

## Supporting information

for

### **Poly(styrene-*graft*-hyperbranched polyglycidol): Synthesis and Solution Behavior of a Hyperbranched Polyelectrolyte**

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## Reagents

All reagents were purchased from Sigma-Aldrich and used as received unless otherwise specified. Inhibitor was removed from the styrene and 4-acetoxystyrene monomers by passing them through a neutral aluminum oxide column on the day of polymerization. Diphenylmethyl potassium (DPMK) was synthesized by treating diphenylmethane with a slight excess of potassium metal, and it was subsequently degassed and ampulized using high vacuum line techniques. Glycidol was purified by vacuum distillation over  $\text{CaH}_2$  and ampulized. Tetrahydrofuran (THF) was used directly from the high vacuum line where it was stirred over sodium/potassium alloy. Toluene was dried over  $\text{CaH}_2$ .

## Instrumentation

$^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker Avance 400 MHz system referenced to acetone- $d_6$  and DMSO- $d_6$  purchased from Cambridge Isotope Laboratories, Inc.

Number-average molecular weight ( $M_n$ ) and polydispersity index ( $M_w/M_n$ ) of the hypergrafted copolymer were determined using size exclusion chromatography (SEC), consisting of a Waters 510 model pump, a Rheodyne model 7725(i) manual injector with a 200  $\mu\text{l}$  loop, and a Knauer Smartline model 2300 RI detector. The following column set was used in DMF + 0.1M LiBr at a flow rate of 1mL/min: four PSS (Polymer Standards Services) GRAM; 8x300 mm; 10  $\mu\text{m}$  100; 1000, and 3000  $\text{\AA}$  long with an 8x50, 10  $\mu\text{m}$  guard. The columns are calibrated with a set of PS standards covering the molecular weight range from 600 to 7,500,000 g/mol. The poly(styrene-*co*-4-acetoxystyrene) and poly(styrene-*co*-4-hydroxystyrene) precursor copolymers were characterized using an

SEC equipped with Knauer's K-501 HPLC pump, K-2301 RI detector and K-2501 UV detector. The columns used were 60 cm PSS SDV-gel: 1x10 $\mu$ /100 Å, 1x5 $\mu$ /linear: 10<sup>2</sup>-10<sup>6</sup> Å. The copolymer precursors were run in THF at 1.0 mL/min, toluene flow marker, and reported values of  $M_n$  and  $M_w/M_n$  are relative to linear PS standards.

A TA Instruments Q-1000 differential scanning calorimeter (DSC) was used from -50°C to 200°C at a heating rate of 10 °C/min with a 2 minute isothermal hold at the maximum and minimum temperatures. Reported glass transition temperatures were measured on the second (of three) heating scans.

Morphological measurements were performed using a Multimode Scanning Probe Microscope (SPM) in tapping mode on samples spin cast from DMF at 2000 rpm from concentrations of 0.1, 0.5, and 1.0 mg/mL onto a mica wafer.

Dilute solution viscometry was performed using a Schott Instruments ViscoSystem AVS 370 Viscometer. The automated system utilizes the Dilute 4.0 Software which is computer controlled performed multiple dilutions using a type 531-10 viscometer (0.64 mm capillary) in DMF and 0.1M LiBr/DMF solution at 25°C.

Dynamic Light Scattering Light scattering measurements were performed in an ALV/DLS/SLS-5022F Compact Goniometer System using a 22-mW He-Ne-Laser with a wavelength of 632.8 nm, and four detector units covering 16 angles from 20° to 146°. The scattering wave vector,  $q$ , is calculated as  $q = (4\pi n_o/\lambda) \sin(\theta/2)$ , where  $n_o$  is the

solvent refractive index,  $\lambda$  is the laser wavelength (632.8 nm), and  $\theta$  is the scattering angle. The scattering intensity autocorrelation function,  $g(2)(t) - 1$ , profiles at each angle were analyzed using the CONTIN algorithm to determine the distribution of decay rates which provides information on the existence of one or more populations in solution. For systems showing one decay mode, a single exponential decay was used to determine the characteristic decay time,  $\Gamma$ .

### **Synthesis of poly(styrene-*co*-4-acetoxystyrene)**

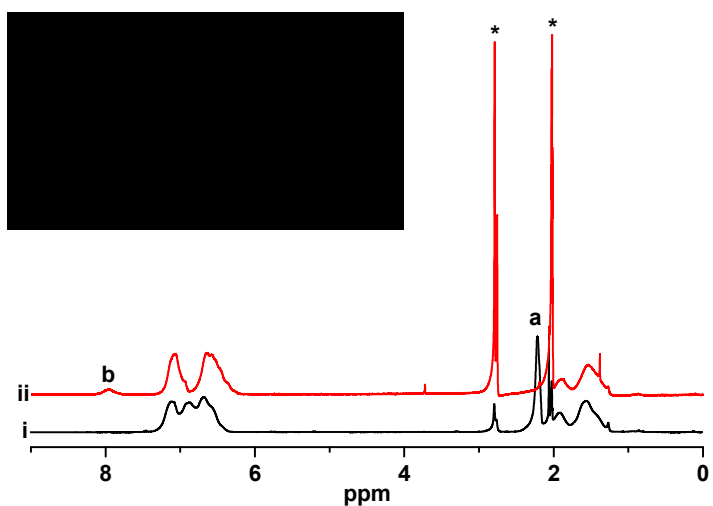
4-acetoxystyrene (13 mmol), styrene (19 mmol), S-1-dodecyl-S'-( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -acetic acid)trithiocarbonate (DDMAT) ( $4.12 \times 10^{-2}$  mmol), and azobisisobutyronitrile (AIBN) ( $4 \times 10^{-3}$  mmol) were added by syringe into a simple tube-reactor containing a glass encapsulated stir bar. The DDMAT chain transfer agent was synthesized prior to the polymerization in a 3-neck round bottom flask equipped with an overhead stirrer, N<sub>2</sub> gas inlet, and an addition funnel. The reaction mixture was cooled using an ice water bath following the procedure previously published by Lai et al. and resulted in a 45% yield.<sup>1</sup> The polymerization reactor was placed on a high-vacuum line and subjected to 3 freeze/thaw cycles. Dried toluene (5 mL) was distilled into the reactor to reduce the viscosity and an additional 3 freeze/thaw cycles were performed. The reactor was flame sealed from the vacuum line and placed into a heated oil bath (60-70 °C) and allowed to react for 30 h. The resulting polymer was precipitated in methanol and vacuum dried overnight.

### **Synthesis of poly(styrene-*co*-4-hydroxystyrene)**

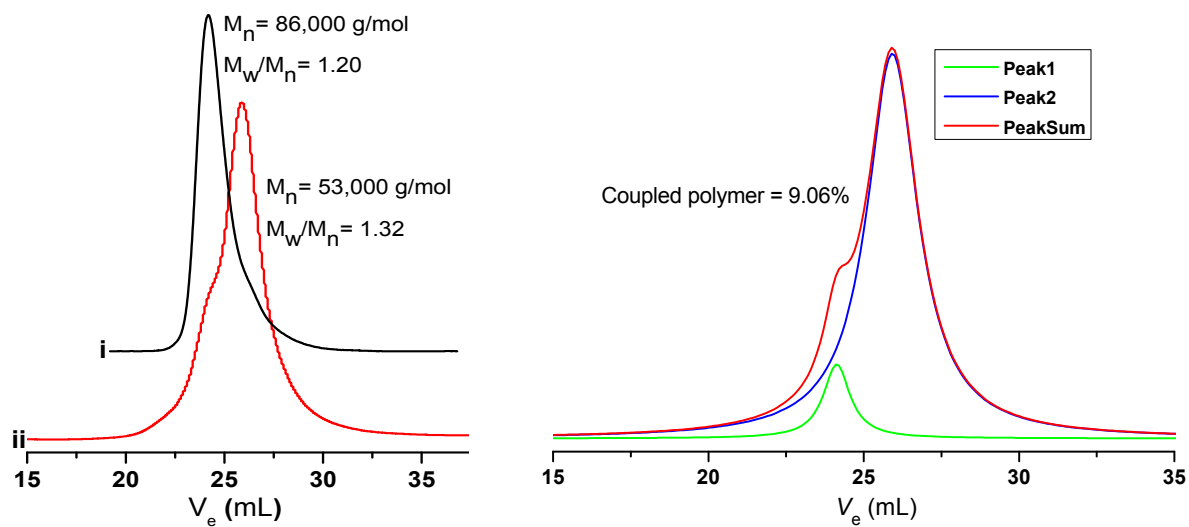
The dried PS-*co*-PAS polymer was dissolved into 1,4 dioxane in a round bottom flask, containing a stir bar, under nitrogen atmosphere and capped. Excess hydrazine (5x) was added drop-wise by syringe into the round bottom flask. After stirring for 48 h, the product was precipitated in cold methanol, filtered, and dried overnight at 80 °C.

### **Synthesis of poly(styrene-*co*-4-acetoxystyrene)-*graft*-hyperbranched glycidol**

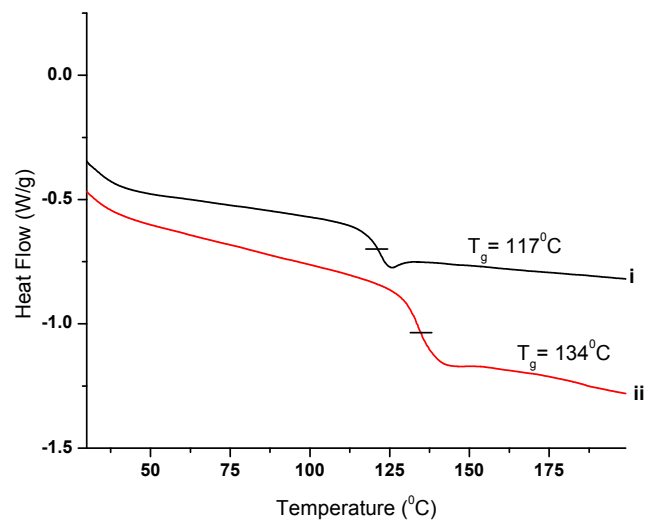
The polymerization was carried out in a flame-dried reactor containing a titrating finger. The apparatus was washed with DPMK in THF, and after washing the excess THF was re-distilled from the purge section into the main reactor for the polymerization. An ampule containing PS-*co*-HS in THF was introduced into the reactor. DPMK was slowly titrated in. This procedure achieved dissolution of the deprotonated macroinitiator close to 2:1 mole ratio of 4-hydroxystyrene monomer units-to-potassium. When the DPMK/macroinitiator solution began to turn from transparent to opaque, with a small amount of precipitant forming, the initiator ampule was flame cut from the reactor and the solution was heated to 35-40 °C. After the solution was heated the small amount of precipitant was re-dissolved and the solution remained opaque until the glycidol monomer was introduced at 35 °C. Shortly after the introduction of glycidol the reaction mixture again became transparent for the remainder of the reaction. The mixture was allowed to react for 48 h and was quenched using methanol. The polymer was precipitated into methanol and vacuum dried at 60 °C overnight.



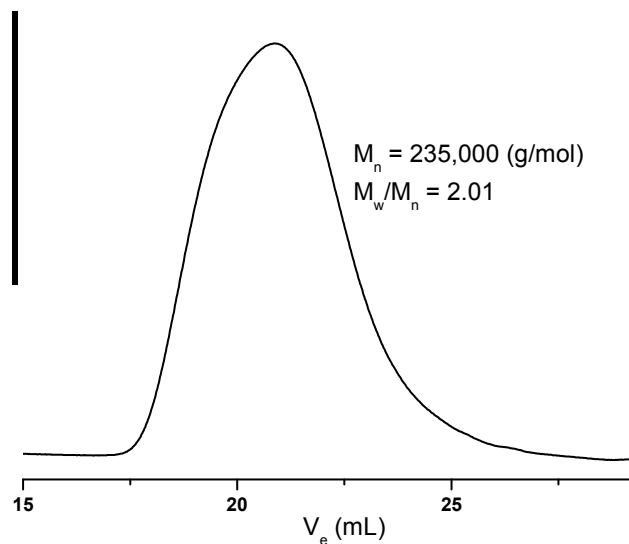
**Figure S1.**  $^1\text{H}$ -NMR spectra of PS-*co*-AS (i) and PS-*co*-HS (ii), indicating the signals (a) and (b) used for copolymer composition determination. Acetone- $d_6$  was used as the solvent (\*).



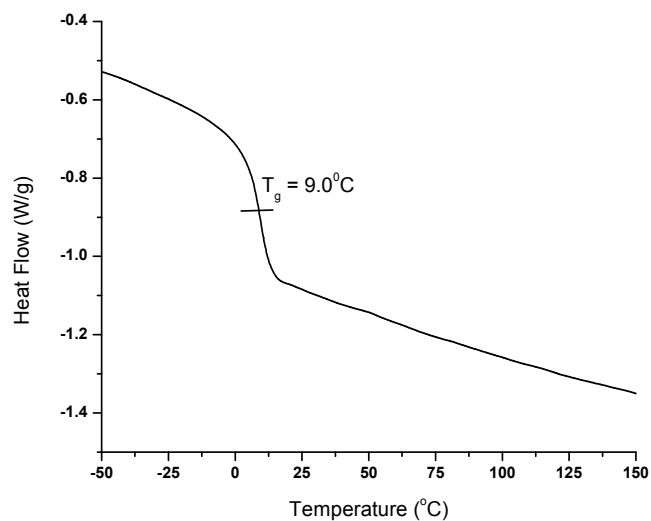
**Figure S2.** SEC chromatogram of PS-*co*-AS (i) and PS-*co*-HS (ii) (left) and end group coupling calculation for PS-*co*-HS (right).



**Figure S3. DSC thermogram of PS-co-AS (i) and PS-co-HS (ii).**



**Figure S4.** SEC chromatogram of hypergrafted polyglycidol. DMF was used as a solvent, eluting at 1mL/min, with toluene as a flow marker and standardized to linear PS.



**Figure S5.** DSC thermogram of hypergrafted polyglycidol.

#### References.

1. Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, 35, (18), 6754-6756.