

# Supporting Information: Hyperbranched Alternating Block Polymers using Thiol-Yne chemistry: Materials with Tuneable Properties

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## Experimental

### Chemicals

All reagents were used as obtained unless otherwise stated. Prop-2-yl-1-ol, 2,2-dimethoxy-2-phenyl-acetophenone (DMPA), isopropyl amine, (3-dimethylaminopropyl)-ethylcarbodiimide (EDC), 4-(dimethylamino)pyridine (DMAP), styrene (Sty), 2,2'-Azobisisobutyronitrile (AIBN), dimethyl acrylamide (DMAm), 1,4 dioxane were purchased from Aldrich. N,N-dimethyl formamide (DMF) and tert-butyl acrylate (tBA) were purchased from Fluka. 2-(butylthiocarbonothioylthio)propanoic acid or (propanoic acid)yl butyl trithiocarbonate (PABTC) was received from Dulux Australia. Toluene, sodium hydroxide pellets and 32% hydrochloric acid were obtained from Ajax. AIBN was recrystallized from ethanol, and styrene was passed over basic alumina to remove the inhibitor. The inhibitor was removed from tBA and DMAm by passing the monomer 3 times over an inhibitor removal column. 1,4 dioxane was distilled under reduced pressure. The linear Acrylic Acid-Styrene block copolymers were synthesized by Meiliana Siau, following the method outlined by Ganeva et al.<sup>1</sup>

### Nuclear Magnetic Resonance (NMR)

All NMR analysis was performed on a Bruker AVANCE200 NMR Spectrometer, with an Oxford narrow bore magnet and 5mm dual(CH) probes with z-gradients. NMR analysis was performed on the XWINNMR3.5 and iNMR 0.7 software.

### **Size Exclusion Chromatography with DMF as the eluent (DMF-SEC)**

Molecular weights of the DMAM, DMAM-Sty linear polymers were determined using a Polymer Laboratories GPC-50-Plus SEC system with a Polymer Laboratories Polar-Gel 8 $\mu$ M guard column and two Polymer Laboratories PolarGel columns. The system was equipped with a PL-RI Differential Refractive Index detector (DRI). The eluent was DMF + 0.1% LiBr at 50 °C at a flow rate of 0.5 mL/min. The system was calibrated using polystyrene standards in the range 38,640-162 g/mol, and all analysis was performed using the Cirrus Software.

### **Size Exclusion Chromatography with THF as the eluent. (THF-SEC)**

All molecular weights of the tBA and tBA-Sty polymers were determined using a Shimadzu SEC system equipped with a Polymer Laboratories 10  $\mu$ m guard column, two Polymer Laboratories Mixed-B columns, and a differential refractive index detector (Shimadzu, RID-10A). Tetrahydrofuran at 40 °C was used as the eluent at a flow rate of 1 mL/min. The system was calibrated using polystyrene standards in the range 915,000-580 g/mol, and all analysis was performed using the Cirrus Software.

### **Multiple Detection Size Exclusion Chromatography**

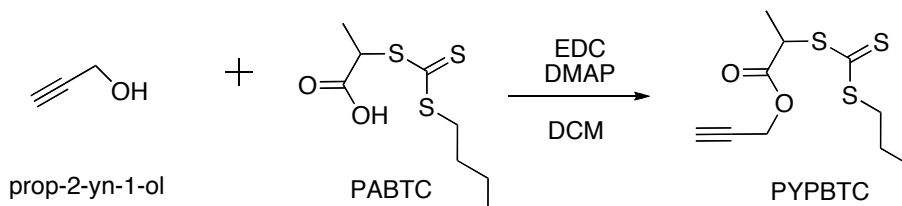
Molecular weights of the DMAM-Sty and AA-Sty hyperbranched polymers were determined using a Polymer Laboratories GPC-50-Plus SEC system with a Polymer Laboratories Polar-Gel 8 $\mu$ M guard column and two Polymer Laboratories PolarGel columns. The system was equipped with a PL-RI Differential Refractive Index detector (DRI) and a PL-BV 400RT Viscometer (Visc). The eluent was DMF + 0.1% LiBr at 50 °C at a flow rate of 0.5 mL/min. The system was calibrated using polystyrene standards in the range 38,640-580 g/mol, with the intrinsic viscosities determined from the Mark-

Houwink equation, using the parameters given in reference.<sup>2</sup> All analysis was performed using the Cirrus Software.

### Dynamic Light Scattering (DLS)

All particle sizes were determined using a Malvern ZetaSizer Nanoseries (Nano-ZS) DLS system, using the Dispersion Technology Software version 5.00.

### Synthesis of (prop-2-ynyl propanoate)yl butyl trithiocarbonate (PYPBTC) RAFT agent



Scheme S1. Synthesis of the RAFT agent PYPBTC.

PABTC (1.030g) was dissolved in 50 mL of DCM and the solution was cooled to 0 °C. Prop-2-yn-1-ol (1.21g) was added to the mixture. To this solution EDC (1.65g) and DMAP (0.5521g) were added. The solution was stirred at 0 °C for 2h and then at ambient temperature overnight. This gave the crude product prop-2-ynyl 2-(butylthiocarbonothioylthio)propanoate or (prop-2-ynyl propanoate)yl butyl trithiocarbonate (PYPBTC). The crude PYPBTC was washed with deionized water (4 × 30 mL then 2 × 50 mL), and passed over a pad of silica using an eluent of 90% toluene and 10% ethyl acetate. The first fraction was collected and dried under vacuum to yield the product PYPBTC (1.08g at 72% yield) as a dark yellow liquid. This reaction is shown in Scheme S1. The purity of the product was confirmed by proton NMR. <sup>1</sup>H-NMR(200MHz, CDCl<sub>3</sub>) δ ppm, 2.509 (1H, t, *J* = 2.46 Hz, H-C≡C), 4.744(2H, d, 2.14 Hz, C≡C-CH<sub>2</sub>-O) 4.871 (1H, q, *J* = 7.38 Hz, C(O)-C(S)H-CH<sub>3</sub>), 1.485 (3H, d, *J* = 7.39 Hz, C(S)H-CH<sub>3</sub>) 3.384(2H, t, *J* = 7.23 Hz, S-CH<sub>2</sub>-CH<sub>2</sub>), 1.71 (2H, q, *J* = 7.61 Hz, S-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.429 (2H, s, *J*=7.95 Hz, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>) 0.953(3H, t, *J* = 7.24 Hz CH<sub>2</sub>-CH<sub>3</sub>).

**PYPBTC mediated synthesis of DMAm-Sty block copolymer.**

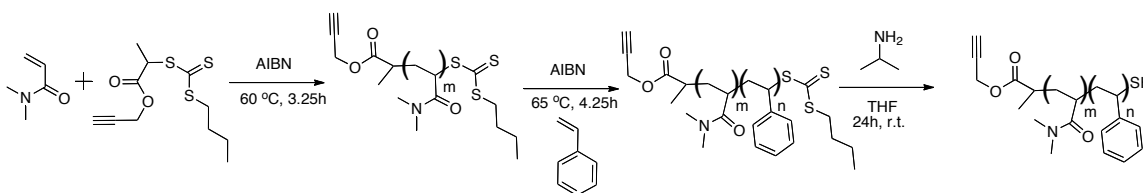
PYPBTC (0.2002 g, 0.7242 mmol) was placed in a vial and had AIBN (0.0119 g, 0.0725 mmol) added to it. To this mixture DMAm (0.7296 g, 7.360 mmol) was added. Toluene (0.8115 g, 8.807 mol) was added to this vial, and the solution was homogenized by shaking at room temperature. This solution was transferred to a round bottom flask equipped with a magnetic stirrer bar, capped with a rubber septum and deoxygenated by bubbling nitrogen through the solution for 10 min. The solution was placed in an oil bath at 60 °C and polymerized for 3.25 hours. After polymerization the conversion was determined by <sup>1</sup>H-NMR and the polymer was precipitated 3 times from hexane at 0 °C. The molecular weight was determined by both <sup>1</sup>H-NMR and DMF-SEC, and the DMAm macroRAFT was dried under vacuum overnight.

The block extension was performed by adding AIBN (0.0097 g, 0.059 mmol) to the DMAm macroRAFT agent (0.6285 g, 0.5616 mmol). Styrene (1.8372 g, 17.640 mmol) was added to this mixture, and homogenized by shaking. This solution was placed in a round bottom flask equipped with a magnetic stirrer bar, capped with a rubber septum and deoxygenated by bubbling nitrogen through the solution for 10 min. The solution was placed in an oil bath at 65 °C and polymerized for 4.25 h. The conversion was determined by <sup>1</sup>H-NMR and the styrene monomer was removed under reduced pressure. The molecular weight was determined by both <sup>1</sup>H-NMR and DMF-SEC.

**Aminolysis of DMAm-Sty block copolymer.**

The DMAm-Sty diblock polymer (1.1257 g, 0.5616 mol) was dissolved in THF (2.5082 g, 34.78 mmol), placed in a round bottom flask equipped with a magnetic stirrer bar and deoxygenated by bubbling nitrogen for 10 min. In a separate vial, isopropyl amine (1.6931 g, 28.64 mmol) was deoxygenated by bubbling nitrogen for 10 min, and

transferred by syringe to the flask containing the polymer in THF. This solution was stirred at 25 °C for 24 h. The polymer was precipitated 3 times from hexane at -78 °C. The polymer was characterized by both <sup>1</sup>H-NMR and DMF-SEC, with the removal of the trithiocarbonate group confirmed by the disappearance of the terminal methyl group of the trithiocarbonate after the aminolysis and the DMAM-Sty polymer was stored under nitrogen. This polymer is called Alkyne Dimethyl Acrylamide Styrene Thiol, or ADMAST.



Scheme S2. Synthesis of DMAM-Sty diblock with an alkyne and thiol as the terminal groups (ADMAST).

### Photopolymerization of ADMAST

The ADMAST (1.0711 g) polymer was placed in a vial, and DMPA (0.0533 g, 0.2079 mmol) was added to the vial. This mixture was dissolved in DMF (1.1174 g, 15.29 mmol), and the solution divided into 4 vials. Each vial was capped with a rubber septum, and deoxygenated by passing nitrogen through the vial for 2 min. These vials were placed in a dark box and illuminated by a Spectroline ENF-280C/FE lamp irradiating at 365 nm for 5 hours. These vials were stirred every 1.5 hours. After 5 hours under the UV lamp, the contents of these vials were combined and the polymer was analyzed by DMF-SEC. This yielded the hyperbranched dimethyl acrylamide-styrene polymer.

### Self-Assembly of DMAM-Sty hyperbranched Polymers.

The hyperbranched DMAM-Sty polymer (14.8 mg) in DMF (15.4 mg) was placed in a vial equipped with a magnetic stirrer bar, and dissolved in acetone (0.6060 g, 10.43

mmol). The vial was capped with a rubber septum, and deionized water (2.400 mL) was added to this solution at a rate of 0.2 mL/hour. After stirring for 18 hours, the system was studied by DLS.

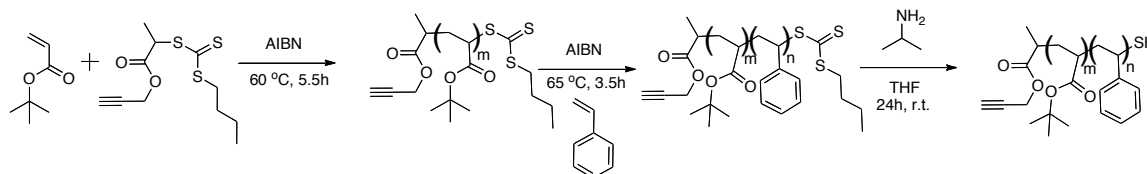
#### **RAFT synthesis of tBA-Sty block copolymer**

PYPBTC (0.2000 g, 0.7235 mmol) was placed in a vial and had AIBN (0.0061 g, 0.037 mmol) added to it. To this mixture tBA (0.9359 g, 7.302 mmol) was added. Toluene (0.9987 g, 10.83 mmol) was added to this mixture, and the solution was homogenized by shaking at room temperature. This solution was transferred to a round bottom flask equipped with a magnetic stirrer bar, capped with a rubber septum and deoxygenated by bubbling nitrogen through the solution for 10 min. The solution was placed in an oil bath at 60 °C and polymerized for 5.5 hours. After polymerization the conversion was determined by <sup>1</sup>H-NMR and the residual monomer and solvent was removed under reduced pressure. The molecular weight was determined by both <sup>1</sup>H-NMR and THF-SEC, and the tBA macroRAFT was dried under vacuum overnight.

The block extension was performed by adding AIBN (0.0092 g, 0.056 mmol) to the tBA macroRAFT agent (0.8491 g, 0.7235 mmol). Styrene (2.1566 g, 20.70 mmol) was added to this mixture, and homogenized by shaking at room temperature. This solution was placed in a round bottom flask equipped with a magnetic stirrer bar, capped with a rubber septum and deoxygenated by bubbling nitrogen through the solution for 10 min. The solution was placed in an oil bath at 65 °C and polymerized for 3.5 h. The conversion was determined by <sup>1</sup>H-NMR and the styrene monomer was removed under reduced pressure. The molecular weight was determined by both <sup>1</sup>H-NMR and THF-SEC.

#### **Aminolysis of tBA-Sty block copolymer**

The tBA-Sty diblock polymer (1.3389 g, 0.7235 mmol) was dissolved in THF (2.5724 g, 35.67 mmol), placed in a round bottom flask equipped with a magnetic stirrer bar and deoxygenated by bubbling nitrogen for 10 min. In a separate vial, isopropyl amine (1.6650 g, 28.17 mol) was deoxygenated by bubbling nitrogen for 10 min, and transferred by syringe to the flask containing the polymer in THF. This solution was stirred at 25 °C for 24 h. The polymer was precipitated from 5% (v/v) water in methanol at -78 °C. The polymer was characterized by both <sup>1</sup>H-NMR and THF-SEC, with the removal of the trithiocarbonate group confirmed by the disappearance of the terminal methyl group of the trithiocarbonate after the aminolysis and the tBA-Sty polymer was stored under nitrogen. This polymer is called Alkyne-*tert*-Butyl Acrylate Styrene Thiol (AtBAST)



Scheme S3. Synthesis of tBA-Sty diblock with an alkyne and thiol as the terminal groups (AtBAST).

### Photopolymerization of AtBAST

The AtBAST (0.8818 g) polymer was placed in a vial, and DMPA (0.0441 g, 0.172 mmol) was added to the vial. This mixture was dissolved in DMF (1.0154 g, 13.89 mol), and the solution divided into 4 vials. Each vial was capped with a rubber septum, and deoxygenated by passing nitrogen through the vial for 2 min. These vials were placed in a dark box and illuminated by a Spectroline ENF-280C/FE lamp irradiating at 365 nm for 5 hours. These vials were stirred every 1.5 hours. After 5 hours under the UV lamp, the contents of these vials were combined and the polymer was analyzed by THF-SEC. The DMF was removed from polymer by dissolving the polymer in diethyl ether and washing with deionized water (3 × 30 mL). The ether layer was collected, and the solvent removed

under reduced pressure. This yielded the hyperbranched *tert*-butyl acrylate styrene polymer.

### **Hydrolysis of *tert*-butyl ester groups**

The selective hydrolysis of the *tert*-butyl esters was achieved by adapting the method of Davis and Matyjaszewski<sup>3</sup> and Cai et. al,<sup>4</sup> for the selective hydrolysis of *tert*-butyl esters. The hyperbranched *tert*-Butyl Acrylate styrene polymer (0.7687g) was dissolved in 1,4 dioxane (3.1297 g, 35.52 mmol) and the solution was placed in a flask equipped with a magnetic stirrer bar. To this mixture a solution of HCl (0.9858 mL, 1.68 mmol) was added and the solution was heated at reflux for 6 hours. The volatiles were removed under reduced pressure and the polymer was analyzed by <sup>1</sup>H-NMR in deuterated acetone, and showed incomplete hydrolysis of the *tert*-butyl ester. The partially hydrolyzed polymer was redissolved in dioxane (3.1000 g, 35.18 mmol) and the solution was placed in a flask equipped with a magnetic stirrer bar. To this mixture a solution of HCl (0.6362 mL, 1.06 mmol) was added and the solution was heated at reflux for a further 6 hours. After this reaction, the solution became homogeneous, and the volatiles removed under reduced pressure. The <sup>1</sup>H-NMR in deuterated acetone showed a significant decrease of the *tert*-butyl ester groups, with the integral after acid hydrolysis in the region 1.4-1.6 ppm being only 13% of the initial tBA-Sty hyperbranched material. This value is an overestimate of the number of *tert*-butyl groups in the final material since this region of NMR spectrum also overlaps with the polymer backbone. The resulting hyperbranched acrylic acid-styrene polymer was characterized by DMF-SEC.

### **Self-Assembly of AA-Sty hyperbranched Polymers at low pH.**



The hyperbranched AA-Sty polymer (15.2 mg) was placed in a vial equipped with a magnetic stirrer bar, and dissolved in acetone (0.6026 g, 10.38 mmol). The vial was capped with a rubber septum, and 0.0129 M HCl in deionized water (2.400 mL) was added to this solution at a rate of 0.2 mL/hour. After stirring for 18 hours, the pH found to be 1.90 and the system was studied by DLS.

#### **Self-Assembly of AA-Sty hyperbranched Polymers at high pH.**

The hyperbranched AA-Sty polymer (15.4 mg) was placed in a vial equipped with a magnetic stirrer bar, and dissolved in acetone (0.6036 g, 10.39 mmol). The vial was capped with a rubber septum, and 0.0185 M NaOH in deionized water (2.400 mL) was added to this solution at a rate of 0.2 mL/hour. After stirring for 18 hours, the system was studied by DLS. After an initial study by DLS the solution was filtered through a 0.45  $\mu\text{m}$  cellulose acetate filter and studied again by DLS. Size distribution of the filtered sample was similar to the unfiltered sample, and subsequently used for the analysis. The pH of the solution was found to be 7.66.

#### **PABTC mediated synthesis of DMAm-Sty block copolymer.**

PABTC (0.1499 g, 0.6288 mmol) was added to a vial and had AIBN (0.0104 g, 0.0633 mmol) added to it. To this mixture DMAm (0.6444 g, 6.501 mmol) was added. Toluene (1.1655 g, 12.65 mol) was added to this vial, and the solution was homogenized by shaking at room temperature. This solution was transferred to a round bottom flask equipped with a magnetic stirrer bar, capped with a rubber septum and deoxygenated by bubbling nitrogen through the solution for 10 min. The solution was placed in an oil bath at 60 °C and polymerized for 3 hours. After polymerization the conversion was determined by  $^1\text{H}$ -NMR and the polymer was precipitated 2 times from hexane at 0 °C.

The molecular weight was determined by both  $^1\text{H-NMR}$ , and the DMAm macroRAFT was dried under vacuum overnight.

The block extension was performed by adding AIBN (0.0085 g, 0.052 mmol) to the DMAm macroRAFT agent (0.6144 g, 0.5437 mmol). Styrene (1.5689 g, 15.06 mmol) was added to this mixture, and homogenized by vigorous shaking. This solution was placed in a round bottom flask equipped with a magnetic stirrer bar, capped with a rubber septum and deoxygenized by bubbling nitrogen through the solution for 10 min. The solution was placed in an oil bath at 65 °C and polymerized for 5 h. The conversion was determined by  $^1\text{H-NMR}$  and the polymer was precipitated 2 times into hexane at -78 °C. The molecular weight was determined by  $^1\text{H-NMR}$ .

#### **Self-Assembly of DMAm-Sty Linear Diblock Polymers**

The linear DMAm-Sty polymer (16.2mg) was placed in a vial equipped with a magnetic stirrer bar, and dissolved in acetone (0.6075 g, 10.46 mmol). The vial was capped with a rubber septum, and deionized water (2.400 mL) was added to this solution at a rate of 0.2 mL/hour. After stirring for 18 hours, the system was studied by DLS. After an initial study by DLS the solution was filtered through a 0.45  $\mu\text{m}$  cellulose acetate filter and studied again by DLS. The size distribution of the filtered sample was similar to the unfiltered sample, and subsequently used for the analysis.

#### **Self-Assembly of AA-Sty Linear Polymers at low pH.**

The linear AA-Sty polymer (16.0 mg) was placed in a vial equipped with a magnetic stirrer bar, and dissolved in acetone (0.6013 g, 10.35 mmol). The vial was capped with a rubber septum, and 0.0135 M HCl in deionized water (2.400 mL) was added to this

solution at a rate of 0.2 mL/hour. After stirring for 15 hours, the system was studied by DLS. The pH of the final solution was found to be 2.13.

### **Self-Assembly of AA-Sty Linear Polymers at high pH.**

The linear AA-Sty polymer (16.1 mg) was placed in a vial equipped with a magnetic stirrer bar, and dissolved in acetone (0.6077 g, 10.46 mmol). The vial was capped with a rubber septum, and 0.0184 M NaOH in deionized water (2.400 mL) was added to this solution at a rate of 0.2 mL/hour. After stirring for 15 hours, the system was studied by DLS. After an initial study by DLS the solution was filtered through a 0.45  $\mu\text{m}$  cellulose acetate filter and studied by DLS. The size distribution of the filtered sample was similar to the unfiltered sample, and subsequently used for the analysis. The pH of the final solution was found to be 6.84.

### **Additional Characterization**

#### **DMAm-Sty Blocks and Hyperbranched Polymer.**

Table S1 shows the conversion of both the PYPBTC mediated polymerization of DMAm and the chain extension with styrene. In addition the table S1 shows the theoretical molecular weight and the number averaged degree of polymerization of each block, as determined by NMR.

Monomer	Reaction time (h)	Conversion (NMR)	$M_n$ theory	$DP_n$ theory	$DP_n$ NMR (of Block)
DMAm (60 °C)	3.25	0.88	887	9	8.5
Sty (65 °C)	4.25	0.33	1911	10	8.5

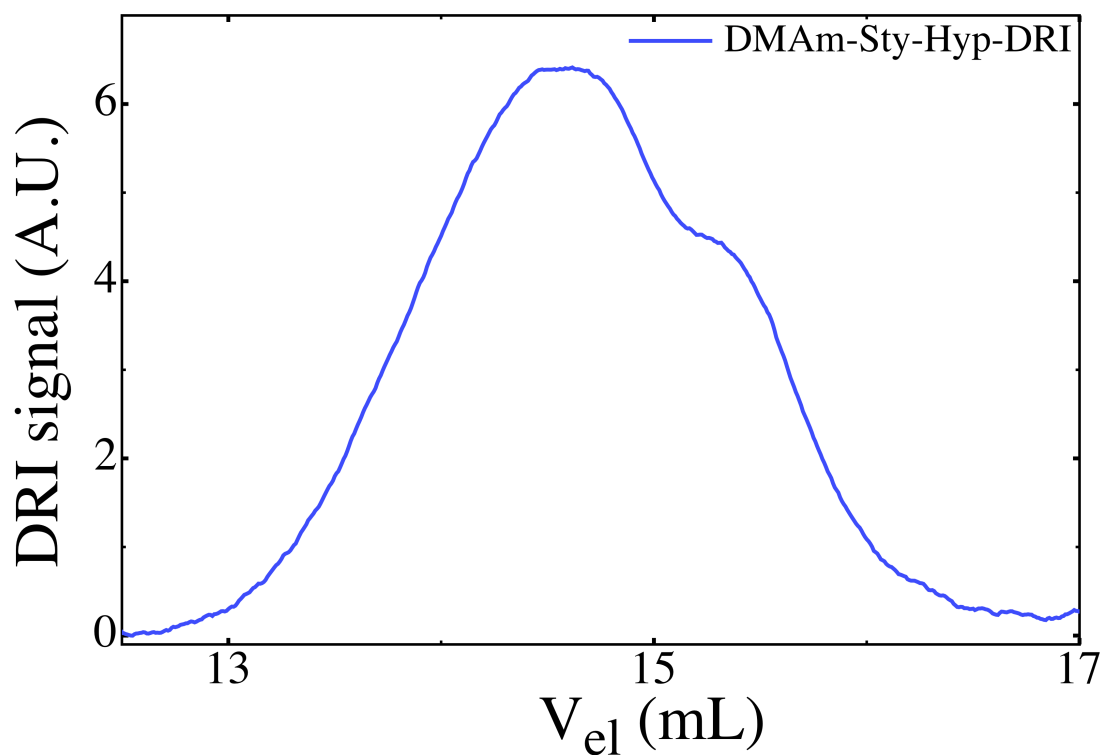
Table S1: Conversion and NMR molecular weight data for the PYPBTC synthesized DMAm-Sty polymers.

Table S2 show the average molecular weight data for the DMAm-Sty based polymers determined by SEC. In general for the linear polymers the theoretical molecular weight from Table S1 agrees well with the average molecular weight determined by conventional SEC. In the case of the hyperbranched polymer the molecular weight was

determined by viscometric/DRI SEC, which gives accurate molecular weights.<sup>5</sup> These multiple detection SEC traces are given in Fig. S1.

Sample	$M_n$ (g/mol) (SEC)	$M_w$ (g/mol) (SEC)	$PDI$ (SEC)
DMAm	623	708	1.14
DMAm-Sty-RAFT	1603	1890	1.18
DMAm-Sty-SH	1618	1920	1.19
Hyperbranched (Visc/DRI)	4200	15000	3.5

Table S2: DMF-SEC molecular weight data for the PYPBTC synthesized DMAm-Sty polymers.



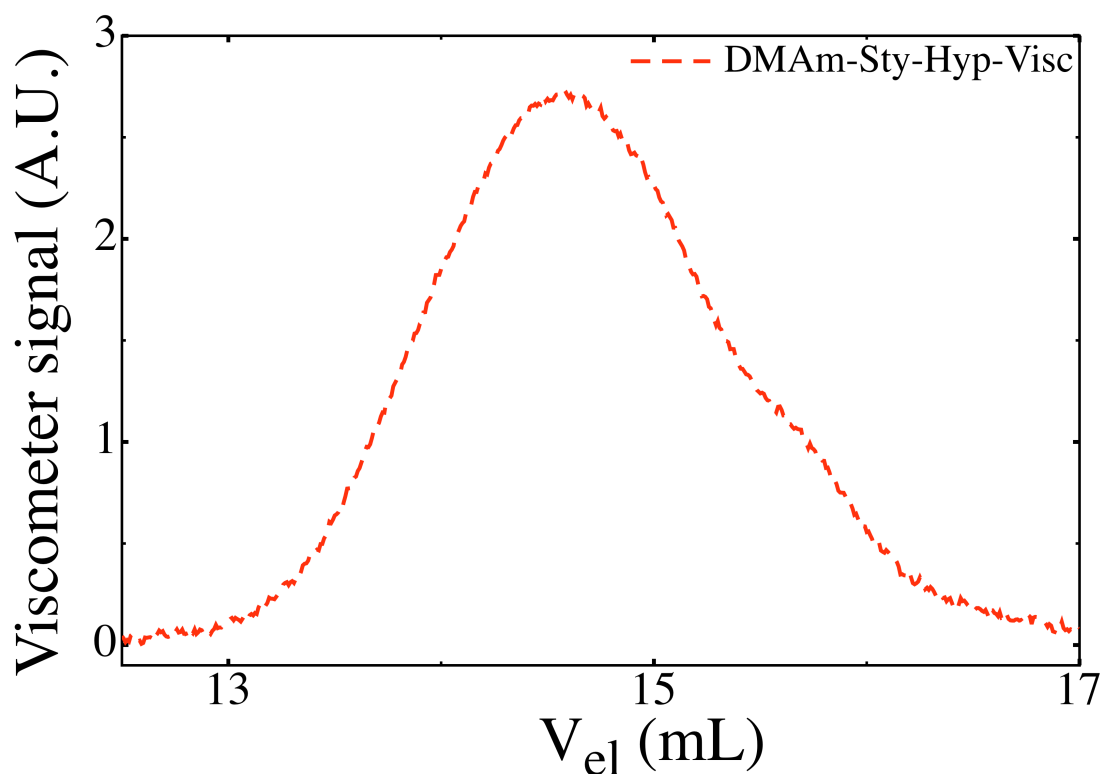


Fig. S1: SEC distribution of the DMAm-Sty hyperbranched polymer detected by DRI (top) and Viscometry (Bottom)

#### tBA-Sty blocks and Hyperbranched Polymer.

Table S3 shows the conversion of both the PYPBTC mediated polymerization of tBA and the chain extension with styrene. In addition the table S3 shows the theoretical molecular weight and the number averaged degree of polymerization of each block, as determined by NMR. In general there is good agreement between the theoretical degree of polymerization and the degree of polymerization determined using NMR.

Monomer	Reaction time (h)	Conversion (NMR)	M <sub>n</sub> theory	DP <sub>n</sub> theory	DP <sub>n</sub> NMR (of Block)
tBA (60 °C)	5.5	0.90	1163	9	7
Sty (65 °C)	3.5	0.25	1906	7.5	6.5

Table S3: Conversion and NMR molecular weight data for the tBA polymerization and the styrene chain extension.

Table S4 show the average molecular weight data for the tBA-Sty based polymers determined by SEC. In general for the linear polymers the theoretical molecular weight from Table S3 agrees well with the average molecular weight determined by SEC. For the hyperbranched polymer there is a clear increase of the average molecular weight of the polymer, relative to the starting diblock. Since this analysis only used DRI detection and polystyrene standards to determine the molecular weight, the true molecular weight of the branched polymer will be higher than the apparent molecular weight of the hyperbranched polymer shown in table S4. This is because the branched polymer should have a more compact size than a linear equivalent. This can be seen in the subsequent section, where multiple detection SEC is employed, and gives a very large molecular weight for the AA-Sty hyperbranched polymer, which results from selective hydrolysis of the tBA groups to acrylic acid.

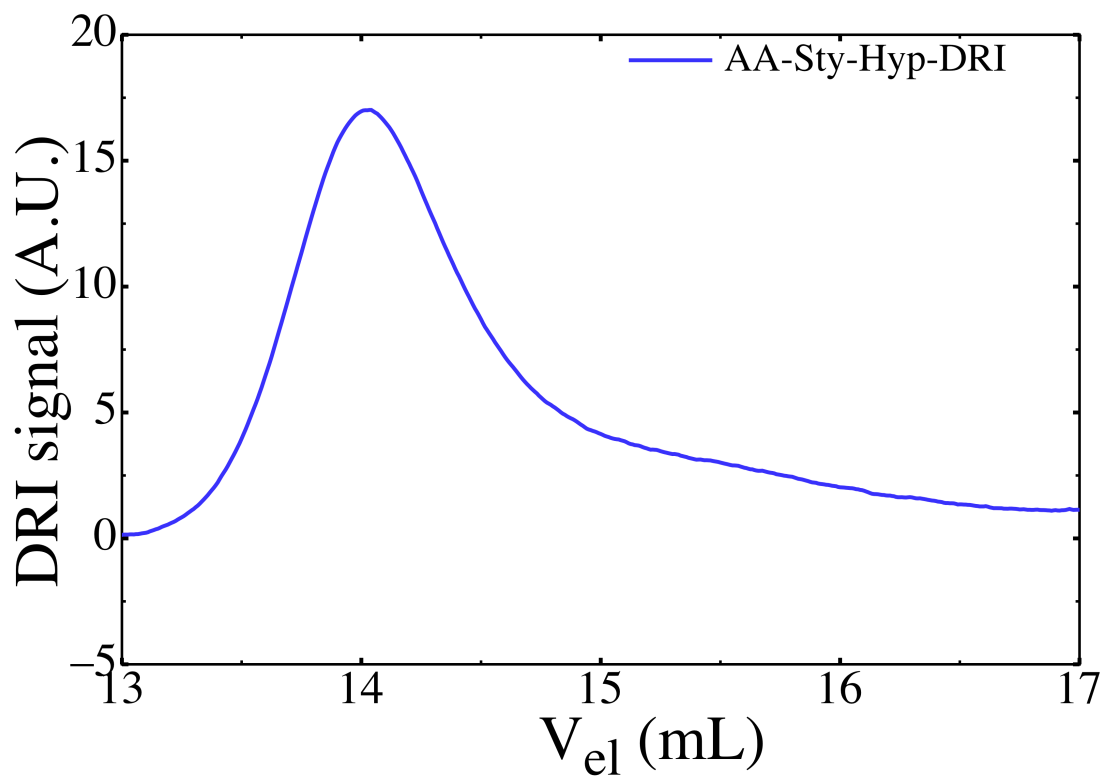
Sample	M <sub>n</sub> (g/mol) (SEC)	M <sub>w</sub> (g/mol) (SEC)	PDI (SEC)
tBA	1200	1400	1.13
tBA-Sty-RAFT	1800	2000	1.15
tBA-Sty-SH	1800	2200	1.22
Hyperbranched	5100 (apparent)	13000 (apparent)	2.5 (apparent)

Table S4: THF-SEC molecular weight data for the tBA-Sty based polymers polymerization

#### DMF-SEC of Acrylic Acid-Styrene Hyperbranched polymer

Fig S2 shows the SEC trace of the hyperbranched acrylic acid-styrene polymer that results from acid hydrolysis of the *tert*-butyl ester. In this case, both viscometric and DRI detection is used. As seen in Fig. S2 the distribution of the polymer is very broad which is consistent with retention of the hyperbranched structure. Table S5 shows the number and weight averaged molecular weight data of the AA-Sty hyperbranched polymer as well as the PDI. The molecular weight of these polymers is large, and the PDI broad, suggesting

selective conversion of the tBA groups to AA groups, with minimal hydrolysis of the other bonds in the polymer. This is very similar to other reports of selective hydrolysis of the *tert*-butyl group under similar conditions.<sup>4</sup>



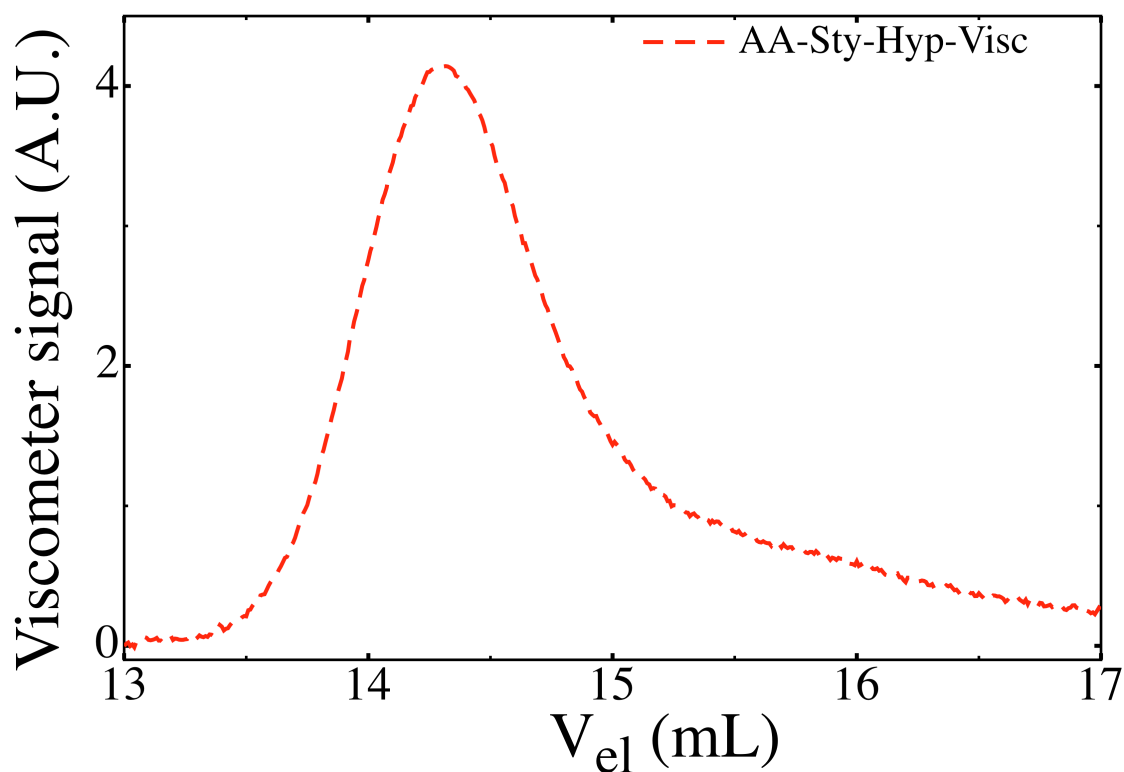


Fig. S2: SEC distribution of the AA-Sty hyperbranched polymer that results from hydrolysis of the tBA groups detected by DRI (top) and Viscometry (Bottom)

Sample	$M_n$ (g/mol)	$M_w$ (g/mol)	PDI
AA-Sty Hyperbranched (Visc/DRI)	5000	37000	7.4

Table S5: Molecular weight data for the acrylic acid-styrene polymers.

#### Deconvolution of Hyperbranched SEC traces.

The SEC traces of the hyperbranched polymers were deconvolved by fitting two Gaussian functions under the DRI distribution of the DMAM-Sty and tBA-Sty hyperbranched polymers. These two Gaussian functions correspond to the linear polymer population and the branched polymer population. The tBA polymer was used in this fitting, but because the hydrolysis of tBA to acrylic acid is selective and efficient the AA trace will give similar results. The yield of the reaction is found by calculating the area under the two Gaussian curves and determining the area in the branched fractions. The



area of the branched materials are 93 % for the DMAm polymer and 94% for the tBA polymer. The deconvolved traces are shown in Fig. S3. This shows the experimental data, overall fit, and the low and high molecular weight fractions.

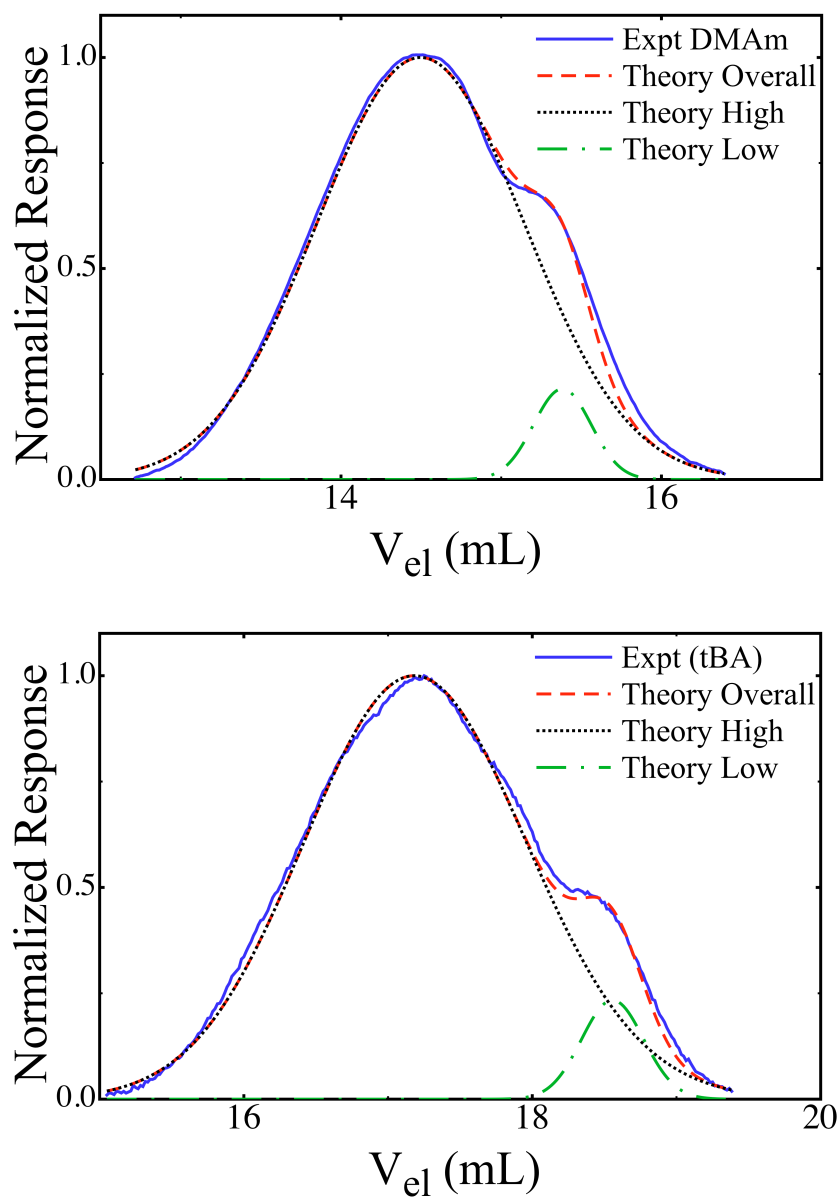


Fig. S3: Deconvolution of the DRI-SEC traces of the DMAm-Sty hyperbranched polymer (top) and tBA-Sty hyperbranched polymer (bottom).

### Synthesis of the linear DMAm-Sty Polymer.

Table S6 shows the conversion of both the PABTC mediated polymerization of DMAm and the chain extension with styrene. In addition the table S6 shows the theoretical molecular weight and the number averaged degree of polymerization of each block, as determined by NMR. In general there is good agreement between the theoretical degree of polymerization and the degree of polymerization determined using NMR. These block lengths are similar to those obtained in the PYPBTC synthesis of DMAm-Sty.

Monomer	Reaction time (h)	Conversion (NMR)	M <sub>n</sub> theory	DP <sub>n</sub> theory	DP <sub>n</sub> NMR (of Block)
DMAm (60 °C)	3	0.97	957	10	9
Sty (65 °C)	5	0.42	2193	11.5	10

Table S6: Conversion and NMR molecular weight data for the PABTC synthesis of DMAm and styrene polymers.

### Self-Assembly of the linear DMAm-Sty Polymer.

Fig. S4 shows the size distribution of the self assembled linear DMAm-Sty polymers in 20% (wt/wt) acetone in water. As seen in this figure, the size distribution of the linear polymers is quite narrow and well defined, and centered around ~10 nm. In particular this system shows minimal run-to-run variation, unlike the hyperbranched DMAm-Sty.

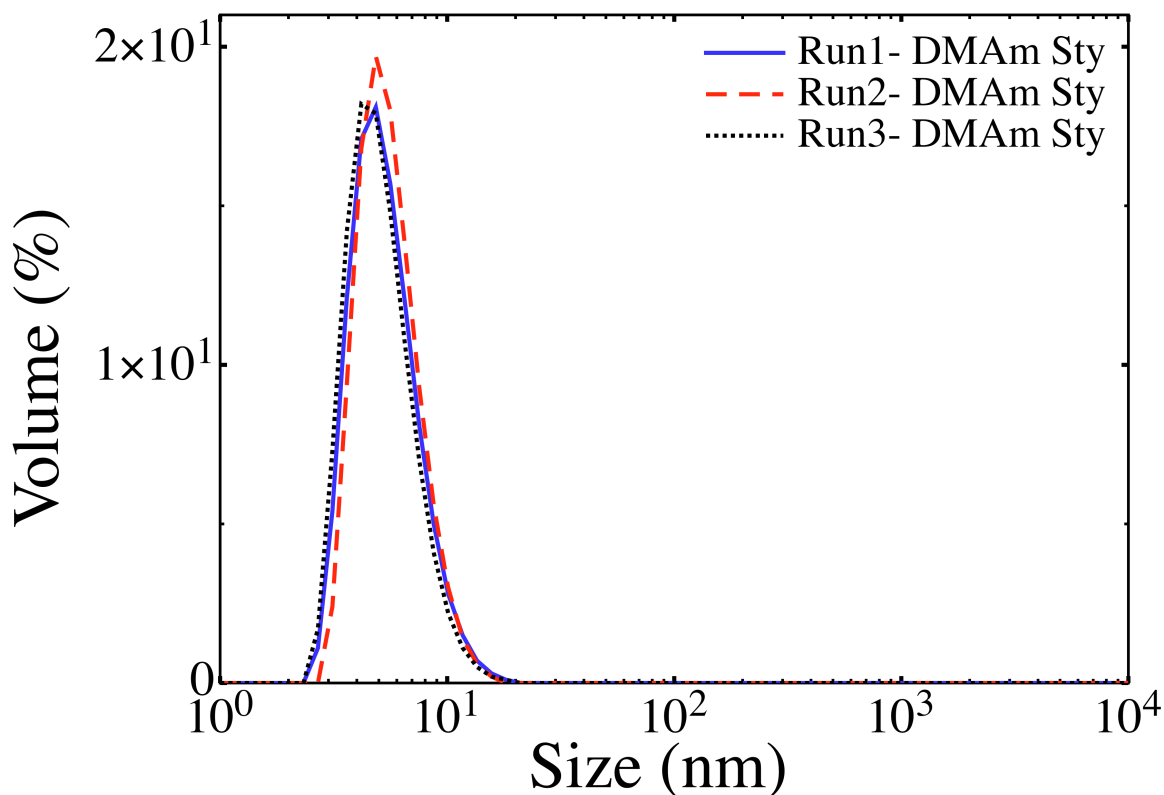


Fig. S4: DLS-Size distribution of the self assembled linear DMAm-Sty polymers in 20% (wt/wt) acetone in water.

#### Self-Assembly of the linear AA-Sty Polymers at low pH.

Fig. S5 shows the size distribution of the self assembled linear AA-Sty polymers in 20% (wt/wt) acetone in water at pH 2.13. As seen in this figure, the size distribution of these self assembled materials is quite poorly defined and has significant run to run variation. In particular, later runs show more of the small particles, centered around ~50 nm. While earlier runs show more of the large aggregates centered around 1000 nm. This is due to the sedimentation of the large aggregates and instability of the system. The large aggregates and run to run variation is consistent with the results observed for the hyperbranched AA-Sty system. However, the aggregates in the linear system appear to be larger and less stable than the hyperbranched case.

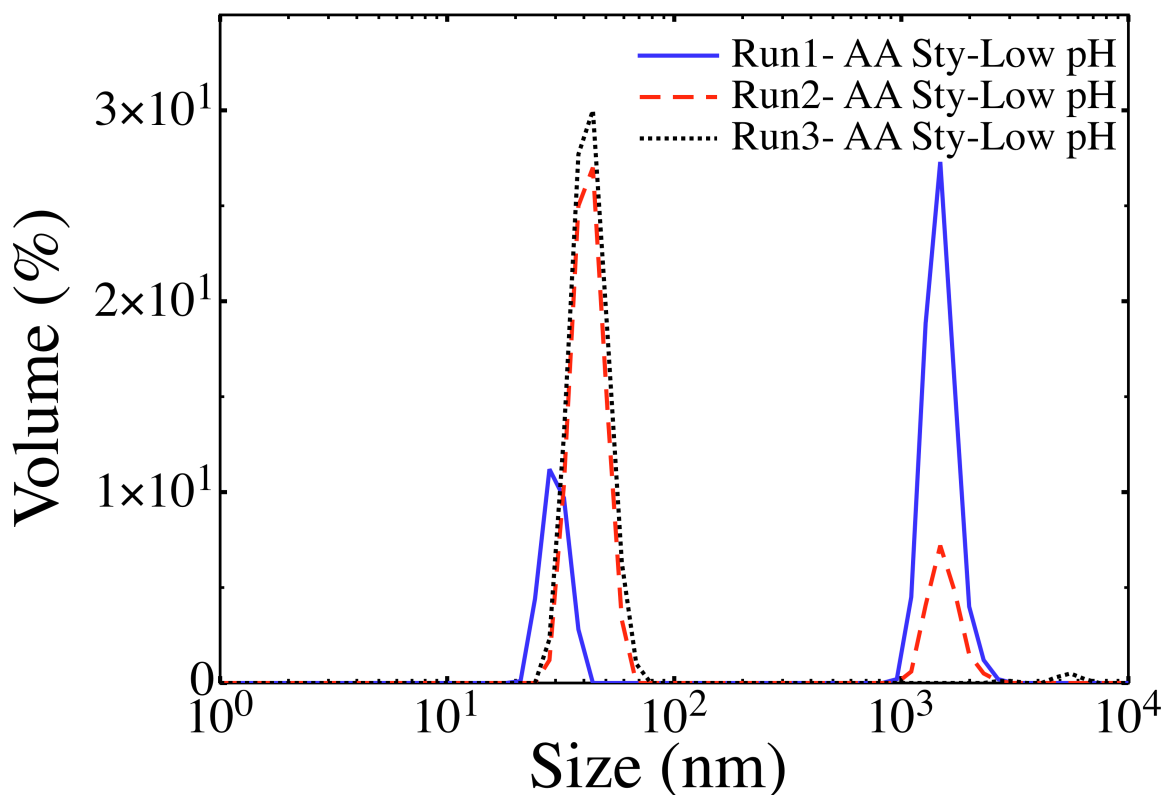


Fig. S5: DLS-Size distribution of the self assembled linear AA-Sty polymers in 20% (wt/wt) acetone in water at pH 2.13.

#### Self-Assembly of the linear AA-Sty Polymers at high pH.

Fig. S6 shows the size distribution of the self assembled linear AA-Sty polymers in 20% (wt/wt) acetone in water at pH 6.84. As seen in this figure, the size distribution of these linear polymers is quite narrow and well defined, and centered around ~10 nm. This system also shows minimal run-to-run variation. These sizes are similar to the hyperbranched AA-Sty system. However, the linear polymer must aggregate with other polymers to form a micelle, whereas, the hyperbranched polymer could adopt a similar structure as a unimolecular particle.

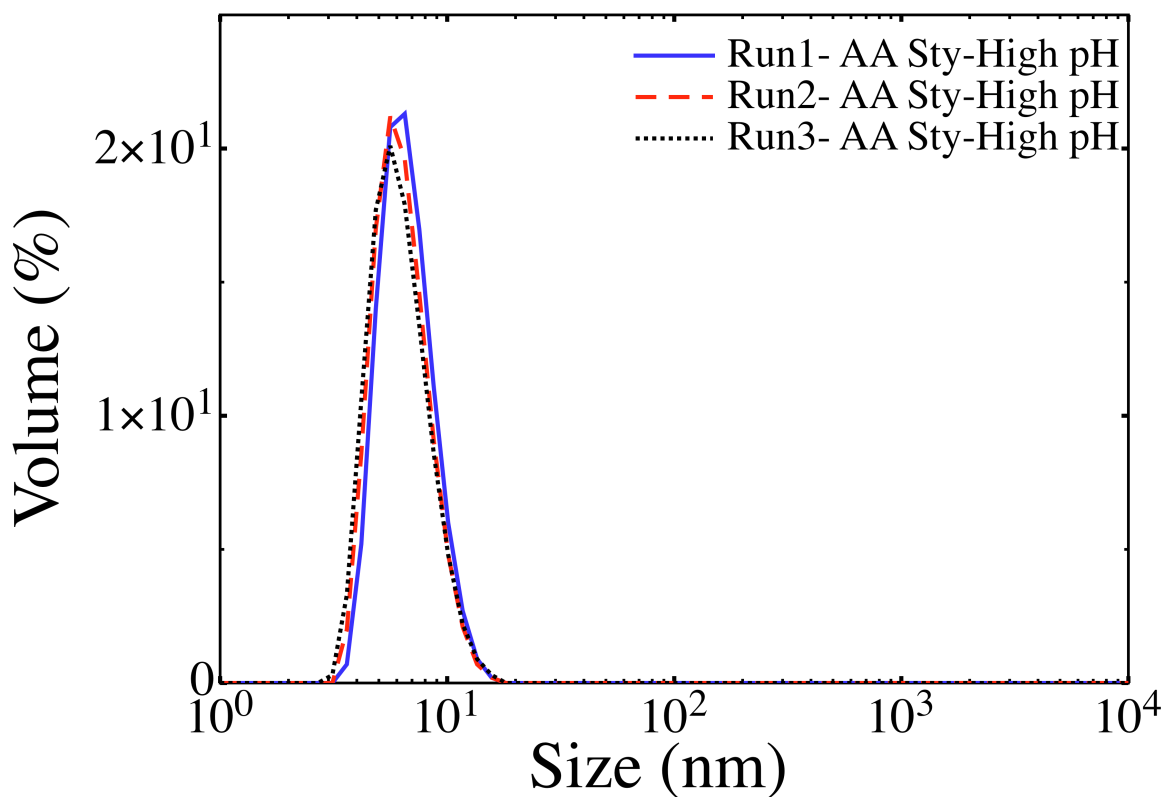


Fig. S6: DLS-Size distribution of the self assembled linear AA-Sty polymers in 20% (wt/wt) acetone in water at pH 6.84.

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