

Glucose-Functionalized Polystyrene Particles Designed for Selective Deposition of Silver on the Surface

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Materials

α -D-(+)-Glucose (anhydrous, 96%), methyl acrylate (99%), silver nitrate (>99%) and styrene (99%) were purchased from Sigma Aldrich. Styrene was degassed and stored under nitrogen. Prior to use it was purified through column chromatography on aluminum oxide to remove the inhibitor. Divinylbenzene, *tert*-butanol (p.a.), tin(II) chloride (anhydrous), aqueous ammonia (25 wt-%) and hexamethylenetetramine were purchased from Merck. Potassium peroxydisulfate (>99%) was purchased from Fluka. Polyvinylpyrrolidone (PVP, dry, molecular weight ~40,000) was purchased from VWR BDH Prolabo. Novozyme 435 (Lipase B from *Candida Antarctica* immobilized on a macroporous acrylic resin, 10,000 U/g) was purchased from Novo Nordisk, dried *in vacuo* at room temperature for 24 hours and stored under nitrogen atmosphere.

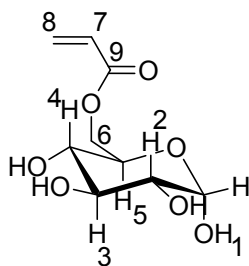
Measurements

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 FT-NMR spectrometer at 400 and 100 MHz, respectively. Deuterated dimethyl sulfoxide (DMSO- d_6) was used as solvent and tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a Thermo Nicolet Nexus 470 spectrometer. The spectra were measured using an ATR unit, SMART SPLITPEA fitted with a Si crystal. For one spectrum 400 scans were collected. Dynamic light scattering (DLS) and zeta potential measurements were performed at 25°C using a Zetasizer Nano Series (Malvern Instruments). Field emission scanning electron microscopy (FESEM) images were acquired using a Hitachi S4800 FE-SEM. For sample preparation one droplet of the particle dispersion was placed on a silicon wafer and dried at room temperature. The samples were sputtered with gold. Particle diameters from FESEM images were determined using MATLAB. For average diameter and standard deviation at least 200 particles per sample were measured. TEM studies were performed using a JEOL ARM 200 probe corrected TEM, operated at 200 kV. Imaging of the particles was performed in high-angle annular dark field (HAADF) – Scanning TEM (STEM) mode. Energy Dispersive X-ray Spectroscopy (EDS) spectra were recorded using a 100 mm² Centurio SDD detector. EDS mappings were obtained in STEM mode by acquiring full spectra in grids of either 256*256 or 512*512 pixels. All mappings were obtained by summation of 50-100 frames, each having 0.1 msec acquisition time per pixel per frame. In this way, the particles remained unaffected by the impact of the incident electron beam. Thermogravimetric analysis (TGA) was performed using a Discovery TGA (TA Instruments). Samples were loaded in platinum pans and ramped at 10°C/min to 900°C under dry air with a flow rate of 20 mL/min.

Glucose acrylate

Table S1. Lipase catalyzed transacylation reactions of glucose and methyl acrylate; starting materials and reaction conditions:

No	Methyl acrylate:glucose mol/mol	$T / ^\circ\text{C}$	Solvent
1	1:1	35	<i>tert</i> -butanol
2	1:1	55	<i>tert</i> -butanol
3	1:1	70	<i>tert</i> -butanol
4	2.5:1	55	<i>tert</i> -amyl alcohol
5	2.5:1	55	<i>tert</i> -butanol



^1H NMR (DMSO- d_6): δ (ppm) = 6.22- 5.85 (H⁷, H⁸), 4.91 (H¹), 3.8- 3.5 (H⁶, H⁴), 3.4 (OH), 6.22- 5.85 (H², H³, H⁵).

^{13}C NMR ($\text{DMSO-}d_6$): δ (ppm) = 168 (C^9), 131.5 (C^8), 128.2 (C^7), 96.85 (C^1), 76.33 (C^5), 74.63 (C^3), 73.33 (C^2), 72.12 (C^4), 64.16 (C^6).

IR (Si) (cm^{-1}): 3316 (OH), 1724 (ester), 1636 (alkene).

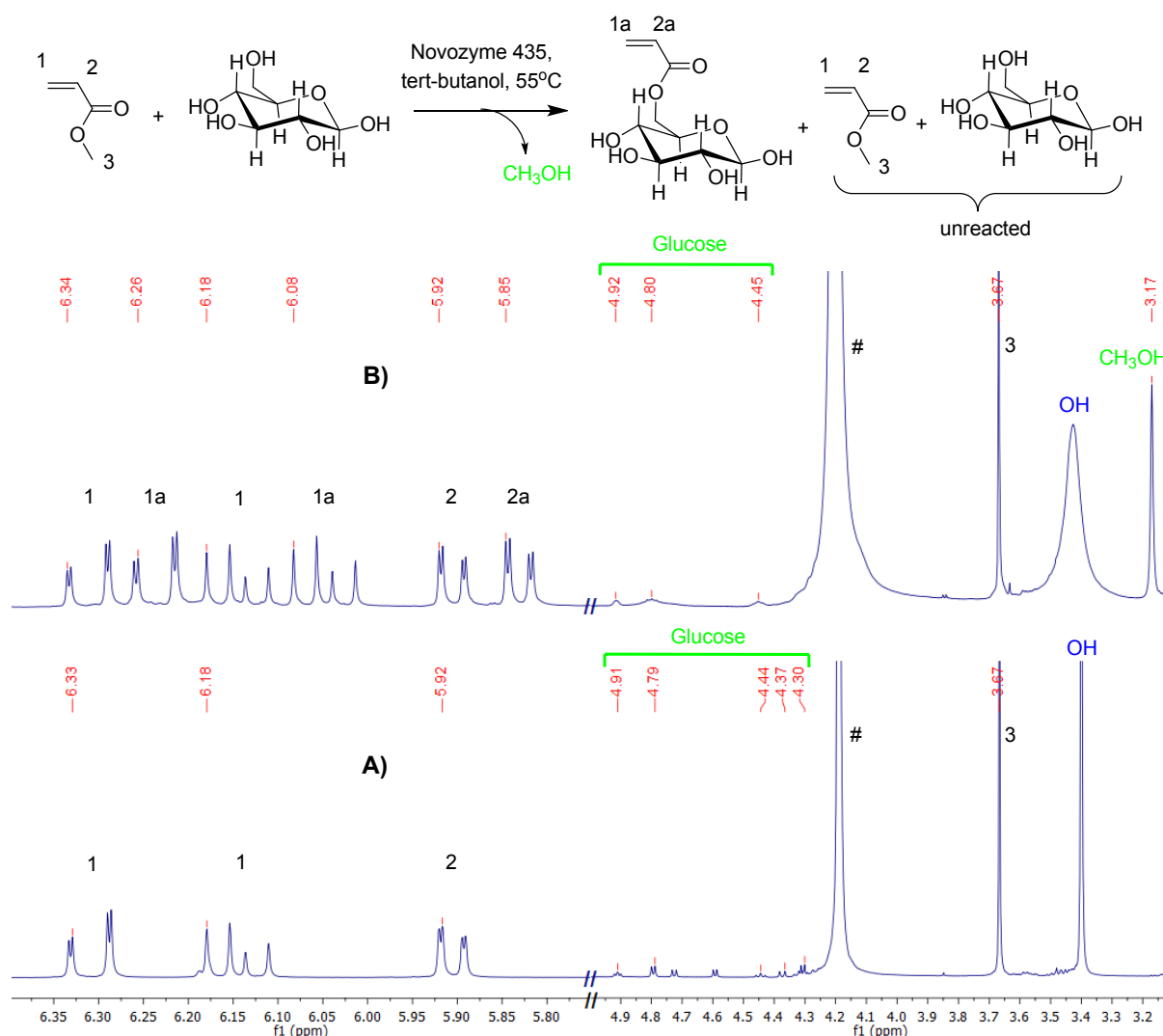


Figure S1. ^1H NMR spectra of (A) the mixture of methyl acrylate and glucose – starting materials (MA: glucose in the reaction feed 2.5:1) and (B) the mixture after transacylation (24 hours) (In the product mixture, MA : MeOH = 1.87:1 and MA: glucose acrylate = 1.8:1) (# = solvent peaks (*tert*-butanol)).

Kinetic study

To a suspension of glucose (**1**) (230 mg, 1.28 mmol) in tertiary alcohol (40 mL), methyl acrylate (**2**) (290 mg, 3.34 mmol) was added. The reaction was initiated by the addition of Novozyme 435 (1.00 g) and the mixture was stirred for 24 hours in inert gas atmosphere at 55°C. Periodically samples were withdrawn from the reaction mixture and the consumption of substrate (methyl acrylate) and formation of glucose acrylate (**3**) was followed via ^1H NMR spectroscopy.

For studying the conversion/time dependence and the effect of solvent on the transacylation reaction the experiments 4 and 5 of table S1 were analyzed.

Glucose was reacted with methyl acrylate (mole ratio glucose: methyl acrylate = 1: 2.5) using Novozyme 435 as catalyst at 55°C in *tert*-butanol or in *tert*-amyl alcohol. At different reaction times samples were analyzed via ^1H NMR spectroscopy and the conversion of methyl acrylate was determined (Figure S2). It was found that the conversion of methyl acrylate was higher, when the reaction was performed in *tert*-butanol. In all experiments the reaction reaches equilibrium after 6 hours and after this the conversion remains constant. The maximum conversion was around 35% in *tert*-butanol and 30 % in *tert*-amyl alcohol.

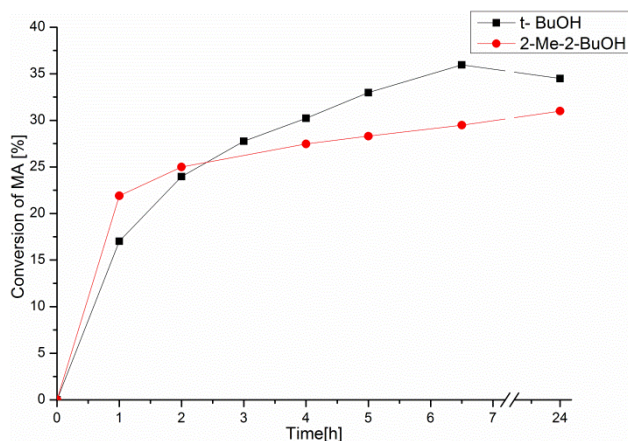


Figure S2. Transacylation of glucose using methyl acrylate as acyl donor and Novozyme 435 as catalyst. Conversion/time dependence in *tert*-butanol and *tert*-amyl alcohol as solvents.

Polystyrene particles

Glucose acrylate (12.5 mg, 1.0 wt. % with respect to styrene) was dissolved in degassed water (50 mL). Then, styrene (1.25 g) and divinylbenzene (62.5 mg, 5.0 wt.-%) were added. The resulting reaction mixture was heated to 80°C and stirred with a magnetic bar at a speed of 240 rpm. Subsequently, potassium peroxydisulfate (12.5 mg, 1.0 wt. %) was added and the mixture was stirred at 80°C for 14 h. The filtered dispersion was centrifuged at 11000 rpm for 30 minutes after which the supernatant was removed and the residue was dispersed in demineralized water (50 mL) using an ultrasonic bath for 15 minutes. This procedure was repeated one time.

All other latex syntheses were performed according to this procedure (Table S2).

Table S2. Polystyrene particles **4A-D**; average particle diameter and polydispersity index (PDI) were determined by DLS analysis and were calculated from FESEM images.

Latex particle	Glucose acrylate		Particle diameter DLS [nm]	PDI DLS	Zeta potential [mV]	Particle diameter SEM [nm]	Size distribution SEM	yield [%]
	mg	wt.-% ^{a)}						
4A	12.5	1	402	0.024	-40.1	391	0.036	96
4B	25	2	353	0.034	-45,7	339	0.032	96
4C	50	4	260	0.019	-37.0	267	0.041	92
4D	100	8	221	0.042	-34.2	218	0.050	89

a) Weight percent with respect to amount of styrene used.

Zeta potential study

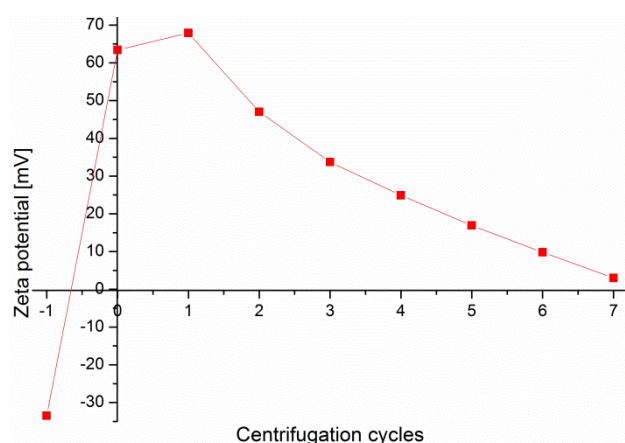


Figure S3. Zeta potential measurements of Sn²⁺-sensitized polystyrene particles **4D** after various centrifugation cycles; value at -1 cycle represents zeta potential of pure latex particles.

Polystyrene-Ag composites

Latex dispersion (300 μL, 1.2 wt. %) was added to a solution of tin(II) chloride in water (40 mL, 2.2 x 10⁻² M). The mixture was stirred for one hour at room temperature and afterwards centrifuged three times for 30 minutes at 6000 rpm and redispersed in demineralized water (40 mL) using an ultrasonic bath. Subsequently the mixture was added to a solution of

silver nitrate (24 mg) and aqueous ammonia (75 μL , 25 wt-%) in water (40 mL). The resulting reaction mixture was stirred for one hour at 75°C. Then, hexamethylenetetramine (20 mg) was added and the mixture was stirred for one hour at 75°C. To prevent agglomeration of the resulting polystyrene-silver CSPs, PVP (250 mg) was added after cooling to room temperature. The dispersion was centrifuged at 4000 rpm for 30 minutes after which the supernatant was removed and the residue was dispersed in demineralized water using an ultrasonic bath for 15 minutes. This procedure was repeated one time.

Table S3. Wt.-% of Ag and polystyrene (PS) of polystyrene-Ag composites **5A-D** determined by TGA.

Polystyrene-Ag composites	Wt.-% of Ag	Wt.-% of PS
5A	28%	72%
5B	37%	63%
5C	43%	57%
5D	50%	50%

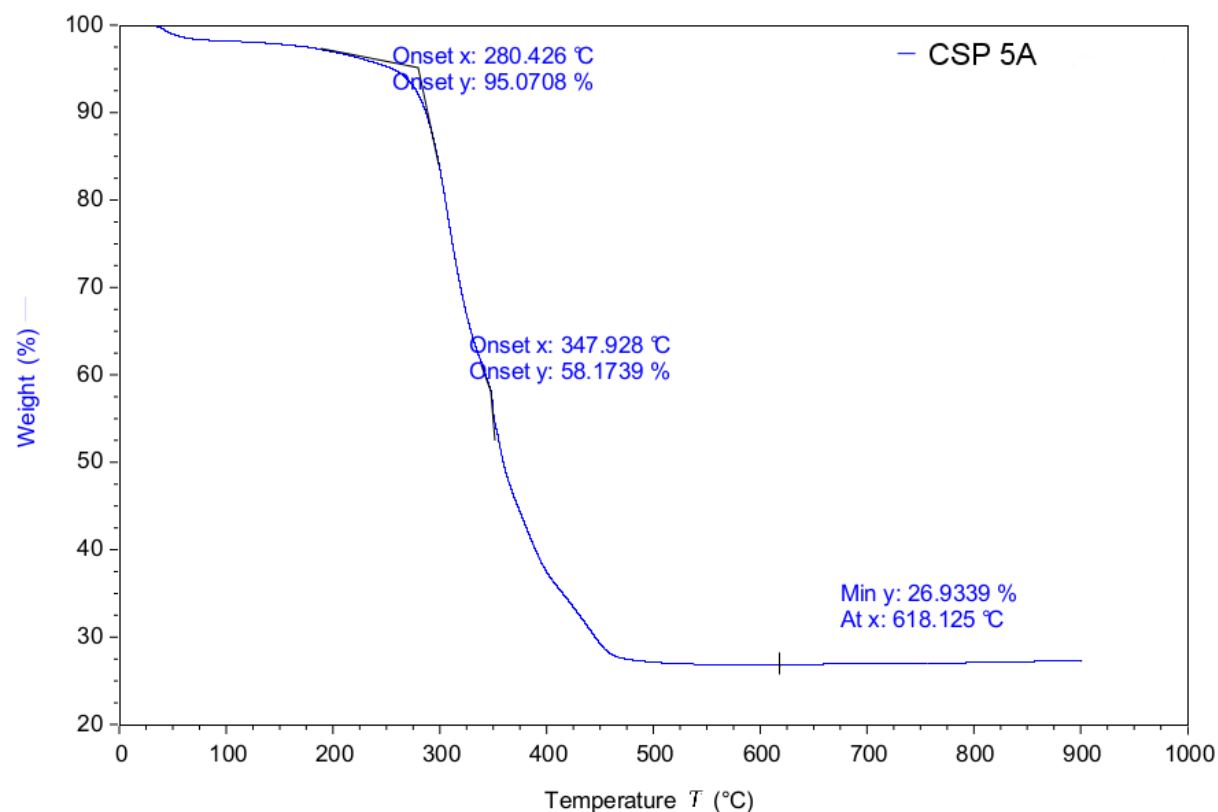


Figure S4. TGA curve of polystyrene-Ag composites 5A; polystyrene started to decompose at 280°C; at 618°C only Ag exists.

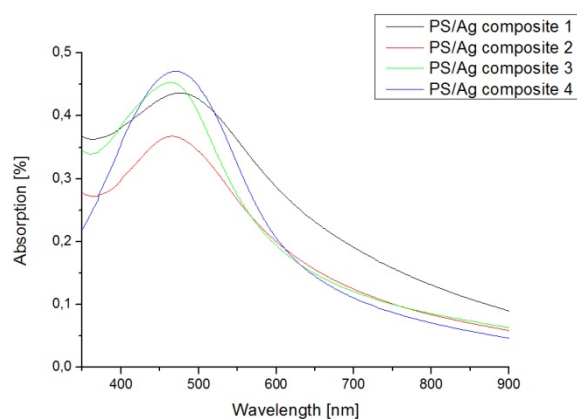


Figure S5. UV/Vis absorption spectra of polystyrene-Ag composites 5A-D with absorption maxima between 470 and 490 nm.