CHEMISTRY OF MATERIALS

General Route toward Chemically Anisotropic Colloids

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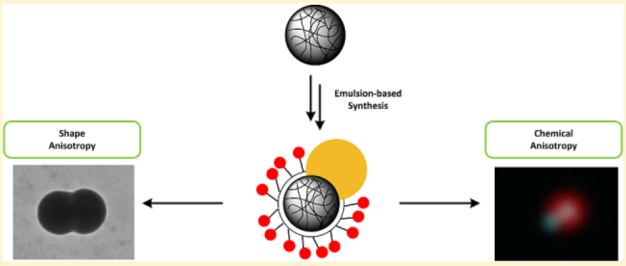
Supporting Information

ABSTRACT: We report a versatile emulsion-based synthesis for the preparation of nanometer-sized dumbbell-shaped particles that contain two chemically different patches. One patch consists of solely polystyrene and is therefore chemically inert toward most chemical reactions. The other patch contains reactive surface chlorine groups. To achieve this, we prepared seed particles with a chlorinated surface that were transformed into dumbbell-shaped particles by introducing a liquid styrene protrusion on the surface, which was polymerized to form a solid, anisotropic colloidal particle. The chlorinated layer on the seed particles provides both sufficient hydrophilicity to set a finite contact angle between the liquid protrusion and the seed particle and a chemical handle for further site-specific modification of the reactive patch. The chlorine groups can be easily converted to other functionalities, making these particles an ideal platform for the preparation of colloids with complex (surface) properties. As an example, it was shown that this patch could participate in copper-catalyzed Huisgen 1,3-dipolar cycloaddition reactions after conversion of the chlorines to azides. This very robust form of click chemistry allows us to decorate the reactive patch with a wide variety of molecules.



KEYWORDS: *anisotropic colloids, click chemistry, emulsion polymerization, patchy particles, surface chemistry*

INTRODUCTION

Currently there is an increasing interest in colloidal particles with anisotropic shape or surface properties.[1] These can be considered as building blocks that can self-assemble into complex structures. Preparing particles with functional patches (i.e., DNA or magnetic material) is of particular interest because this can lead to directional interactions between the colloids and even more advanced superstructures.[2] The synthetic procedures generally used to prepare these particles, such as selective deposition, surface templating, and lithography, are difficult to carry out and suffer from low yields, which makes it hard to study these systems systematically. To circumvent this problem, emulsion-based syntheses can be used. A number of papers have reported these types of procedures to produce polymeric or polymeric/inorganic hybrid dumbbell-shaped particles.[3] The general strategy relies on the internal phase separation of a monomer-swollen, cross-linked polymer particle.[4a,b] Upon swelling of the polymer network of the cross-linked particle, an elastic stress is induced. This stress can be relieved by heating the swollen particles, which results in a contraction of the polymer network. Upon contraction, excess monomer is expelled from the particle. If the surface properties of the colloid are tuned well (i.e., if there is a finite contact angle between the expelled monomer and the surface of the polymer particle), the monomer will form a liquid protrusion on the surface. Polymerization of this liquid droplet results in solid, dumbbell-shaped colloids. Tuning of the contact angle is usually achieved by adding hydrophilic layers [poly(vinyl acetate) or poly(acrylic acid)] on the seed particles.[2]

In this article, we show that a functional, slightly hydrophilic coating of vinyl benzyl chloride (VBC) can be applied to the surface of cross-linked polystyrene particles. These functional particles can then be successfully used as seeds for the formation of dumbbell-shaped colloids. The resulting particles contain a well-defined chlorinated and therefore reactive patch that allows for localized, site-specific modification of the nanosized colloids. The chlorine functionality provides a general chemical handle that can be the starting point for surface modifications via a wide variety of chemistries, providing the possibility to introduce virtually any desired molecule onto the surface. As an example, we show that the particles can be modified using click chemistry, further expanding the possibilities for tuning the patch characteristics.

EXPERIMENTAL SECTION

Materials. Styrene (St, 99%), divinylbenzene (DVB, 55% mixture of isomers, tech. grade), vinylbenzyl chloride (VBC, ≥90%, tech. grade), fluoresceinamine (for fluorescence, mixture of isomers, ≥75%), dimethylformamide (DMF, ≥99%), bromotris(triphenylphosphine)-copper(I) [$Cu(PPh_3)_3Br$, 98%], *N,N*-Diisopropylethylamine (DIPEA, ≥98%), 4-pentynoic acid (95%), propargyl alcohol (99%), and propargyl amine (98%) were obtained from Sigma-Aldrich. Hydro-

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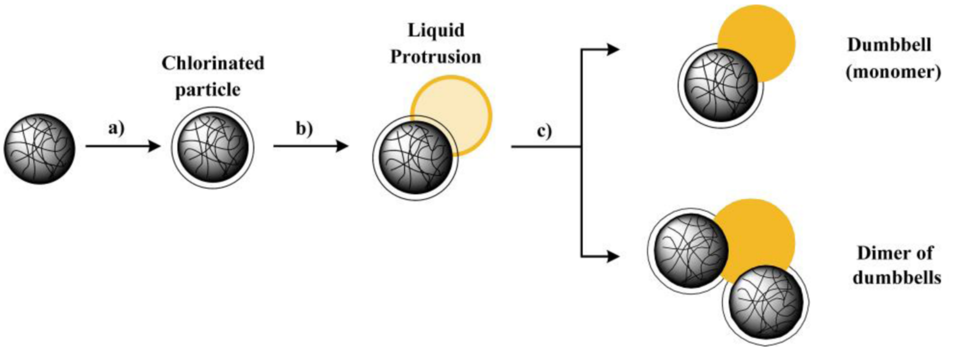
Scheme 1. Schematic Representation of the Synthetic Procedure To Give Anisotropic Particles with Chlorinated Patches[a]



[a]Step (a): introduction of a chlorinated shell (in white) on cross-linked polystyrene particles. Step (b): swelling of the chlorinated seeds with a mixture of divinylbenzene and styrene, and subsequent heating to form a liquid protrusion. Step (c): polymerization of the liquid protrusion by addition of an oil-soluble radical initiator (AIBN) to form solid dumbbell-shaped colloids. If fusion of the liquid protrusion occurs before polymerization, dimers of dumbbells are formed.

quinone (99%) was purchased from Riedel-de Haën, sodium azide (NaN_3, 99%) from VWR, and sodium dodecyl sulfate (SDS) from BDH. Potassium persulfate (KPS, >99% for analysis), sodium bisulfite ($NaHSO_3$, ACS reagent) and azobis(isobutyronitrile) (AIBN, 98%) were purchased from Acros Organics. All of the chemicals were used as received. The water used throughout all of the syntheses was purified using a Milli-Q water purification system.

Synthesis of Chlorinated Seed Particles. Cross-linked polystyrene (CPs) particles were synthesized using a standard emulsion polymerization method described in literature.[3a] A 500 mL round-bottom flask equipped with stir bar was placed in an oil bath at 80 °C. Water (200 mL) was charged into the reactor and allowed to reach the bath temperature. Styrene (21.15 g), DVB (0.635 g), and SDS (0.25 g) dissolved in water (50 mL) were added. The complete mixture was allowed to heat up to the temperature of the bath. Finally, the addition of of KPS (0.39 g dissolved in 37.5 mL of water) initiated the polymerization. The reaction was allowed to continue for 24 h at 80 °C. The resulting latex had a solid content of 7% (measured gravimetrically). The resulting particles had a radius of 125 nm with a polydispersity of 3.8% as determined with TEM.

The synthesized particles were used as seeds in the second step, in which chlorine groups were introduced at the colloidal surface.[5] Crude seed dispersion (25 mL) and 10 mL of water were introduced into a 50 mL round-bottom flask equipped with a magnetic stir bar. The mixture was degassed with nitrogen for 30 min. VBC (1 mL premixed with 20 μL of DVB) was added under an inert atmosphere. The seeds were swollen for 1 h at 30 °C, after which the temperature was raised to 60 °C. When this temperature was reached, 0.04 g of KPS and 0.03 g of sodium bisulfite dissolved in 2.5 mL of water were added. The reaction was allowed to run for 4 h. The particles were washed by centrifugation and redispersion in water. The solid content of the resulting dispersion was adjusted to 5%. A particle radius of 155 nm and polydispersity of 4.4% were measured using TEM. The presence of the chlorine groups was confirmed using FT-IR (ATR) and XPS.

Synthesis of Anisotropic Particles Based on Chlorinated Seeds. The spherical chlorinated seed particles were converted to anisotropic colloids using a method described by Kraft et al.[3a] SDS (84 mg) was introduced into a small reactor tube containing a magnetic stir bar. To this tube were added 2.5 mL of chlorinated seeds (solid content = 5%) and 2.5 mL of water. The particles were swollen for 48 h with a mixture consisting of 550 μL of styrene and 20 μL of DVB (swelling ratio ≈ 5; the mass of added monomer divided by the mass of polymer in the seed particles). After this swelling period, the mixture was heated at 80 °C for 2 h, causing the formation of a liquid protrusion at the surface of the seed particles. After the 2 h period, the mixture was allowed to cool to room temperature. In order to polymerize this liquid protrusion, 4.8 mg of AIBN dissolved in 230 μL of styrene was added as well as 0.5 mL of a hydroquinone solution (46 mg in 50 mL of water). Hydroquinone was added to prevent polymerization in the aqueous phase. The reaction was allowed to continue for 24 h at 80 °C. The resulting particles were washed using centrifugation and redispersion in water in order to remove unwanted aggregates and secondary nuclei. The washed dispersion had a solid content of 1%. The particle size and shape were investigated with TEM. The majority of the particles were dumbbell-shaped, consisting of nearly equally sized lobes (~185 nm radius). Besides the dumbbells, a small fraction of dimers of dumbbells was also observed, in agreement with ref 3a. No attempts to separate the dumbbells from the dimers were carried out.

Covalent Attachment of Fluoresceinamine to Chlorinated Dumbbells. In order to prove that only one side of the dumbbells contained chlorine groups, the surface chlorine groups were reacted with the amine functionality of fluoresceinamine. A 1 mL aliquot of the dispersion containing the dumbbell-shaped particles (solid content = 1%) was used. First, water was replaced by DMF by centrifugation and redispersion (three times). Fluoresceinamine (3.5 mg) was added to the DMF dispersion, and the mixture was heated to 90 °C for 24 h. The particles were washed with DMF and ethanol to remove excess dye, and finally the particles were redispersed back in water. Confocal microscopy was used to investigate the distribution of the fluorescence signal over the particles.

Conversion of Chlorine Groups to Azides on Dumbbells. NaN_3 (13.5 mg) was added to 6 mL of chlorinated dumbbells in DMF (solid content = 1%). The mixture was heated for 24 h at 70 °C. After this, the emulsion was washed with DMF and water to remove excess NaN_3. Substitution of chlorine by azides was monitored with FT-IR (ATR). TEM was used to confirm that the particle shape remained unaffected during the reaction.

Click Chemistry on Azide-Functionalized Dumbbells. $Cu(PPh_3)_3Br$ (12.5 mg) was introduced into a 10 mL round-bottom flask equipped with stir bar. To this, 26 μL of DIPEA and 6 mg of 4-pentynoic acid or 5 μL of propargyl amine was added. Finally, a dispersion containing azide-functionalized particles (in DMF, solid content = 1%) was injected. The reaction was allowed to run for 24 h under gentle stirring at 70 °C. After 24 h, the reaction was stopped, and the mixture was washed with DMF. FT-IR (ATR) was used to show successful click reactions. TEM showed the presence of the original dumbbell-shaped particles.

Characterization. Transmission electron microscopy pictures were taken with a Philips Technai10 electron microscope typically operating at 100 kV. The samples were prepared by drying a drop of diluted aqueous particle dispersion on top of polymer-coated copper grids.

The XPS measurements were carried out with a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic small-spot X-ray source and a 180° double-focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminum anode (Al Kα = 1486.6 eV) operating at 72 W and a spot size of 400 μm.

Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The background pressure was 2×10^{-9} mbar, and during measurement the argon pressure was 3×10^{-7} mbar because of the charge-compensation dual-beam source.

IR spectra were obtained using a PerkinElmer Frontier FT-IR/FIR spectrometer. The attenuated total reflectance (ATR) mode was used. Measurements were carried out on powders obtained by drying the particle dispersion.

Confocal images were recorded on a Leica SP8 microscope. The microscope was equipped with a Plan Apo 100× oil immersion lens with a numerical aperture of 1.4. Samples were illuminated by laser beam with a wavelength of 488 nm selected from a white-light laser by means of an acousto-optical beam splitter (AOBS). The scanning was unidirectional at a scanning speed of 600 Hz. The pinhole size was 151.7 μm (Airy disk). We used varying line and frame averaging. Images were captured by combining two imaging channels, with one recording in reflection mode and the other in fluorescence mode. The excitation wavelength of 488 nm was close to the excitation maximum of the dye coupled to the particles. To visualize the lobes that were not labeled, we took advantage of their Mie scattering: the particles were immersed in immersion oil (n = 1.52) which is not perfectly index-matched with polystyrene (n = 1.59). The two channels were recorded in different 8 bit color look-up tables so as to distinguish them: reflection mode in cyan and fluorescence mode in red "glow".

■ RESULTS AND DISCUSSION

We synthesized cross-linked spherical polystyrene colloids (CPs)[3a] that were coated with a thin, cross-linked layer of vinyl benzyl chloride [Step (a) in Scheme 1]. The chlorine groups of vinylbenzyl chloride (VBC) ensure a slightly hydrophilic character of the seed surface and at the same time provide a chemical handle for further surface modification. A core−shell approach was used to ensure that the majority of the added VBC actually ended up at the surface of the particles.[5] In this step, potassium persulfate (KPS) was used together with sodium bisulfite as an initiator system. The addition of sodium bisulfite shifts the mechanism for radical formation from a thermal process to a redox process in which the bisulfite ion acts as a reductor.[6] In this way, the polymerization could be carried out at a lower temperature, suppressing the undesired hydrolysis of the relatively labile chlorine functionality of VBC. Successful incorporation of the chlorine functionality was indicated by both infrared (IR) analysis and X-ray photoelectron spectroscopy (XPS). Comparison of the IR spectra of the bare polystyrene seeds and the chlorinated particles showed a new signal at 1266 cm^{-1}, which corresponds to the $-CH_2-Cl$ vibration of the incorporated VBC (Figure 1). In the XPS spectrum, binding energies of 200 and 270 eV corresponding to chlorine were detected (Figure 2), providing additional proof that chlorine groups were indeed present at the surface, as XPS is a surface elemental analysis technique with a penetration depth of only 1−10 nm. The binding energy at 530 eV can be attributed to oxygen present from the initiator system that was used. The intense signal at 285 eV was obviously caused by the carbon atoms of polystyrene. In the second step, the chlorinated seed particles were used for the preparation of dumbbells (step **b**) in Scheme 1).

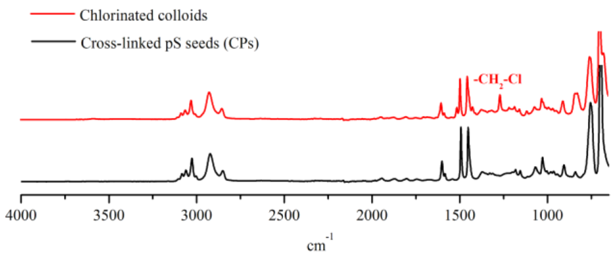


Figure 1. Infrared spectra (recorded in ATR mode) of cross-linked polystyrene seeds (black) and the chlorinated seeds (red).

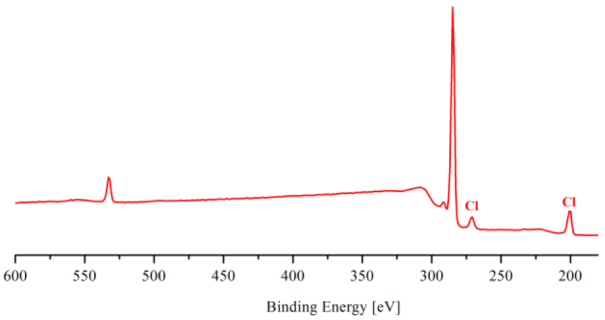


Figure 2. X-ray photoelectron spectrum of chlorinated particles.

The particles were swollen with a mixture of styrene (St) and divinylbenzene (DVB). Because a chlorinated seed was used, we expected that the resulting dumbbells would consist of one lobe covered with surface chlorine groups, while the other lobe (originating from the liquid protrusion) would be solely built up from polystyrene (note: there might be SDS present on this lobe, as SDS was added to stabilize the liquid protrusion during synthesis). It was not likely that the chlorine groups would be distributed over the whole dumbbell, because the chlorine groups were covalently attached to the seed. This argument was also used by Mock and Zukoski[7] when they prepared dumbbells containing lobes with different charges on the surface using a different procedure from the one reported here. Wang et al.[3h] recently used a procedure in which VBC was used as swelling monomer for unfunctionalized polystyrene seeds. In that case it could not be ruled out that a small fraction of residual VBC remained inside the seed particles. As discussed below, we were able to confirm that introduction of the shape anisotropy based on our chlorinated seeds yielded dumbbell-shaped particles with a well-defined chlorinated patch.

Figure 3 shows a representative TEM picture of the colloids after formation and polymerization of the liquid protrusion. Dumbbell-shaped particles were indeed formed and were also the most abundant, although also dimers of dumbbells were observed to a lesser extent (5−10%). These particles were formed when the liquid protrusions of two particles fused together before polymerization.[3a,b] The fraction of dimers

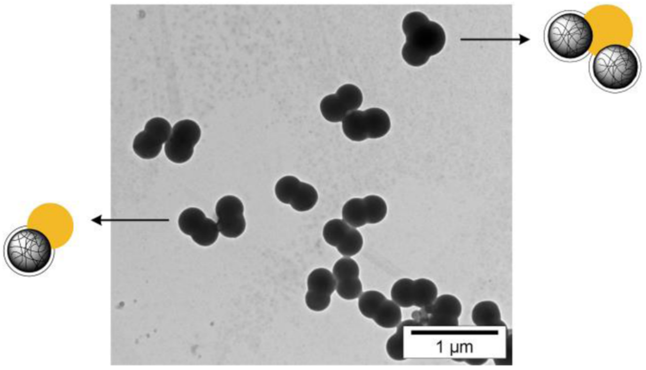


Figure 3. TEM picture of the anisotropic particles synthesized using the chlorinated seeds. The majority of the particles are monomeric dumbbells. A small percentage of dimers is observed.

formed depends on the size of the liquid protrusion, the amount of surfactant to stabilize the oil−water interface of the protrusion, and most likely also the time between the formation of the liquid protrusions and the actual polymerization of these monomer droplets. In our synthesis, polymerization was induced directly after protrusion formation to minimize the number of dimer particles. Nevertheless, a small fraction of dimers was formed, which is inherent to the synthetic procedure. Dumbbells and dimers (or even higher-order aggregates) can be separated from each other using density-gradient centrifugation, as shown by Kraft et al.[3a] This provides a method to obtain dispersions containing solely dumbbells or dimers.

In all cases, the size of the protrusion is almost equal to the size of the seed particle. The contact angle between the protrusion and the seed is very pronounced, indicating that the expelled monomer mixture only partially wets the chlorinated surface. In other words, the introduction of the chlorine functionalities at the surface of the seed particles provides sufficient hydrophilicity to prevent full wetting of the colloidal surface by the apolar protrusion. IR analysis of these particles confirmed that the chlorine functionality was still present (see Figure 5). This signal decreased in intensity compared with the chlorine signal observed for the spherical particles (Figure 1) because of the doubling of the amount of polystyrene by introduction of the protrusion.

From the TEM analysis we conclude that dumbbells form, although with these pictures we were not able to visualize the distribution of the chlorine groups over the whole particle. In order to validate this hypothesis, a dye with an amino group (fluoresceinamine) was mixed with these particles. The reaction between the surface chlorine groups and the amino group of the dye ensured covalent attachment. A large excess of dye was used to let all of the chlorine groups react. Nonreacted or aspecific absorbed dye was washed off after the reaction. High-resolution confocal microscopy was used to analyze the fluorescence of the obtained particles, and the results are shown in Figure 4. The red signal corresponds to fluorescence, while the scattered signal is shown in cyan. Overlaying the two signals revealed that the particles showed significant fluorescence at only one lobe of each particle. The asymmetric fluorescence signal proved that the chlorine groups were asymmetrically distributed across the particles and therefore did not migrate to the protrusion. More confocal pictures can be found in the Supporting Information.

The ability to prepare dumbbell-shaped colloids of which only one lobe contains chlorine groups opens the way to site-specific modification reactions. The chlorines on the surface can be easily converted to other functionalities by straightforward organic chemistry, such as nucleophilic displacements with functional amines or reactive anions of metal salts (i.e., KOH). Numerous examples of possible applications of these particles can be envisioned. Dumbbells with a hydrophobic patch and a hydrophilic patch can be synthesized and used for very efficient stabilization of oil−water interfaces.[8,3f,g] The introduction of well-designed molecules could introduce directional interactions between the particles,[2a,c] and self-propelling particles are accessible in large quantities when proper catalytic complexes are attached.[9] The synthesized particles are therefore a versatile platform for the preparation of a wide variety of complex colloids.

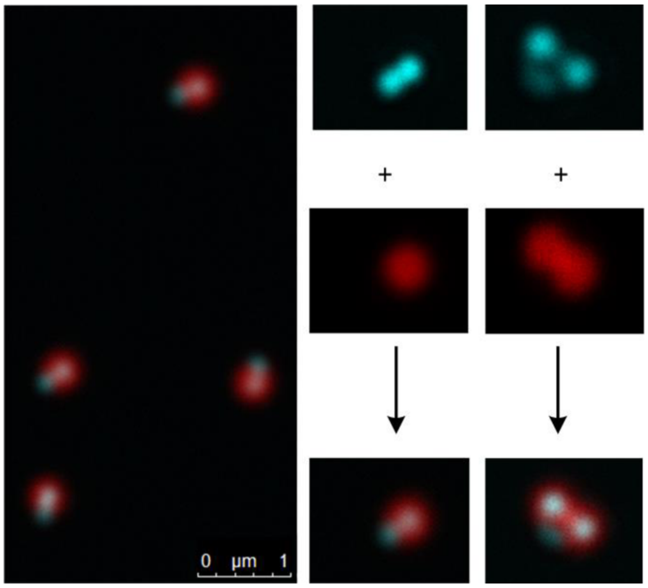
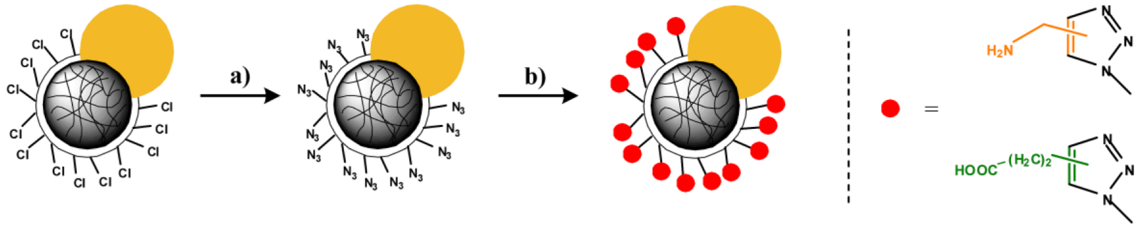


Figure 4. Confocal images of anisotropic particles after functionalization of the chlorinated patch with fluoresceinamine. Left: Image captured by combining two imaging channels, with one recording in reflection mode (cyan) and the other in fluorescence mode (red). Right: enlargement of the two separate imaging channels for both a monomeric dumbbell-shaped particle and a dimer particle.

As a proof of principle, the copper-catalyzed Huisgen 1,3-dipolar cycloaddition (in the remainder of the article termed “click chemistry”) was chosen because of its orthogonal character.[10] The surface reactions were first carried out on the spherical chlorinated seeds to optimize the reaction conditions. Click chemistry was previously used to modify the surface of polystyrene particles;[11] however, the synthesis we present (Scheme 2) is an improvement of the reported method in terms of surface coverage and tunability of the number of functional groups. The results and proof of successful modification reactions can be found in the Supporting Information. In order to use click chemistry for modification, the chlorine groups were first transformed to azides by addition of sodium azide in dimethylformamide (DMF). DMF is known for its poor ability to solvate anions.[12] Therefore, dissolving sodium azide in DMF results in “naked” (i.e., nonhydrated) azide ions. These ions are highly reactive and ensure high conversion of chlorines to azides. Cross-linking of both the seed and protrusion of the dumbbells prevents dissolution of the particles in DMF. IR spectroscopy showed the disappearance of the chlorine signal and the appearance of a relatively strong azide signal at 2096 cm^{-1} (Figure 5). After successful introduction of the azide functionality, two click reactions were carried out with two small alkyne-containing molecules, namely, propagylamine and 4-pentynoic acid. The reactions were carried out in DMF with a conventional catalytic system of bromotris(triphenylphosphine)copper(I) [Cu(PPh$_3$)$_3$Br] and *N*,*N*-diisopropylethylamine (DIPEA). After the reaction, IR analysis showed the complete disappearance of the azide signal (Figure 5), which is a strong indication that the attachment of the alkyne precursors was successful. No characteristic alkyne precursor signals could be observed in the IR spectra.

This in contrast to the spectra obtained after click functionalization of the spherical particles (see the Supporting Information). The lack of these signals can be attributed to the fact that the dumbbells contain roughly twice the amount of polystyrene compared with the spherical seeds. Furthermore, a

Scheme 2. Schematic Representation of the Preparation of Functionalization of Dumbbell-Shaped Colloids Using Click Chemistry[a]



[a]Step (a): substitution of surface chlorine groups with azides by addition of sodium azide (NaN_3) in DMF. Step (b): coupling of propargylamine (orange) or 4-pentynoic acid (green) to the surface using the copper-catalyzed Huisgen 1,3-dipolar cycloaddition reaction.

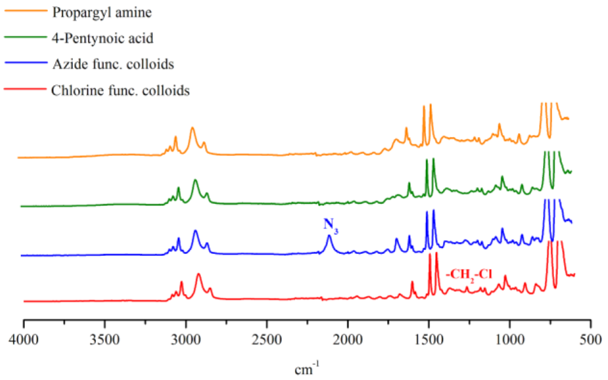


Figure 5. Infrared spectra of dumbbells with a chlorinated patch (red) or an azide-functionalized patch (blue) and the spectra obtained after surface functionalization via click chemistry with 4-pentynoic acid (green) or propargylamine (orange).

part of the surface functionalities are buried under the protrusion after dumbbell formation.

Finally, the particles were imaged after the complete reaction sequence to confirm that the particles kept their shape. shows The TEM picture of particles functionalized with propargylamine (Figure 6) shows that the colloids stayed intact.

■ CONCLUSIONS

We have developed a synthesis route toward anisotropic particles that contain reactive chlorinated lobes and chemically inert lobes. The synthesis is emulsion-based, allowing the preparation of these complex particles in large quantities, which in itself is a significant advantage compared with available methods to date. The chlorine functionality can be used for further modification reactions. As an example, surface modification of the reactive lobe using click chemistry was carried out. The combination of click chemistry and the developed synthesis method provides a route for the preparation of anisotropic particles with a wide variety of functionalities and morphologies.

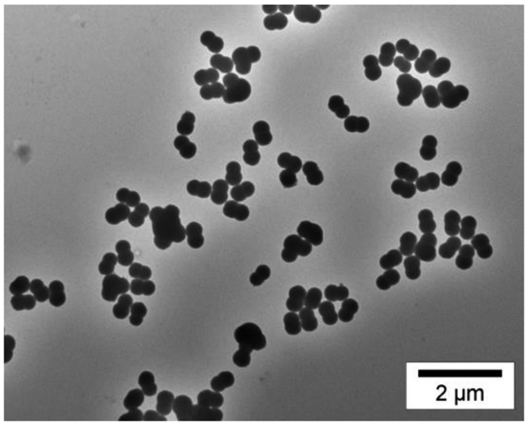


Figure 6. TEM picture of colloids with a patch functionalized with propargylamine via the copper-catalyzed Huisgen 1,3-dipolar cycloaddition reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and optimization of click chemistry on spherical particles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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