

Supporting Information

Sustainable glucose-based block copolymers exhibit elastomeric and adhesive behavior

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Materials and Methods

Materials

4-Cyano-4-[(ethylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CEP) was purchased from Strem Chemicals, Newburyport, MA and was used as received. The tackifier (Sylvalite RE-80HP) was purchased from Arizona Chemicals, Jacksonville, FL and was used as received. All other reagents used in this study were purchased from Sigma-Aldrich, St. Louis, MO and were used as received. Acryloyl chloride and n-butyl acrylate (n-BA) were passed through an activated alumina column to remove the inhibitors and stored at $-20\text{ }^{\circ}\text{C}$ for future use.

Characterization

All ^1H NMR spectra were recorded at room temperature on a Bruker Avance III 500 MHz Spectrometer in CDCl_3 as the solvent. Chemical shifts are reported relative to the Tetramethylsilane (TMS) internal standard peak at 0.00 ppm. Size-exclusion chromatography (SEC) was performed in THF using a Waters Styragel guard column and 3 Waters Styragel columns (HR6, HR4, and HR1) in series with separation ability of $100\text{--}10,000,000\text{ g}\cdot\text{mol}^{-1}$. The columns were contained in an Agilent 1260 Infinity liquid chromatograph equipped with a Wyatt Dawn Heleos II multiangle light scattering detector and a Wyatt Optilab T-rEX refractive index detector. The dn/dc values were calculated from the refractive index signal using a known sample concentration and assuming 100% mass recovery from the column and were used for molar mass calculations. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Differential scanning calorimetry (DSC) measurements were carried out using a TA Instruments Discovery DSC under air. The glass transition temperature, T_g , values were determined on the second heating at a heating rate of 10

°C min⁻¹. Tensile testing was performed using a Shimadzu AGS-X tensile tester at room temperature on tensile bars that had gauge dimensions of approximately 10 mm×8 mm×0.2 mm. All samples were elongated at a speed of 5 mm per minute. Samples were annealed at 140 °C for 1-2 hours before testing. Five replicate tensile bars of each polymer sample were conducted. Small-angle X-ray scattering (SAXS) experiments were performed at the Sector 5-ID-D beamline of the Advanced Photon Source (APS) at Argonne National Laboratories, maintained by the Dow-Northwestern-Dupont Collaborative Access Team (DNDCAT), unless otherwise mentioned. The source produces X-rays with a 0.70 Å wavelength. The sample to detector distance was fixed at 7.491 m. Scattering intensity was monitored using a Mar 165 mm diameter CCD detector operating with a resolution of 2048 by 2048. The two dimensional scattering patterns were azimuthally integrated to afford one-dimensional profiles presented as spatial frequency (q) versus scattered intensity. Samples were annealed at 140 °C for 2 hours before the SAXS experiments.

Sample Preparation for Adhesion Testing:¹

For adhesion testing, solutions of the polymers (or a mixture of the polymer and tackifier) in ethyl acetate (EtOAc) were cast on a polyethylene terephthalate (PETE) film. Rosin esters were used as the tackifier (Sylvalite RE-80HP) and the tackifier concentration was 30 weight percent of the total solid content, where appropriate. The concentration of polymer/tackifier solution was 30 weight percent. As a representative example, 200 mg of P9 was dissolved in 520 µl EtOAc (or when using a tackifier, 140 mg of P9 and 60.0 mg of the Rosin ester tackifier were dissolved in 520 µl EtOAc). Then, the solution was evenly spread on a PETE film using a standard laboratory drawdown rod (two centimeters in diameter). The film was dried at room temperature

open to air in a chemical fume hood overnight. The resultant coated PETE film was cut into 2-cm wide strips for adhesion testing. The strips were approximately 5-cm long.

180° Peel Adhesion Testing:

The peel strength of the polymers were measured using a Shimadzu AGS-X tensile tester at a peel rate of 305 mm per minute. Two centimeter wide strips of the coated PETE films were placed on a clean stainless steel panel, as an adherend. To develop good contact between the adhesive and the steel plate, the coated film was gently pressed against the steel plate by manually rolling an electric tape roll on it. The strip was then peeled from the stainless steel panel. The reported average peel force and standard deviation values were acquired from at least five replicates.

Synthesis of the GATA monomer

A modified version of previously reported procedures^{2,3} was followed. To a dried one liter round bottom flask, anhydrous D-(+)-glucose (30.0 g, 167 mmol), trityl chloride (50.0 g, 180 mmol), and anhydrous pyridine (125 ml) were added sequentially. The mixture was placed in a preheated, well-mixed oil bath at 90°C until everything was fully dissolved. Then, acetic anhydride (90 ml) was added in one portion and allowed to stir at room temperature with the removal of the oil bath for 16 h. Afterward, the solution was slowly poured into a mixture of 4 liters of ice water and 250 ml acetic acid and then vigorously stirred for 4 hours. The resultant white precipitate was filtered and washed with cold water and dried under fume hood overnight. The solid obtained was dispersed in 100 ml ethyl ether and stirred for 10 minutes. The solid obtained was then vacuum filtered to afford 6-trityl-d-glucose-1,2,3,4-tetraacetate (TGTA) (49.5 g, 50.2 % isolated yield). ¹H NMR (CDCl₃): δ 1.60-2.20 (m, 12H, CH₃-CO); 3.05 (dd, 1H); 3.33

(dd, 1H), 3.63-3.75 (m, 1H); 5.10-5.30 (m, 3H); 5.68-5.78 (m, 1H, O-CH-O-CO-CH₃); 7.15-7.50 (m, 15H) ppm (Figure S1a).

Next, TGTA (25.0 g, 42.4 mmol), 2 ml water, and 40 ml dichloromethane were mixed in a 250 ml round bottom flask. 12.5 ml trifluoroacetic acid was slowly added and the mixture stirred at room temperature for 10 minutes. The mixture was diluted with 100 ml dichloromethane and 100 ml water and transferred into a separatory funnel. Another wash with dichloromethane was performed with 200 ml dichloromethane. The organic wash solutions were combined and washed with a saturated solution of NaHCO₃ (250 ml) and then water (2 x 250 ml). The organic layers were then dried over magnesium sulfate and concentrated by rotary evaporation. The resulting viscous solution was dissolved in a minimum amount of anhydrous ether, and agitated with a glass rod to induce recrystallization, which was left in a refrigerator overnight. The resulting white crystals, D-glucose-1,2,3,4-tetraacetate (GTA, 10.8 g, 73.0% isolated yield) were vacuum filtered and dried at ambient conditions. ¹H NMR (CDCl₃): δ 2.00-2.12 (m, 12H, CH₃-CO); 2.21 (dd, 1H, -CH₂-OH); 3.54-3.82 (m, 3H), 5.05-5.15 (m, 2H); 5.31 (t, 1H); 5.72 (d, 1H, O-CH-CH-OH) ppm (Figure S1b).

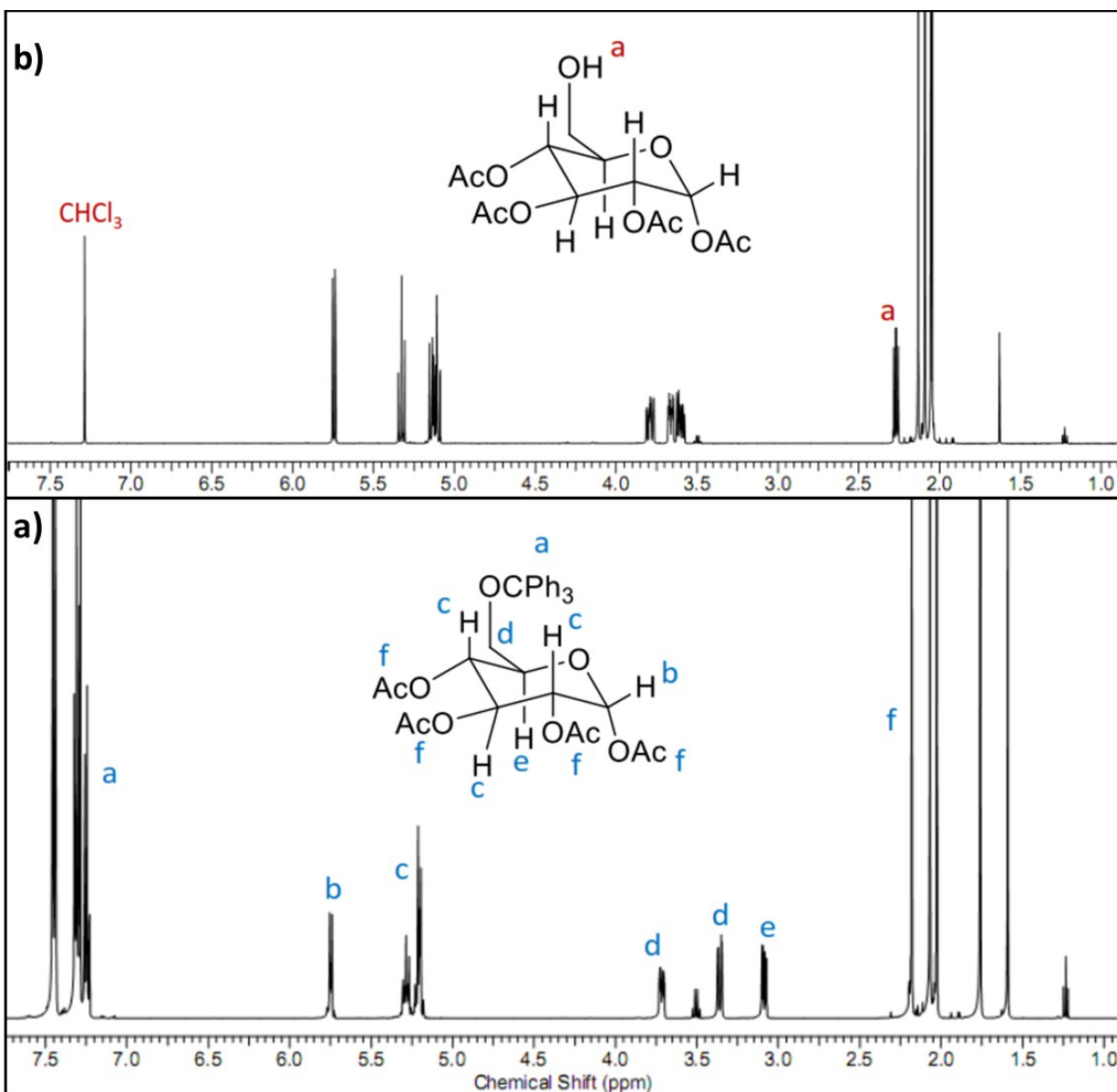


Figure S1. a) ^1H NMR spectrum of TGTA. b) ^1H NMR spectrum of GTA, 500 MHz, CDCl_3 . Non-assigned peaks at 1.25, 1.65, and 3.5 ppm correspond to diethyl ether, water, and diethyl ether, respectively.

Next, a solution of GTA (5.00 g, 14.4 mmol) and triethylamine (4.35 g, 43.1 mmol) in 20 ml dichloromethane was added dropwise to a stirred 0 °C solution of acryloyl chloride (3.60 g, 39.8

mmol) in 100 ml dichloromethane in a 250 ml round bottom flask. After 2 h, the mixture was allowed to warm to room temperature and was stirred for an additional 14 h. The solvent was then removed by evaporation. The remaining solid was dissolved in 10 ml dichloromethane and passed through a plug of silica gel using 500 ml of an ethyl acetate:hexanes (80:20) mixture. The solvent was removed to afford glucose-6-acrylate-1,2,3,4-tetraacetate (GATA, 5.15 g, 88.9% isolated yield). ^1H NMR (CDCl_3): δ 1.95-2.15 (m, 12H, $\text{CH}_3\text{-CO}$); 3.84-3.91 (m, 1H), 4.20-4.30 (m, 2H), 5.08-5.14 (m, 2H), 5.23 (t, 1H), 5.70 (d, 1H, O-CH-CH-OH), 5.86 (d, 1H), 6.12 (dd, 1H), 6.42 (d, 1H) ppm (Figure S2).

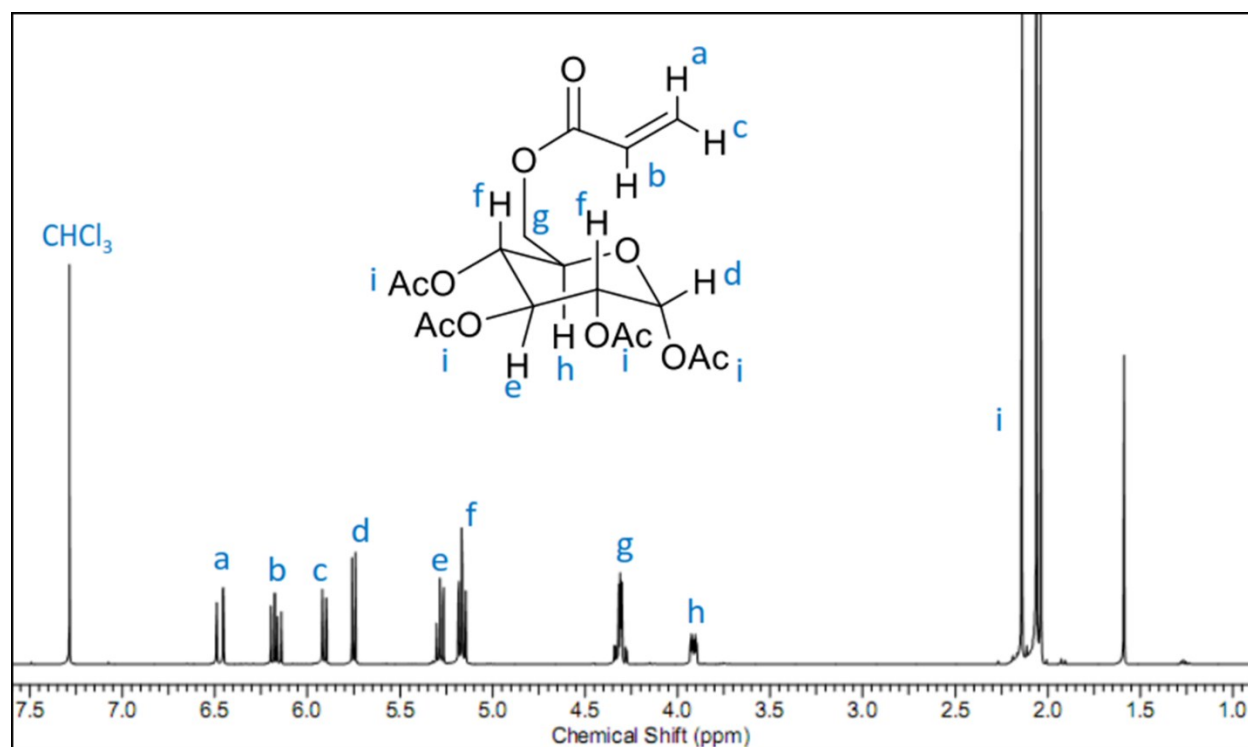


Figure S2. ^1H NMR spectrum of GATA, 500 MHz, CDCl_3 . Non-assigned peak at 1.65 ppm corresponds to water.

Polymer Synthesis

Poly(glucose-6-acrylate-1,2,3,4-tetraacetate) (PGATA):

An illustrative example is provided. P1: To a 10 ml round-bottom flask equipped with a teflon stirring bar was added 4-cyano-4-(ethylsulfanylthiocarbonyl) sulfanylpentanoic acid (CEP) (29.0 mg, 0.110 mmol), AIBN (1.80 mg, 0.011 mmol), GATA (2.00 g, 4.98 mmol), and 3 ml of dimethylformamide (DMF). The flask was sealed and the mixture was degassed by purging with nitrogen at room temperature for 30 minutes. Subsequently, the reaction vessel was submerged into a thermostated oil bath at 70 °C for 13 hours. The polymerization was quenched by immediately placing the flask into liquid nitrogen and opening it to air. The reaction mixture was diluted by adding 2 ml of methylene chloride, and subsequently the polymer was precipitated in 100 ml of ice-cold methanol. The yellow solid was isolated via filtration and the resulting PGATA-CTA powder was dried under vacuum at 40 °C (1.70 g, 85.0% isolated yield). $M_n = 21 \text{ kg}\cdot\text{mol}^{-1}$ (full conversion), $D = 1.17$. $^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 1.4\text{-}2.5$ (br m, CH, CH_2 , CH_3), $3.9\text{-}4.4$ (br m, CH_2 and CH), $5\text{-}5.2$ (br m, CH and CH), $5.3\text{-}5.5$ (br m, CH), $5.7\text{-}5.9$ (br m, CH) ppm.

Poly(glucose-6-acrylate-1,2,3,4-tetraacetate)-*b*-poly(*n*-butyl acrylate) (PGATA-*b*-PnBA):

An illustrative example is provided. P5: To synthesize the PGATA-PnBA block copolymer, AIBN (0.660 mg, 0.004 mmol), the relevant macro-CTA (i.e. PGATA-CEP) (P1) (300 mg, 0.014 mmol), *n*-BA (1.50 ml, 10.4 mmol) and 5 ml of *n*-butyl acetate were mixed in a 10 ml round-bottom flask equipped with a teflon stirring bar. The flask was sealed and the mixture was degassed under inert nitrogen at room temperature for 30 minutes. Subsequently, the reaction vessel was submerged into a preheated, stirred oil bath maintained at 70 °C. After 14 hours, the

reaction was quenched by immediately placing the flask into liquid nitrogen and opening it to air. CH_2Cl_2 (2 ml) was added to the mixture, and subsequently the polymer was precipitated in 150 ml of ice-cold methanol. The precipitates were isolated via gravity filtration and dried under vacuum at 40 °C (1.00 g, 82.8% isolated yield). $M_n(\text{PnBA}) = 65 \text{ kg}\cdot\text{mol}^{-1}$ (68% conversion), $\bar{D} = 1.20$. $^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.9\text{--}1.1$ (m, $\text{CH}_3\text{-PnBA}$), $1.3\text{--}2.4$ (br m, CH-PGATA and PnBA , $\text{CH}_2\text{-PGATA}$ and PnBA , $\text{CH}_3\text{-PGATA}$, $\text{CH}_2\text{-PnBA}$, $\text{CH}_2\text{-PnBA}$), $3.9\text{--}4.4$ (br m, $\text{CH}_2\text{-PGATA}$ and PnBA , CH-PGATA), $5\text{--}5.2$ (br m, CH-PGATA and CH-PGATA), $5.3\text{--}5.5$ (br m, CH-PGATA), $5.7\text{--}5.9$ (br m, CH-PGATA).

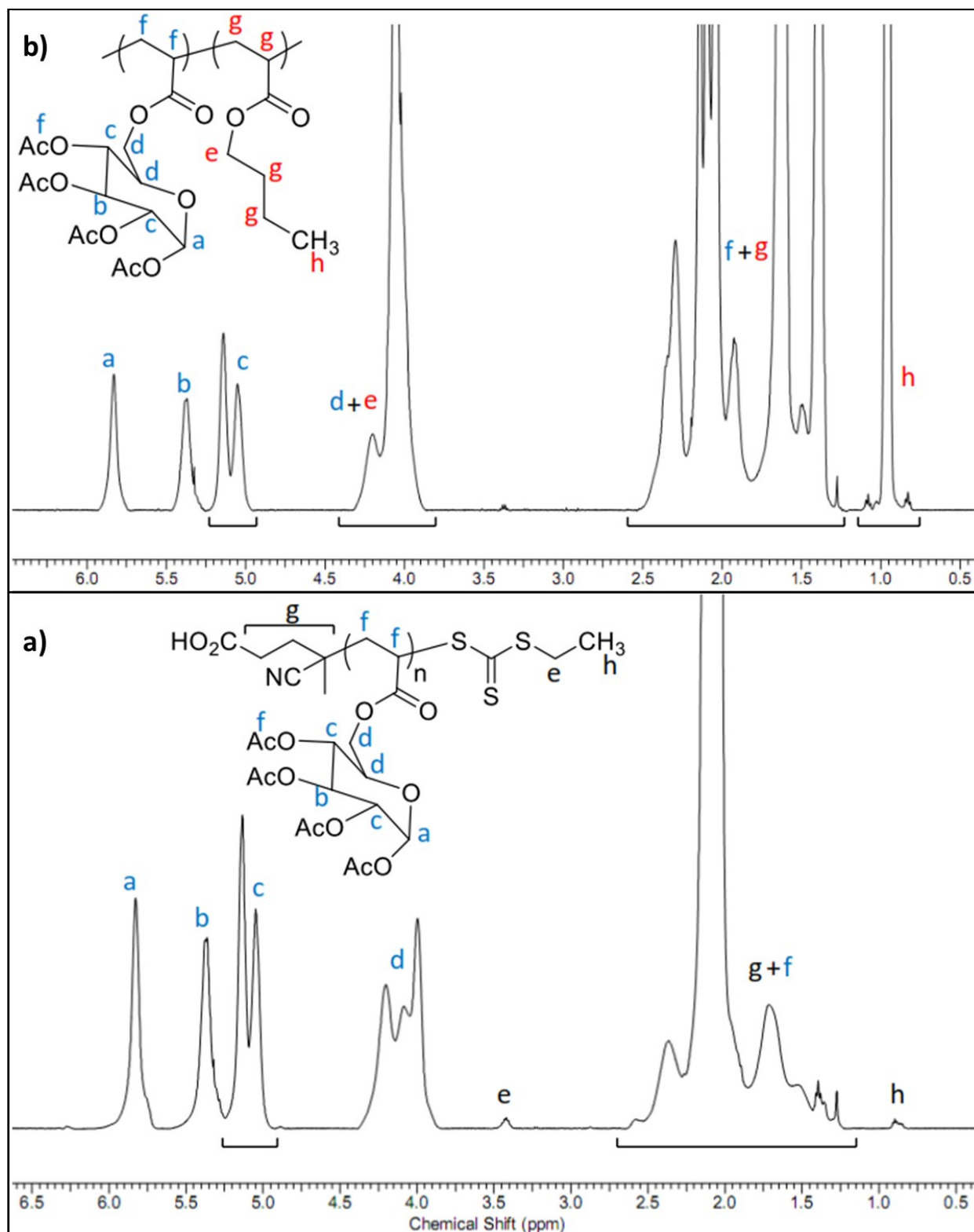


Figure S3. Representative ^1H NMR spectra of a) PGATA and b) PGATA-*b*-PnBA, 500 MHz, CDCl_3 .

Poly(glucose-6-acrylate-1,2,3,4-tetraacetate)-*b*-poly(n-butyl acrylate)-trithiocarbonate-poly(n-butyl acrylate)-*b*-poly(glucose-6-acrylate-1,2,3,4-tetraacetate) (PGATA-*b*-PnBA-trithiocarbonate-PnBA-*b*-PGATA):

An illustrative example is provided. P9: to synthesize the triblock copolymers that carry the trithiocarbonate functionality within the midblock, AIBN (0.500 mg, 0.003 mmol), the relevant macro-CTA (i.e. PGATA-DTC macro-CTA) (P3) (150 mg, 0.007 mmol), n-BA (1.25 ml, 8.69 mmol) and 6 ml of n-butyl acetate were mixed in a 10 ml round-bottom flask equipped with a teflon stirring bar. The flask was sealed and the mixture was degassed under inert nitrogen at room temperature for 45 minutes. Subsequently, the reaction vessel was submerged into a preheated, stirred oil bath maintained at 80 °C. After 52 hours, the reaction was quenched by immediately placing the flask into liquid nitrogen and opening it to air. CH₂Cl₂ (2 ml) was added to the mixture, and subsequently the polymer was precipitated in 200 ml of ice-cold methanol. The precipitates were isolated via gravity filtration and dried under vacuum at 40 °C (750 mg, 73.0% isolated yield). M_n (PnBA)= 126 kg.mol⁻¹ (79% conversion), D =1.16. ¹HNMR (CDCl₃, 500 MHz): δ = 0.9-1.1 (m, CH₃- PnBA), 1.3-2.4 (br m, CH- PGATA and PnBA, CH₂- PGATA and PnBA, CH₃- PGATA, CH₂- PnBA, CH₂- PnBA), 3.9-4.4 (br m, CH₂- PGATA and PnBA, CH- PGATA), 5-5.2 (br m, CH- PGATA and CH- PGATA), 5.3-5.5 (br m, CH- PGATA), 5.7-5.9 (br m, CH- PGATA).

Poly(n-butyl acrylate) (PnBA):

The synthesis of n-butyl acrylate macro-CTA was performed in bulk. AIBN (3.50 mg, 0.021 mmol), 3,5-bis(2-dodecylthiocarbonothioylthio-1-oxopropoxy)benzoic acid (BTCBA) (100 mg,

0.122 mmol), and n-butyl acrylate (9.80 ml, 68.1 mmol) were mixed in a 25 ml round-bottom flask equipped with a teflon stirring bar. The flask was sealed and the mixture was degassed under inert nitrogen at room temperature for 45 minutes. Subsequently, the reaction vessel was submerged into a preheated, stirring oil bath maintained at 70 °C. After 1.5 hours, the reaction was quenched by immediately placing the flask into liquid nitrogen and opening it to air. 10 ml of CH₂Cl₂ was added to the mixture, and subsequently the polymer was precipitated in 400 ml of ice-cold methanol and was left in the freezer for two hours. The precipitates were isolated by decanting off the supernatant fluid. The procedure was repeated three times and precipitates were dried under vacuum at 40 °C (4.15 g, 61.2% isolated yield). M_n (PnBA)= 56 kg.mol⁻¹ (78% conversion), $D = 1.04$. ¹HNMR (CDCl₃, 500 MHz): δ = 0.9-1.1 (m, CH₃), 1.2-2 (br m, CH₂, CH₂, CH₂), 2.2-2.4 (br m, CH), 3.9-4.1 (br m, CH₂).

Poly(glucose-6-acrylate-1,2,3,4-tetraacetate)-*b*-poly(n-butyl acrylate)-*b*-poly(glucose-6-acrylate-1,2,3,4-tetraacetate) (PGATA-*b*-PnBA-*b*-PGATA):

An illustrative example is provided. P12: to synthesize triblock copolymers with the bifunctional CTA, AIBN (0.600 mg, 0.004 mmol), the relevant macro-CTA (i.e. PnBA-BTCBA macro-CTA) (1.00 g, 0.018 mmol), GATA (600 mg, 1.49 mmol), 4 ml of n-butyl acetate, and one ml of dimethylformamide were mixed in a 10 ml round-bottom flask equipped with a teflon stirring bar. The flask was sealed and the mixture was degassed under inert nitrogen at room temperature for 45 minutes. Subsequently, the reaction vessel was submerged into a preheated, stirred oil bath maintained at 70 °C. After 43 hours, the reaction was quenched by immediately placing the flask into liquid nitrogen and opening it to air. CH₂Cl₂ (2 ml) was added to the mixture, and subsequently the polymer was precipitated in 300 ml of ice-cold methanol. The precipitates were isolated via gravity filtration and dried under vacuum at 40 °C (1.10 g, 89.1% isolated yield). M_n

(PGATA) = 13 kg.mol⁻¹ (39% conversion), $\bar{D} = 1.07$. ¹H NMR (CDCl₃, 500 MHz): δ = 0.9-1.1 (m, CH₃- PnBA), 1.3-2.4 (br m, CH- PGATA and PnBA, CH₂- PGATA and PnBA, CH₃- PGATA, CH₂- PnBA, CH₂- PnBA), 3.9-4.4 (br m, CH₂- PGATA and PnBA, CH- PGATA), 5-5.2 (br m, CH- PGATA and CH- PGATA), 5.3-5.5 (br m, CH- PGATA), 5.7-5.9 (br m, CH- PGATA).

Supplementary Figures

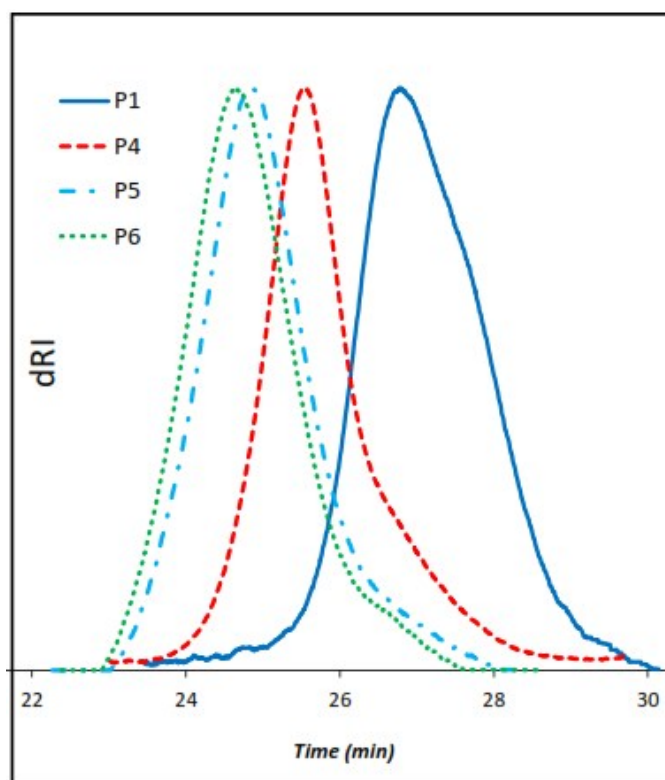


Figure S4. SEC traces of the PGATA-*b*-PnBA diblock copolymers [P4-P6] and the corresponding macro-CTA [P1] (eluent: THF, at room temperature).

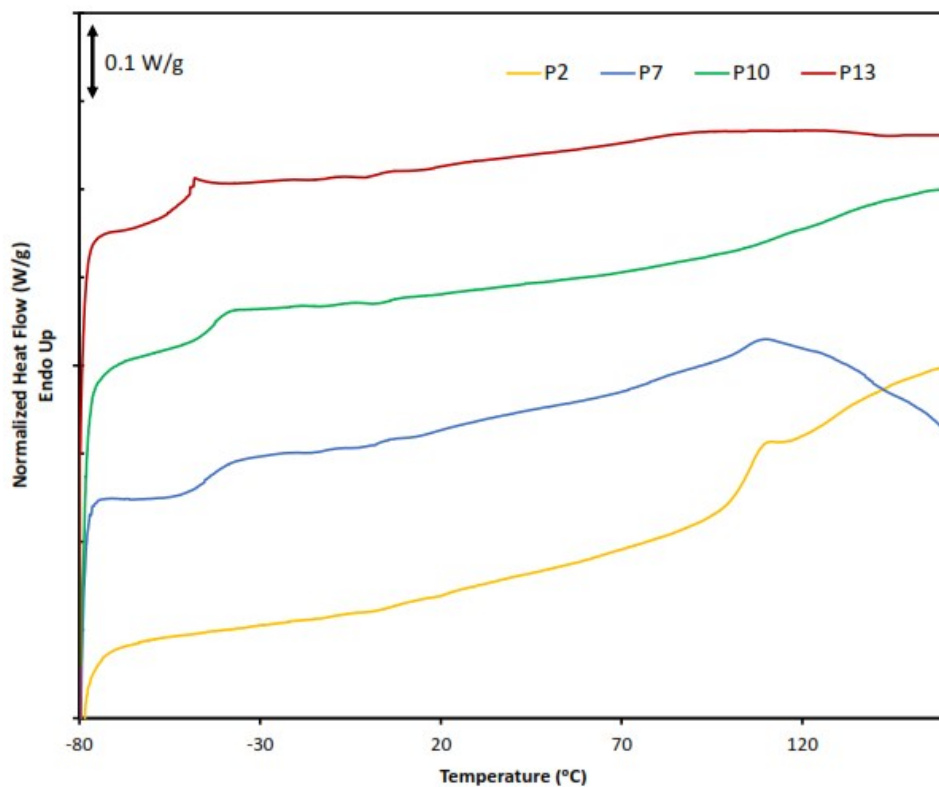


Figure S5. Representative DSC traces of the two groups of the triblock copolymers: P7 (PGATA-PnBA-PGATA: 12-29-12 kDa) and P13 (PGATA-PnBA-PGATA: 9-56-9 kDa), and their corresponding macro-CTAs, P2 and P10, respectively.

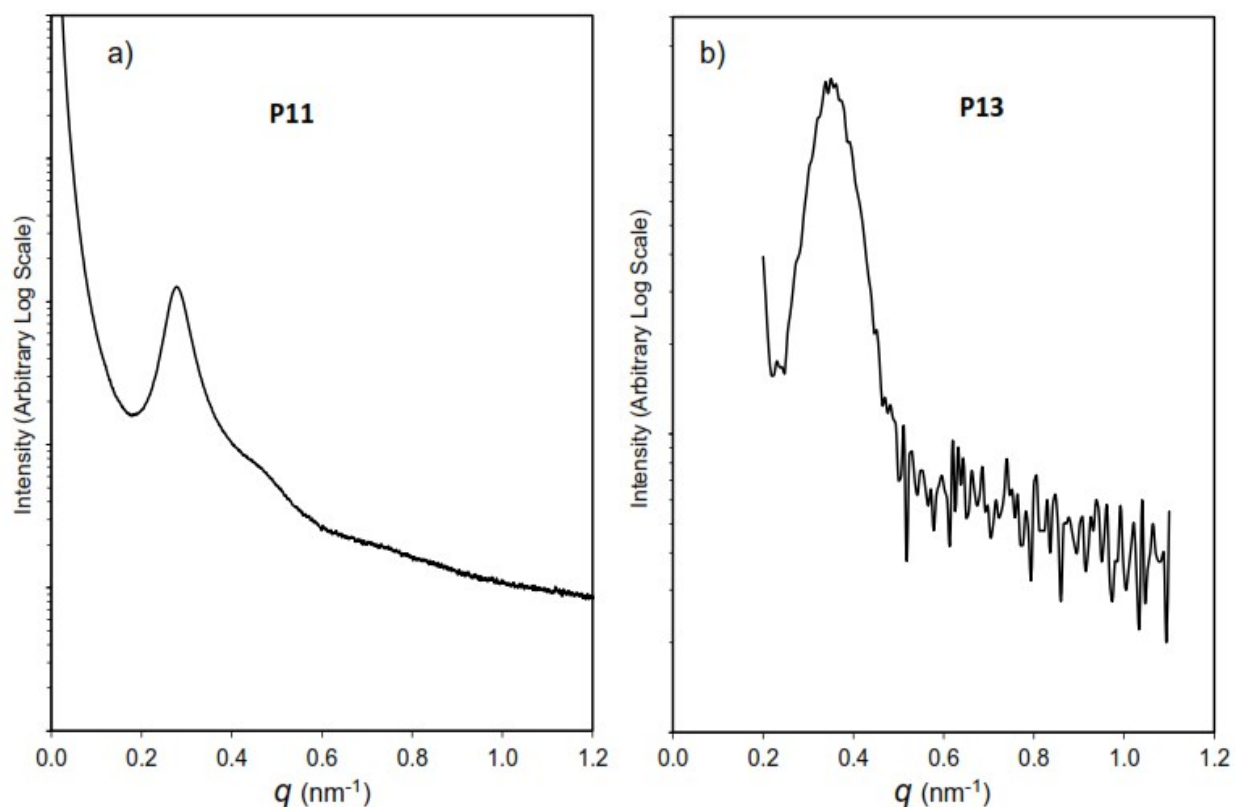


Figure S6. Experimental 1D SAXS profile of a) P11 (PGATA-PnBA-PGATA: 4-56-4 kDa) and b) P13 (PGATA-PnBA-PGATA: 9-56-9 kDa) at 25 °C. b) P13 SAXS data was acquired using a home-built instrument. The sample to detector distance was 2.15 meters and the beam source produces X-rays with 1.54 Å wavelengths.

References

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2. M. Mahkam, *Drug Delivery*, 2007, **14**, 147-153.
3. J. M. Ting, T. S. Navale, F. S. Bates and T. M. Reineke, *Macromolecules*, 2014, **47**, 6554-6565.