# Versatile procedure for site-specific grafting of polymer brushes on patchy particles via Atom Transfer Radical Polymerization (ATRP).

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### **Supporting Information**

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#### S1 Infrared (IR) spectra of spherical, chlorinated seed particles.



**Figure S1.** (a) Infrared (IR) spectra of non-functionalized, cross-linked polystyrene colloids (CPs, bottom black spectrum), spherical chlorinated core-shell particles obtained after coating CPs with a mixture of VBC, styrene and DVB (CPs-CI-75, middle red spectrum) and chlorinated colloids with a shell composed of only VBC and DVB (CPs-CI-100, top blue spectrum). The chlorine signal (1266 cm<sup>-1</sup> of CPs-CI-100 is slightly more intense compared to the signal measured for CPs-CI-75 due to a larger fraction of VBC per particle. (b) X-ray photoelectron spectrum (XPS) of chlorinated seed particles (CPs-CI-100). All signals are labelled with the corresponding element.

#### S2 Distinguishing protrusion from seed lobe by analyzing shape of two-patch particles.

The procedure to prepare the dumbbell-shaped colloids used throughout this paper relies on an internal phase separation from a monomer swollen seed particle (Figure S2, grey spheres). Due to swelling of the cross-linked chlorinated colloids, an elastic stress is induced onto the polymer network. This stress can be relieved by a (thermally induced) phase separation. Upon heating, the polymer network contracts and excess monomer is expelled from the seed in the form of a liquid protrusion (Figure S2, yellow lobe).

These protrusions can in principle merge to lower the total monomer (oil) – water interface present in the system.<sup>1</sup> Upon merging, two-patch particles are formed which consist of two lobes originating from the seed particles and one central liquid lobe having twice the volume of the originally formed liquid protrusion. From the dimensions of this central lobe it can therefore be deduced which lobe of monomeric dumbbells was initially liquid and corresponds to the formed protrusion. Dumbbell-shaped colloids with small protrusion will form more or less linear two-patch particles due to the limited volume of the central lobe. Dumbbells with protrusions larger than the seed will form more spherical two-patch particles with a large central domain.

The orientation of the chlorinated patches is uniform and reproducible. The origin for this reproducible shape is not completely clear, although Kraft et al. speculated that the seed particles are pushed together via a depletion force generated by the formed polymers during polymerization of the central monomer lobe.<sup>2</sup>



**Figure S2.** (a) Schematic representation of the expected geometry of two-patch particles (right) as a function of the size of the protrusion on a monomeric dumbbell (left). Smaller protrusions lead to the formation of more linear two-patch particles. (b) Transmission electron microscopy (TEM) of dumbbell-shaped colloids and their corresponding two-patch particles. All scale bars represent 0.1  $\mu$ m, except the image in the bottom right corner where the scale bar = 0.2  $\mu$ m.

S3 Comparison between chlorinated and bromoisobutyrate functionalized particles as colloidal initiators for the Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) of NIPAM.



**Figure S3.** Infrared (IR) spectra of particles obtained after Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) of NIPAM using spherical chlorinated particles (black, bottom spectrum) or brominated particles (red, top spectrum) as colloidal initiators. Clearly, no p(NIPAM) related signals are present after the attempted grafting reaction if chlorinated seeds are used. This illustrates the incapability of these particles to initiate the NIPAM polymerization. Exploiting the particles functionalized with bromoisobutyrate moieties as initiators yields colloids with significant p(NIPAM) content after SI-ATRP.

## S4 Light microscopy image of partially grafted dumbbells with small bare protrusion in the pure water and dumbbells with large bare protrusions in high ionic strength media.



**Figure S4.** (a) Schematic representation of the absence of aggregation/assembly of the partially grafted dumbbells without the addition of salt. (b) Light microscopy image of a stable dispersion of partially grafted colloids in pure water. Without the addition of salt, no cluster formation was observed. (c) Schematic representation of salt-induced clustering of dumbbells with small p(NIPAM) grafted patches. Addition of salt results in an attraction between the large, bare protrusions (yellow). (b) Light microscopy image of the ill-defined clusters observed after introducing the partially p(NIPAM) grafted dumbbells with a large protrusion in a 100 mM NaCl solution.

S5 Probing the stability of clusters obtained after their salt-induced formation upon dilution.



**Figure S5.** Finite-sized colloidal clusters consisting of dumbbell-shaped colloids with large p(NIPAM) grafted patches prepared by raising the ionic strength (see Figure 6 of main article). Subsequent dilution of the continuous phase with pure water to lower the ionic strength does not lead to disassembly of the clusters. (a) Set of trimers and tetramers of dumbbells and (b) enlarged view of the clusters present after lowering the ionic strength.

#### S6 Verification of specificity of attractions between p(NIPAM) grafted patches.

#### S6.1. Experimental

**S6.1.1. Materials.** The same materials as listed in the main article were used. In addition, 2-bromoisobutyryl bromide (BiBb, 98%), 2-hydroxyethyl acrylate (HEA, 96%, contains 200–650 ppm monomethyl ether hydroquinone as inhibitor), polyvinylpyrrolidone (PVP, average mol. wt. 40000) and polyethylene glycol sorbitan monolaurate (Tween®20) were obtained from Sigma-Aldrich. Azobis(isobutyronitrile) (AIBN, 98%) and pyridine (> 99%) from Acros Organics was used. Dichloromethane (DCM, peptide synthesis) was purchased from Biosolve. 2- (2-bromoisobutyryloxy) ethyl acrylate (BIEA) was prepared following a procedure of Matyjaszewski et al.<sup>3</sup> All additional chemicals were used as received.

**S6.1.2.** Synthesis of brominated colloidal initiators (CPs-Br). A core-shell approach was chosen in which the cross-linked polystyrene particles (CPs) served as seed particles for brominated core-shell particles. To be able to visualize the colloids with optical microscopy, slight bigger CPs were required compared to the ones used in the main article. These larger core particles were prepared using the same procedure as described in the main article, with the only difference being that 0.125 g instead of 0.25 g SDS was used in the emulsion polymerization. The resulting particles had a radius of 225 nm and a polydispersity index (PDI) of 0.031 as determined with dynamic light scattering (DLS).

The crude CPs seed dispersion (25 mL) was introduced in a 100 mL round-bottom flask, together with water (25 mL). The dispersion was heated to 70 °C and purged with nitrogen for 30 min. After degassing, a mixture of styrene (1 mL) and DVB (20  $\mu$ L) was added. The dispersion was stirred for 10 min after which 2-(2-bromoisobutyryloxy) ethyl acrylate (BIEA, 0.75 g) was injected. BIEA contains a polymerizable double bond which enables direct covalent attachment to the colloidal particles. The chemical structure of the ATRP initiating moiety is completely similar to the one immobilized on the dumbbell-shaped colloids in the main article, ensuring similar initiating properties. After 5 min of stirring, the polymerization was started by the addition of a degassed, aqueous KPS solution (32 mg in 5 mL water). The polymerization was allowed to run for 6 h after which the reaction was stopped by removing the flask from the oil bath. The particles were washed with water and ethanol three times. Infrared (IR) spectroscopy was used to confirm successful surface modification (1732 cm<sup>-1</sup>, C=O vibration of BIEA). DLS showed a *Z*-average radius of 255 nm and a PDI of 0.030.

S6.1.3. Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) on CPs-Br. NIPAM (120 mg, 1 mmol) and Cu(I)Br (13 mg, 0.09 mmol) were weighed and transferred directly into an oven-dried Schlenk flask. A MeOH/H<sub>2</sub>O mixture (7:3, v/v) (0.5 mL) was added and the solution was stirred for 5 min to dissolve/disperse the NIPAM and Cu(I)Br. A light green mixture was obtained. PMDETA (63  $\mu$ L, 0.3 mmol) was added resulting in the appearance of a blue/green color. The complete mixture was degassed by evacuation and refilling with nitrogen (three cycles).

In a separate Schlenk flask, the CPs-Br colloids dispersed in a 7:3 (v/v) MeOH/H<sub>2</sub>O mixture (0.5 mL, 2 wt%) were degassed by evacuation and refilling with nitrogen (three cycles). After degassing, the dispersion was injected into the monomer/catalyst mixture under inert atmosphere. The resulting reaction mixture was white/green. The ATRP reaction was allowed to run for 4 h at room temperature, after which the reaction was terminated by exposure of the mixture to air, yielding an intense blue color. The particles were washed several times with MeOH, 50 mM NaHSO<sub>3</sub> solution and water. The NaHSO<sub>3</sub> solution was used to facilitate the removal of the copper catalyst. The presence of p(NIPAM) was probed using IR spectroscopy.

**S6.1.4. Synthesis of micron-sized non-functionalized polystyrene colloids (MPs).** A procedure reported by Kraft et al.<sup>4</sup> and Wolters et al.<sup>5</sup> was followed for the preparation of monodisperse linear polystyrene spheres by dispersion polymerization. For this ethanol (126 mL), water (14 mL), styrene (10 mL), AIBN (0.136 g) and PVP (5.0 g) were introduced into a 200 mL round-bottom flask, closed with a rubber septum and sealed with Teflon tape. To initiate polymerization, the flask was immersed in a 75 °C oil bath with its axis of rotation at approximately a 60° angle. Polymerization was conducted for 20 h while rotating the flask at 60 rpm. The resulting particles were washed with ethanol and water. The synthesis yielded colloids with a diameter of 1.2  $\mu$ m and a polydispersity of 2.9% as determined with transmission electron microscopy (TEM).

**S6.1.5.** In situ observation of the aggregation behavior of a dispersion containing spherical p(NIPAM) grafted particles and non-functionalized polystyrene colloids. MPs colloids were washed several times with a concentrated solution of Tween®20 to substitute PVP for Tween®20 as steric stabilizer. A diluted dispersion (total volume 0.5 mL) of p(NIPAM) grafted colloids (as prepared in S6.1.3) and Tween®20-stabilized micron-sized colloids was prepared. The aqueous phase contained 1 mM Tween®20 and 10 mM NaCl. The resulting dispersion was introduced into a capillary, which was subsequently flame sealed. The capillary was placed on a heating stage, which was mounted on an optical microscope. Regulating the temperature of the heating stage allowed for in situ observation of the temperature-induced cluster formation.

The non-functional micron-sized particles (MPs), which basically mimic the bare, non-grafted protrusion of our dumbbell-shaped colloids, were sterically stabilized with Tween<sup>\*</sup>20. The choice for sterically, and not charged, stabilized particles is justified by the very low zeta ( $\zeta$ ) potentials measured for the bare protrusions of the partially grafted dumbbells (Figure 5 of main article). Tween<sup>\*</sup>20 was chosen as stabilizer, because it does not interfere with the thermo-responsive behavior of p(NIPAM).<sup>6</sup> This was confirmed by conducting temperature dependent DLS measurements. Regardless of the presence of Tween<sup>\*</sup>20 in the dispersion, the p(NIPAM) undergoes a coil-to-globule transition. The obtained hydrophobic polymer brushes still attract each other, resulting in aggregation as was concluded from Figure S7, which shows a clear increase in both hydrodynamic diameter as well as PDI.



**Figure S6.** (a) Optical microscopy image of a dispersion containing p(NIPAM) grafted polystyrene colloids and nonfunctionalized micron-sized polystyrene colloids (MPs). The p(NIPAM) grafted particles are smaller than the micron-sized colloids which makes differentiating between the two types of particles possible. The image was recorded below the lower critical solution temperature (LCST) of p(NIPAM). (b) Optical microscopy image of the same dispersion as shown in a), but now above the LCST of p(NIPAM). The non-functionalized particles are highlighted with the red circle. The formed clusters, which consist of purely p(NIPAM) grafted colloids, are labelled with green circles. (c) Enlargement of the colloidal clusters formed above the LCST of p(NIPAM) to confirm that the non-functionalized colloids (red circles) do not participate in the aggregation process.



**Figure S7.** (a) The temperature dependence of the *Z*-average diameter of particles grafted with p(NIPAM) hairs dispersed in water containing 10 mM NaCl and 1 mM of Tween<sup>\*</sup>20. (b) Polydispersity index (PDI) of p(NIPAM) grafted polystyrene colloids dispersed in an aqueous 10 mM NaCl solution containing 1 mM Tween<sup>\*</sup>20 as a function of temperature. The measurements performed at 40 °C are highlighted with the red areas.

#### S7 Thermo-response of p(NIPAM) grafted, spherical colloids as function of brush height.

#### S7.1. Experimental

**S7.1.1. Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) on CPs-Br.** CPs-Br colloids were prepared as described in S6.1.2. CPs seed particles of 125 nm radius with a polydispersity of 3.8% as determined with transmission electron microscopy (TEM) were used as seed particles (see main article for experimental details). The subsequent ATRP reaction was conducted using the same procedure as outlined in S6.1.3. To control the brush height, ATRP reactions with the initial NIPAM concentration of 1 M (120 mg, 1 mmol), 0.75 M (90 mg, 0.75 mmol) and 0.015 M (1.8 mg, 0.015 mmol) were conducted. All other reaction conditions were kept constant.

#### S7.2. Results and Discussion

Since ATRP is a controlled radical polymerization technique, the resulting hairs are uniform in length. Tuning the hair length is easily achieved by varying the initial monomer concentration in the reaction mixture, as can be seen from the results in Table S1. Initial NIPAM concentration of 1, 0.75 and 0.015 M resulted in polymer brushes of approximately 140, 85 and 10 nm high at room temperature, respectively. These brush heights were obtained by subtracting the hydrodynamic radius of the bare initiator particles (CPs-Br) from the hydrodynamic radius of each of the brush particles. The hydrodynamic radii were measured with dynamic light scattering (DLS).

The DLS results were in agreement with the IR spectra of the particles with different hair lengths. These spectra showed a decrease in the intensity of the p(NIPAM) related signals (3300, 1640 and 1536 cm<sup>-1</sup>) with decreasing initial NIPAM concentrations (Figure S8).

**Table S1.** Hydrodynamic diameters (D<sub>h</sub>) and hair lengths of p(NIPAM) polymers immobilized on polystyrene particles at 20 °C and 40 °C as function of the initial NIPAM concentrations.



**Figure S8.** Infrared (IR) spectra of polystyrene colloids with grafted with p(NIPAM) brushes. The thickness of the brush depends on the initial NIPAM concentration in the reaction mixture. The black spectrum (bottom) was obtained after an ATRP reaction containing an initial NIPAM concentration of 0.015 M, the red spectrum (middle) contained 0.75 M and the blue spectrum was obtained after reaction in a mixture with 1 M NIPAM (top).

The thermo-responsive behavior of the resulting brush particles was first measured in pure water. We found that heating a dispersion of p(NIPAM) grafted colloids in pure water above the lower critical solution temperature (LCST) of p(NIPAM) induces a coil-to-globule transition of the grafted polymers without affecting the colloidal stability of the dispersion. The lack of aggregation is easily rationalized by the fact that the polystyrene core particles are heavily charged, due to the choice of KPS as initiator during the particle formation reactions (see Experimental section of main article and section S6.1.2 of this supporting information). When these surface charges are not screened, the electrostatic repulsion between the colloids prevent them to aggregate via the hydrophobic attraction generated by the collapsed p(NIPAM) brush.

The particles functionalized with the two thickest polymer brushes showed a convincing decrease in hydrodynamic diameter (entry 1 and 2, Table S1 and Figure S9a and e) when the dispersion was heated above



**Figure S9.** (a) Hydrodynamic diameter (black squares) and polydispersity index (PDI; red triangles) of p(NIPAM) grafted polystyrene colloids (140 nm brush, entry 1, Table S1) in deionized water as function of temperature. (b) Hydrodynamic diameter of p(NIPAM) grafted polystyrene colloids (entry 1, Table S1) dispersed in an aqueous 10 mM NaCl solution as function of temperature. (c) PDI corresponding to the DLS measurements shown in b). (d) Macroscopic appearance of the DLS samples which were measured to obtain the data depicted in b) and c). (e) Hydrodynamic diameter (black squares) and PDI (red triangles) of p(NIPAM) grafted polystyrene colloids (85 nm brush, entry 2, Table S1) in deionized water as function of temperature. (f) Hydrodynamic diameter of p(NIPAM) grafted polystyrene colloids (entry 2, Table S1) dispersed in an aqueous 10 mM NaCl solution as function of temperature. (g) PDI corresponding to the DLS measurements shown in f). (h) Macroscopic appearance of the DLS samples which were measured to obtain the data depicted in grafted polystyrene colloids (entry 2, Table S1) dispersed in an aqueous 10 mM NaCl solution as function of temperature. (g) PDI corresponding to the DLS measurements shown in f). (h) Macroscopic appearance of the DLS samples which were measured to obtain the data depicted in f) and g). (i) Hydrodynamic diameter (black squares) and PDI (red triangles) of p(NIPAM) grafted polystyrene colloids (10 nm brush, entry 3, Table S1) in deionized water as function of temperature. (j) Similar DLS measurements as depicted in i), but now with a continuous phase containing 10 mM NaCl. In all panels, the measurements performed at 40 °C are highlighted with the red areas.

the LCST of p(NIPAM). This collapse was not measured for the particles with the thinnest brush (entry 3, Table S1 and Figure S9i). This either indicates the absence of a coil-to-globule transition for these thin brushes or that we cannot measure the temperature-induced change in hydrodynamic diameter. Since the extent to which the brush collapses seems to scale with the total length of the brush (Table S1), this last option is likely.

Addition of salt to the particle dispersions to screen the surface charges present enables reversible aggregation mediated by the hydrophobic p(NIPAM) brushes. The results of temperature dependent DLS measurements are summarized in Figure S9. In agreement with the thermo-response measured without the addition of salt (10 mM), the colloids equipped with the thicker p(NIPAM) brushes (entry 1 and 2, Table S1) clearly aggregated in a thermo-reversible fashion. The aggregation was apparent from both the DLS measurements, which show a distinct increase in hydrodynamic diameter (Figure S9b and f) and polydispersity index (PDI) (Figure S9c and g) at elevated temperatures, and from the macroscopic appearance of the colloidal dispersions (Figure S9d and h). In contrast, the particles with the thinnest p(NIPAM) brush (entry 3, Table S1) did not aggregate. Both hydrodynamic diameter and PDI did not significantly change upon raising the temperature above the LCST of p(NIPAM). Apparently, the p(NIPAM) brush does not turn hydrophobic or at least does not provide enough attraction to drive the aggregation process. Increasing the ionic strength even further to 50 mM to screen the surface charges on the polystyrene core even more did not change this picture.

From these temperature dependent DLS measurements we conclude that there exists a critical brush height that is required to induce thermo-reversible aggregation. Below this critical length, no (dominating) attractions between the p(NIPAM) grafted particles are generated.



S8 Thermo-response of dumbbell-shaped colloids with large p(NIPAM) grafted patches.

**Figure S10.** (a) The temperature dependence of the *Z*-average diameter of colloidal dumbbells grafted with p(NIPAM) measured with dynamic light scattering (DLS). Dumbbells with initiator patches (grey) larger than the protrusion (yellow) were used (top left). Transmission electron microscopy (TEM) images of the used particles are shown in Figure 1d of the main article. (b) The temperature dependence of the *Z*-average diameter of colloidal dumbbells grafted with p(NIPAM) hairs measured with DLS. Dumbbells with initiator patches (grey) smaller than the protrusion (yellow) were used (top right). TEM images of the used particles are shown in Figure 7d of the main article. The DLS measurements were conducted in aqueous solution containing 10 mM NaCl and 1 mM of Tween\*20. The measurements conducted at 40 °C are highlighted with the red areas.

Clusters observed with optical microscopy and macroscopic appearance of a dispersion containing dumbbell-shaped colloids with (c) initiator patches larger than the protrusion and (d) initiator patches smaller than the protrusion after heating above the lower critical solution temperature (LCST) of p(NIPAM).

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