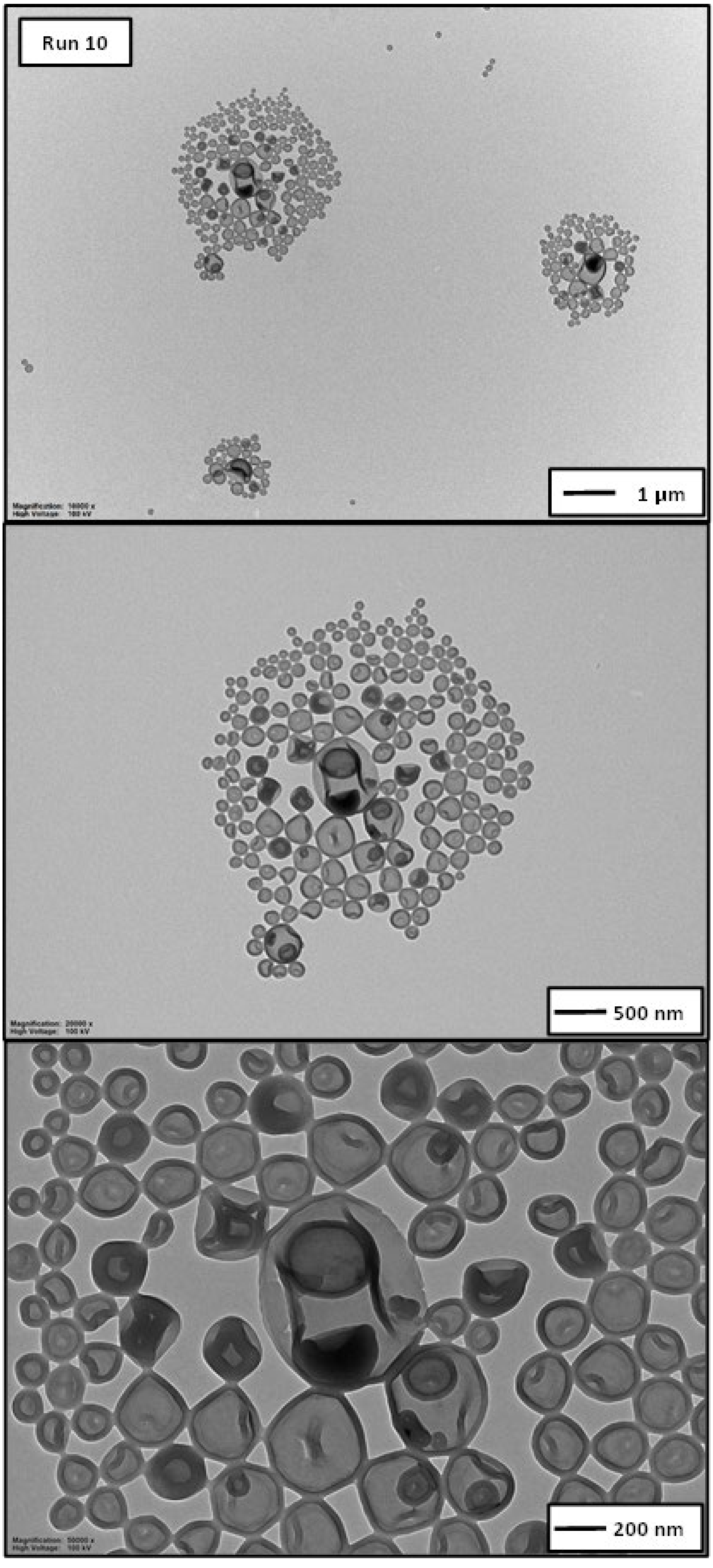
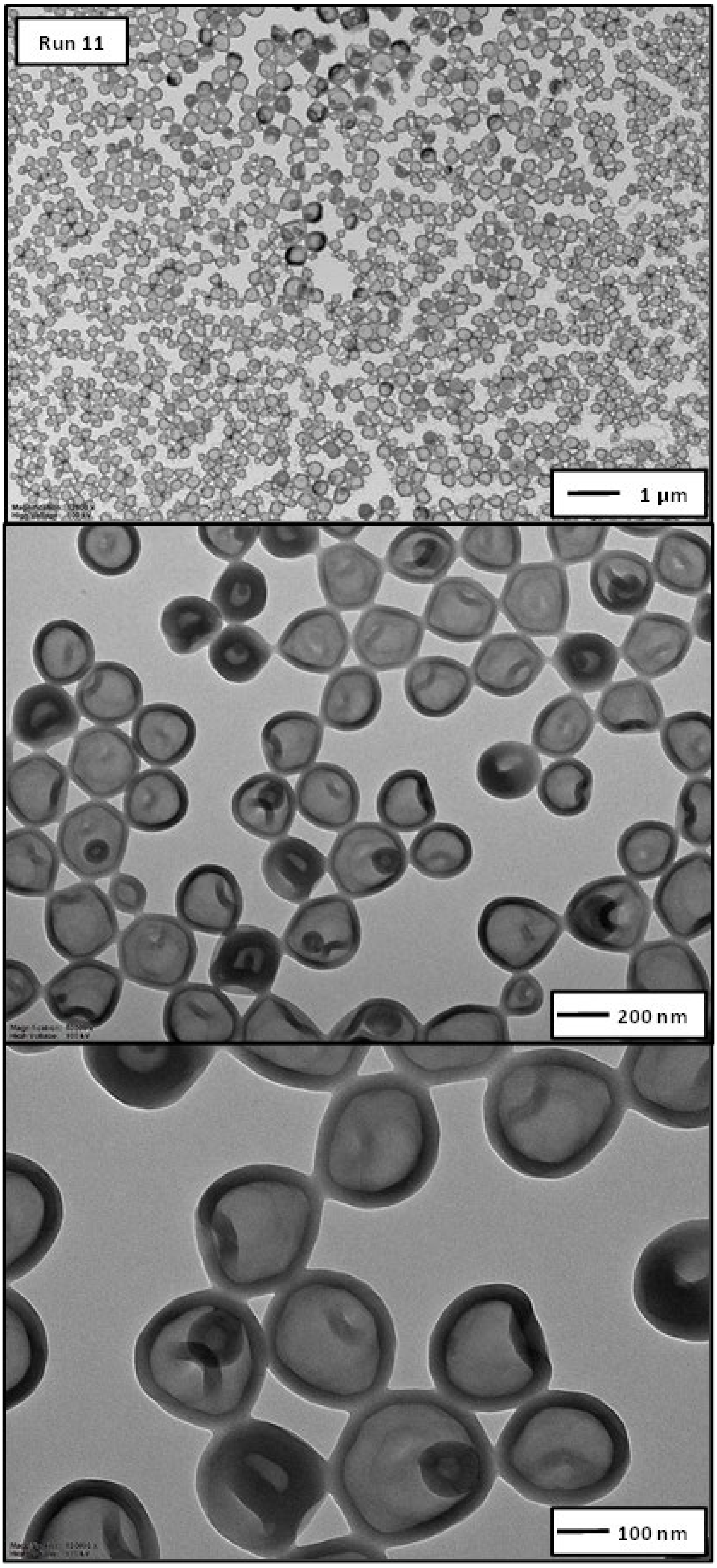


**Fig. S15** Additional TEM images for the dispersion polymerization in Fig. 4 (Run 11).



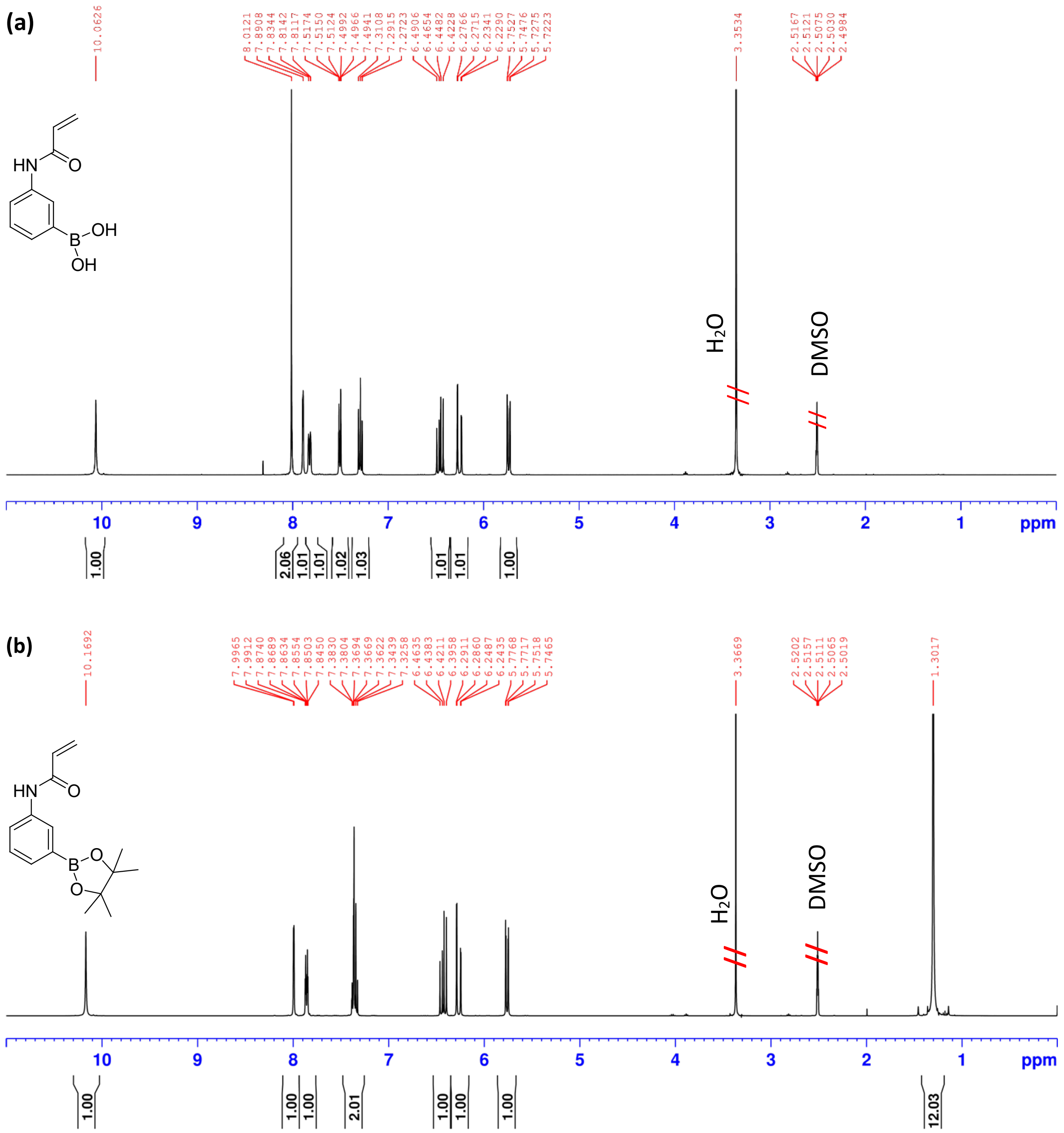


**Fig. S16 (a)** $^1$H NMR spectrum of 3-BAPhA: $\delta_H$ (400 MHz) ($D_6$-DMSO) $\delta$ = 5.74 (dd, J = 10.1, 2.0 Hz, 1H, *cis*-H), 6.25 (dd, *J* = 17.0, 2.0 Hz, 1H, *trans*-H), 6.46 (dd, *J* = 17.0, 10.1 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.49 – 7.52 (m, 1H), 7.81 – 7.83 (m, 1H), 7.89 (s, 1H, 2-H), 8.01 (s, 2H, B-OH), and 10.06 (s, 1H, NH). **(b)** $^1$H NMR spectrum of 3-BAEPhA: $\delta_H$ (400 MHz) ($D_6$-DMSO), 1.30 (s, 12H), 5.76 (dd, *J* = 10.0, 2.1 Hz, 1H, *cis*-H), 6.27 (dd, *J* = 17.0, 2.1 Hz, 1H, *trans*-H), 6.43 (dd, *J* = 17.0, 10.1 Hz, 1H, *vicinal*-H), 7.33 – 7.38 (m, 2H), 7.85 – 7.87 (m, 1H), 7.80 (d, *J* = 2.1 Hz, 1H, 2-H), and 10.17 (s, 1H, NH).

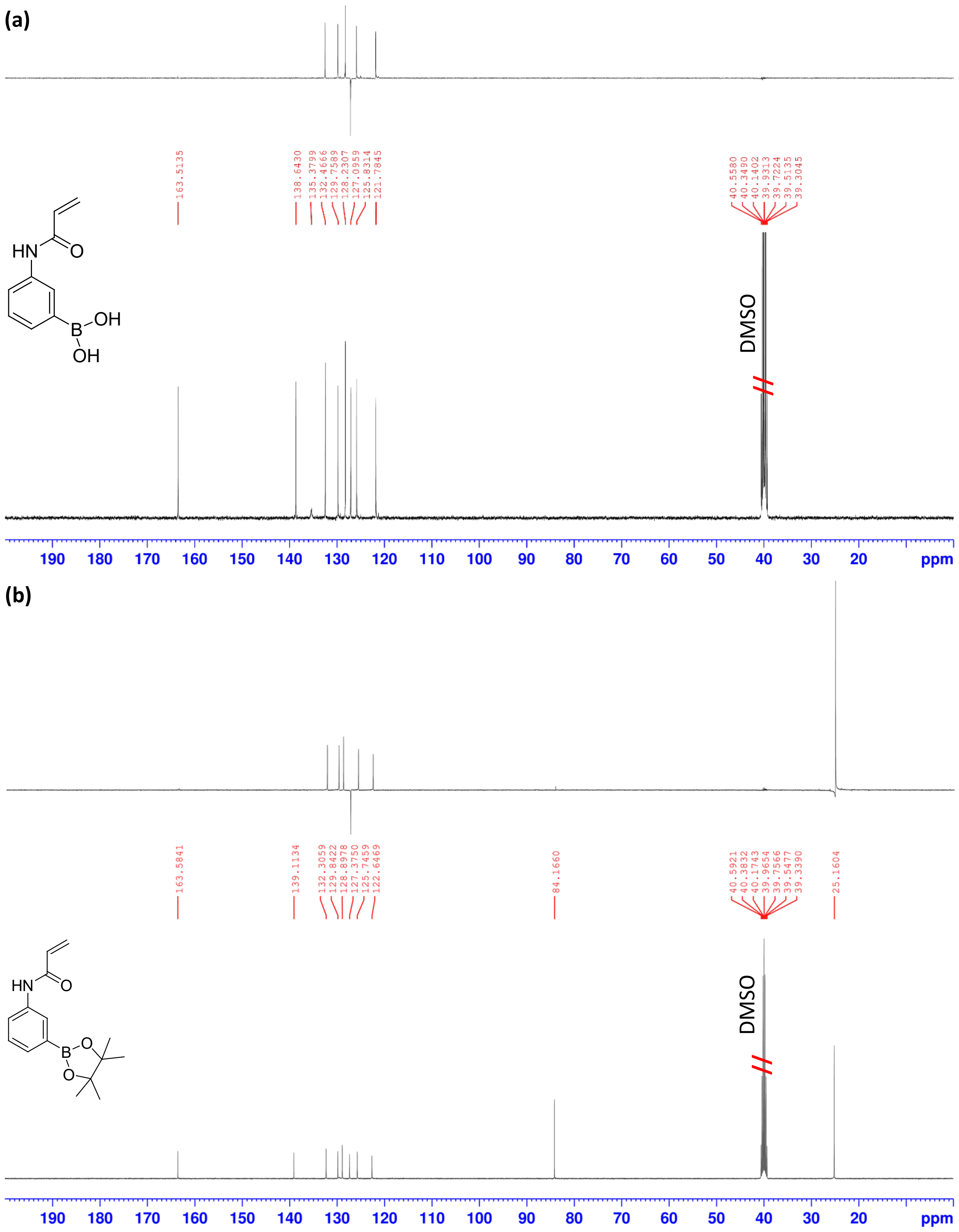
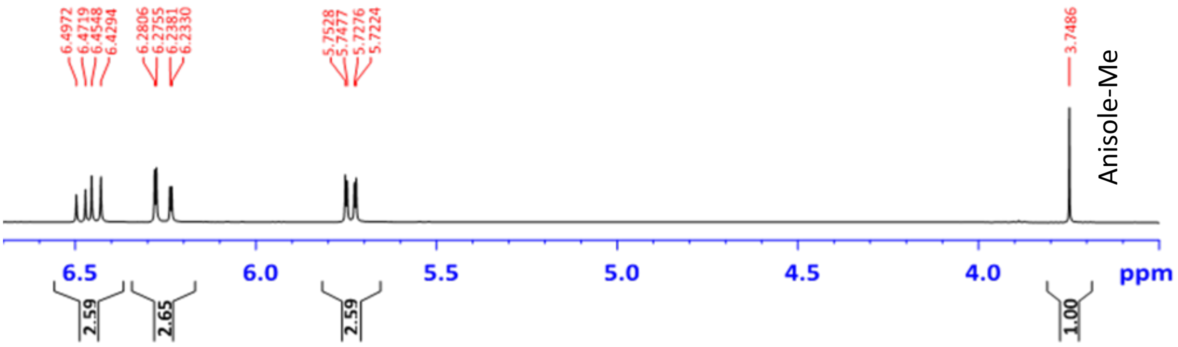


**Fig. S17 (a)** $^{13}$C NMR spectrum of 3-BAPhA: $\delta_C$ (100 MHz) ($D_6$-DMSO), 121.8 (CH), 125.8 (CH), 127.1 ($CH_2$), 128.2 (CH), 129.8 (CH), 132.5 (CH), 135.4 (C), 138.6 (C), and 163.5 (C=O). **(b)** $^{13}$C NMR spectrum of 3-BAEPhA: $\delta_C$ (100 MHz) ($D_6$-DMSO), 25.2 ($CH_3$), 84.2 (C), 122.7 (CH), 125.8 (CH), 127.4 ($CH_2$), 128.9 (CH), 129.8 (CH), 132.3 (CH), 139.1 (C), and 163.6 (C=O).

**(a)** t = 0



**(b)** t = 2 h

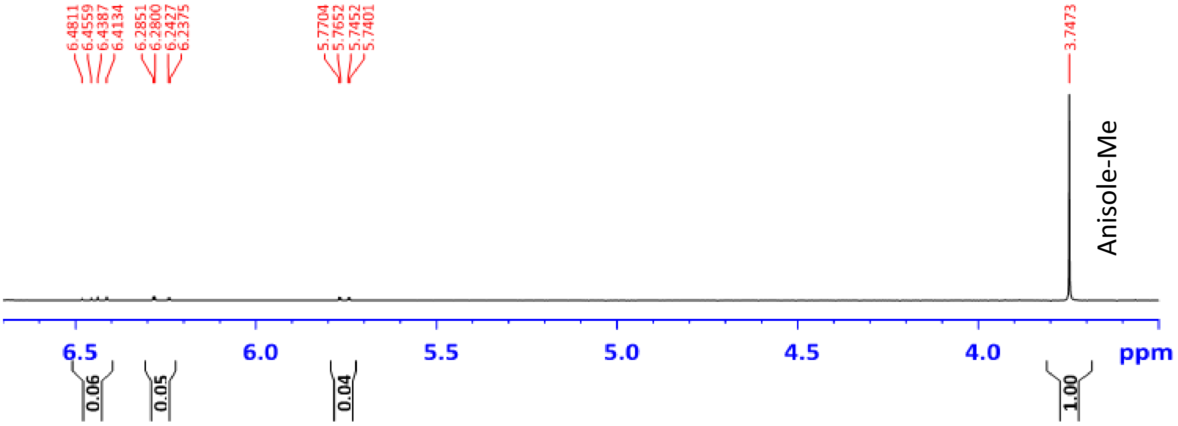


**Fig. S18** Representative conversion measurement: $^1$H NMR of Run 4 **(a)** before and **(b)** after polymerization.

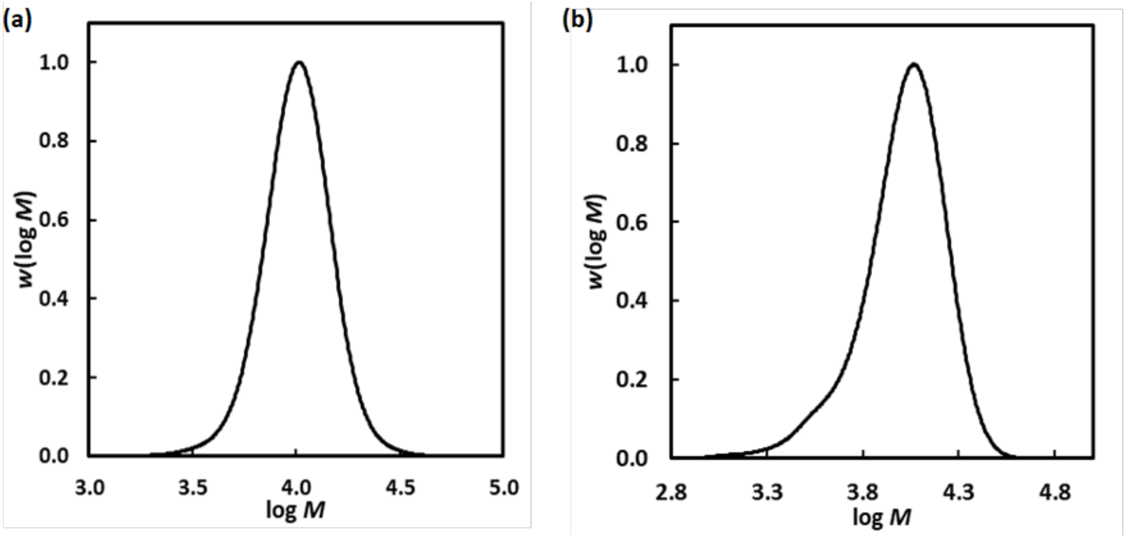


**Fig. S19** GPC of **(a)** poly(3-BAPhA) homopolymer ($M_n$ = 9,400 gmol$^{-1}$, $Đ$ = 1.16) and **(b)** poly(3-BAEPhA) ($M_n$ = 8,700 gmol$^{-1}$, $Đ$ = 1.31) homopolymer for preliminary solubility studies.