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Stimuli-Responsive Bicomponent Polymer Janus Particles by "Grafting from"/"Grafting to" Approaches

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ABSTRACT: We report preparation of stimuli-responsive bicomponent polymeric Janus particles and investigation of their switching behavior. The first polymer was immobilized on one side of silica particles using the surface-initiated atom transfer radical polymerization, "grafting from" approach. The second polymer was immobilized using the "grafting to" method by reaction between reactive terminating groups of polymer chains and functional groups on the particle surface. On the example of mixed oppositely charged polyelectrolyte Janus particles decorated with poly(acrylic acid) and poly(2-vinylpyridine) chains, we demonstrate stimuli-responsive aggregation/disaggregation behavior upon pH changes.

Introduction

Asymmetry is intrinsic to natural systems and is widely used by living organisms for efficient adaptation and mimicry. Janus particles (JPs), i.e., the colloidal particles having different properties (such as charge, polarity, and optical and magnetic properties) at opposite sides, are an example of synthetic asymmetrical systems.[1−8] Because of anisotropy of properties, the JPs are unique among other micro- and nanoparticles. Recently, the JPs demonstrated huge potential as drug carriers,[9] emulsion stabilizers,[4,10,11] microrheological probes, and functional elements for design of electronic paper.[12,13] Moreover, because of asymmetrical structures, the JPs are able to aggregate into fascinating hierarchical structures,[5,7,14−18] thereby building blocks for complex superstructures.

Mono- and bicomponent JPs based on different low and high molecular weight materials were recently prepared using the microfluidic technique,[5,9,13,19−21] controlled phase separation phenomena,[22−24] template-directed self-assembly,[25,26] controlled surface nucleation,[19,27−29] and toposelective surface modification.[6,30−34] A particularly interesting group of JPs comprises the ones specifically responding to change of environmental conditions. For, example, immobilization of stimuli-responsive polymers to one side of colloidal silica particles was recently used for synthesis of temperature/pH sensitive Janus particles.[35−37] Apparently, grafting of two polymers with different sensitivities on opposite sides can further diversify responsive properties of JPs.

In this article, we report on the synthesis and switchable properties of JPs decorated with two sorts of stimuli-responsive polymers immobilized to the opposite sides of micrometer sized silica particles. The first polymer was immobilized on one side of the silica particles using the surface-initiated atom transfer radical polymerization (ATRP), "grafting from" approach. The second polymer was immobilized using the "grafting to" method by reaction between reactive terminating groups of polymer chains and functional groups on the particle surface. Finally, pH-responsive properties of JPs decorated by two oppositely charged polyelectrolytes are demonstrated.

Experimental Section

Materials and Methods. Silica particles (800 nm in diameter) were purchased from Kisker (Germany). *N*-Isopropylacrylamide (NIPAAm, Aldrich), acetone (Aldrich), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDTA, Aldrich), ethyl 2-bromoisobutyrate (EBiB), 3-aminopropyltriethoxysilane (APS, ABCR), α-bromoisobutyric acid (Biba, Fluka), anhydrous dichloromethane (Fluka), triethylamine (Fluka), L-ascorbic acid (Sigma), fluorescein *o*-acrylate (FA, Aldrich), copper(II) bromide (Aldrich), 4,4′-azobis(4-cyanovaleric acid) (ACVA, Fluka), hydroxybutyl acrylate (HYBA, Aldrich), THF, 4-(dimethylamino)pyridine (DMAP), 1,3-dicyclohexylcarbodiimide (DCC), *N*-hydroxysuccinimide (NHS, Aldrich), 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDC, Pierce), MES hydrate (Sigma), phosphate buffered saline (PBS, Aldrich), and rhodamine B (Aldrich) were used as received. 2-Vinylpyridine (2VP, Polymer Source) and *tert*-butyl acrylate (tBA, Fluka) were distilled under nitrogen steam prior to the polymerization.

Synthesis of Rhodamine B−Hydroxybutyl Acrylate Monomer (RhHYBA). Rhodamine B (3 g, 6.26 mmol) was dissolved in 40 mL of anhydrous methylene chloride under nitrogen. DMAP (0.08 g, 0.65 mmol) and HYBA (1.5 mL, 10 mmol) were added to the flask at 0 °C. DCC (6.26 mL of 1.0 M solution in methylene chloride) was injected into the reaction flask with stirring. The reactive mixture was stirred for 30 min at 0 °C and then was allowed to slowly warm to room temperature. Reaction was stopped after 12 h. Methylene chloride was removed via rotary evaporation, and the reaction mixture redissolved in 50 mL of acetonitrile and filtered. The fluorescent monomer was purified using column chromatography (packed material: silica gel; eluent: acetonitrile).

Synthesis of Carboxy-Terminated Rhodamine-Labeled Poly(2-vinylpyridine). 2VP (5 mL, 46.35 mmol), RhBHYBA (0.1 g, 0.16 mmol), and ACVA (65.7 mg, 0.23 mmol) were dissolved in THF (9 mL). The reaction mixture was sealed and purged with nitrogen for 30 min. Polymerization was carried out at 80 °C and stopped after 72 h. The polymer mixture was precipitated in 200 mL of toluene at 0 °C.

Modification of Silica Particles and Preparation of Colloidosomes. Silica particles were washed three times in dichloromethane followed by drying in a vacuum oven at 110 °C. APS was chemisorbed from a 2 wt % ethanol solution for 24 h. To remove nonadsorbed APS, the particles were rinsed and centrifuged five times in ethanol. A similar procedure was used to adsorb APS onto the planar silicon wafers. The thickness and wetting properties of the APS layer were determined by null ellipsometry and contact

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Table 1. Values of Molecular Weight, Mass Fraction According to TGA and FTIR, Calculated Values of Grafting Density (Γ), Distance between Grafting Sites (*D*) of Polymers, and Thickness (*H*) of Polymer Layer[a]

sample ID	polymer	M_n, g/mol	M_w, g/mol	mass % TGA	mass % FTIR	Γ, chains/nm^2	*D*, nm	*H*, nm
PtBA JPs	PtBA	184 000	466 000	10.05	10.34	0.15	2.46	44
PNIPAAm JPs	PNIPAAm	60 000	148 000	3.00		0.12	2.84	13
PtBA−P2VP JPs	PtBA	184 000	466 000	10.05	10.34	0.15	2.46	44
	P2VP	17 000	28 000			0.10	3.07	4

[a] Γ, *D*, and *H* were estimated using results of FTIR for PtBA and PNIIPAAm and null ellipsometry for P2VP. It was considered that first (PtBA) and second (P2VP) grafted polymers occupy 75% and 25% of particle surface, respectively.

angle measurements, respectively. Preparation of colloidosomes was done by the Pickering emulsion approach proposed by Granick and co-workers.[6]

Immobilization of ATRP-Initiator. Next, ATRP-initiator was immobilized onto the surface of amino-modified particles. First, the colloidosomes were treated by the alkali solution of α-bromoisobutyl bromide (2.5 mmol) and EDC (3 mmol) prepared at 4 °C. The pH value of the mixture was adjusted to pH = 10 with triethylamine. The reaction was carried out at ambient conditions for 17 h under stirring at 800 rpm. Afterward, modified colloidosomes were filtered off and washed several times with pure water to remove unattached particles. Then, particles were dried in a vacuum oven at 20 °C overnight. Next, wax was dissolved in chloroform.

Grafting of PNIPAAm and PtBA Using Surface-Initiated ATRP. Fluorescein-labeled poly(*N*-isopropylacrylamide) was grafted on the initiator-modified particles as follows: NIPAAm (2 g, 1.75×10^{-2} mol), FA (40 mg, 1×10^{-4} mol), EBIB (0.65 mg, 3.3×10^{-6} mol), $CuBr_2$ (0.35 mg, 1.6×10^{-6} mol), and PMDTA (1.3 mg, 8×10^{-6} mol) were dissolved in 2 mL of acetone.[38,39] The reaction solution was added to the tube containing initiator-modified silica particles. After the tube was sealed with a rubber septum, a solution of L-ascorbic acid (18 mg, 1×10^{-4} mol) in water (0.06 mL) was injected. The vial was placed in a 70 °C oil bath. The polymerization was carried out under stirring and was stopped after 225 min. The polymer obtained in solution was collected by precipitation in diethyl ether and used for determination of molecular weight (Table 1). It is believed that these values should be close to those of the grafted polymer brushes. DMAC/2% H_2O/LiCl (3 g/L) was used as eluent for GPC. A similar procedure was used for grafting of PtBA on initiator-modified particles. Briefly, initiator-modified particles (50 mg) and fluorescein *o*-acrylate (20 mg) were mixed together with 5 mL of freshly distilled *tert*-butyl acrylate. The particles were dispersed by ultrasonication for several minutes. $CuBr_2$ (0.4 mg, 1.8×10^{-6} mol), PMDTA (1.5 mg, 8.7×10^{-6} mol), and EBIB (1.2 mg) were dissolved in 1 mL of acetone and added to the monomer solution. After the tube was sealed with a rubber septum, a solution of 300 μL of Sn(II) 2-ethylhexanoate in 1 mL of anisole was injected, and polymerization was started. The polymerization was carried out under stirring for 7 h at 70 °C.

Grafting of Carboxy-Terminated Rhodamine-Labeled Poly(2-vinylpyridine) Using "Grafting to" Approach. For grafting of the second polymer on JPs modified by the first polymer (PtBA), the "grafting to"[40−43] approach was used. Silica particles with the grafted first polymer were dispersed in 2 mL of 1 wt % solution of carboxy-terminated polymers carboxy-terminated rhodamine-labeled poly(2-vinylpyridine) and stirred for 2 h. Solvent was removed by evaporation. The particles were annealed at 150 °C for 2 h. The ungrafted polymer was removed by multiple circles of redispersing of particles in chloroform and subsequent centrifuging.

Fluorescence Microscopy. Fluorescence images were obtained using an Axiovert 200 M inverted microscope with a 40× and 100× objectives (Zeiss, Oberkochen, Germany) equipped with a FluoArc lamp. For data acquisition a standard TRITC (excitation: HQ 535/50; dichroic: Q 565 LP; emission: HQ 610/75, Chroma Technology) and FITC (excitation: HQ 480/40; dichroic: Q 505 LP; emission: HQ 535/50, Chroma Technology) filter sets in conjunction with a Micromax 512 BFT camera (Photometrics, Tucson, AZ) and a MetaMorph imaging system (Universal Imaging, Downingtown, PA) were used.

Scanning Electron Microscopy (SEM). All SEM micrographs were acquired on an environmental scanning electron microscope (ESEM), (DSM 982 Gemini, ZEISS, Germany) operating at 50 kV in the secondary electron (SE) mode. In order to enhance electron density contrast samples were stained with OsO_4. Exposure to OsO_4 leads to a preferential staining of the P2VP phase.

FTIR-ATR Spectroscopy. FTIR-ATR spectra were taken with an IFS 55 (Bruker, Germany) spectrometer for all prepared systems.

Diffuse Reflection IR Spectroscopy. Diffuse reflection IR spectroscopy was used for determination of grafted amount of polymer. Details of the calibration procedure are given elsewhere.[43] Briefly, the grafted amount was estimated using calibration curves plotted from the absorbency spectra of the samples, made from a mixture of the polymer and particles (50 mg). The characteristic bands at 1740 cm^{-1} (for PtBA) and 1590/1570 cm^{-1} (for P2VP) were used for the estimation of grafted amount of polymers.

The grafting density of polymer (Γ), the distance between grafting sites (*D*), and thickness of grafted polymer layer (*H*) were estimated as follows:

$$\Gamma = R\rho_{\mathrm{SiO2}}\phi_{\mathrm{POL}}N_{\mathrm{A}}/3M_{\mathrm{n}}\varphi_{\mathrm{POL}}(1 - \phi_{\mathrm{POL}})$$

$$D = \Gamma^{-0.5}$$

$$H = \Gamma M_{\mathrm{n}}/\rho_{\mathrm{POLYMER}}N_{\mathrm{A}}$$

where R is the radius of silica particle; ρ_{SiO2} and ρ_{POLYMER} are the mass density of silica and polymer, respectively, ϕ_{POL} is the mass fraction of polymer (obtained using FTIR and TGA), M_{n} is the average number molecular weight of polymer chains, N_{A} is the Avogadro number, and φ_{POL} is the fraction of particle surface cover by the polymer ($\varphi_{\mathrm{POL}} = 0.75$ for a first polymer, $\varphi_{\mathrm{POL}} = 0.25$ for a second one).

Dynamic Light Scattering (DLS). A Zetasizer Nano ZS by Malvern Instruments/UK was used for determination of particle size. The device is equipped with a 633 nm laser and with a noninvasive backscatter (NIBS) technology for increasing particle size sensitivity.

Electrokinetic Measurements. The electrophoretic mobility was measured as a function of pH using the same equipment as above. The pH of the prepared suspensions was controlled by adding 0.1 M KOH or HCl aqueous solutions.[44] The samples have been prepared by the dilution of native or modified silica particles (2 mg) in 13 mL of 10^{-3} M KCl solution. Three measurements were recorded for each sample at each value of pH. The ζ potentials were calculated from the electrophoretic mobility using the Smoluchowsky equation[45]

$$\mu_{\mathrm{e}} = \frac{\varepsilon_{\mathrm{r}}\varepsilon_0\xi}{\eta}$$

where μ_{e} is the electrophoretic mobility, η is the liquid viscosity, and ε_{r} and ε_0 are the permittivity of a vacuum and the relative permittivity of the medium, respectively.

Contact Angle Measurements and Surface Energy Evaluation. Static water contact angles were measured by the sessile drop method using a conventional drop shape analysis technique (Krüss DSA 10, Hamburg, Germany). Deionized reagent grade water was used for contact angle measurements. Liquid droplets (10 μL) were dropped carefully onto the sample surface, and the average value of five measurements, made at different positions of the same sample, was adopted as the average values of contact angles of

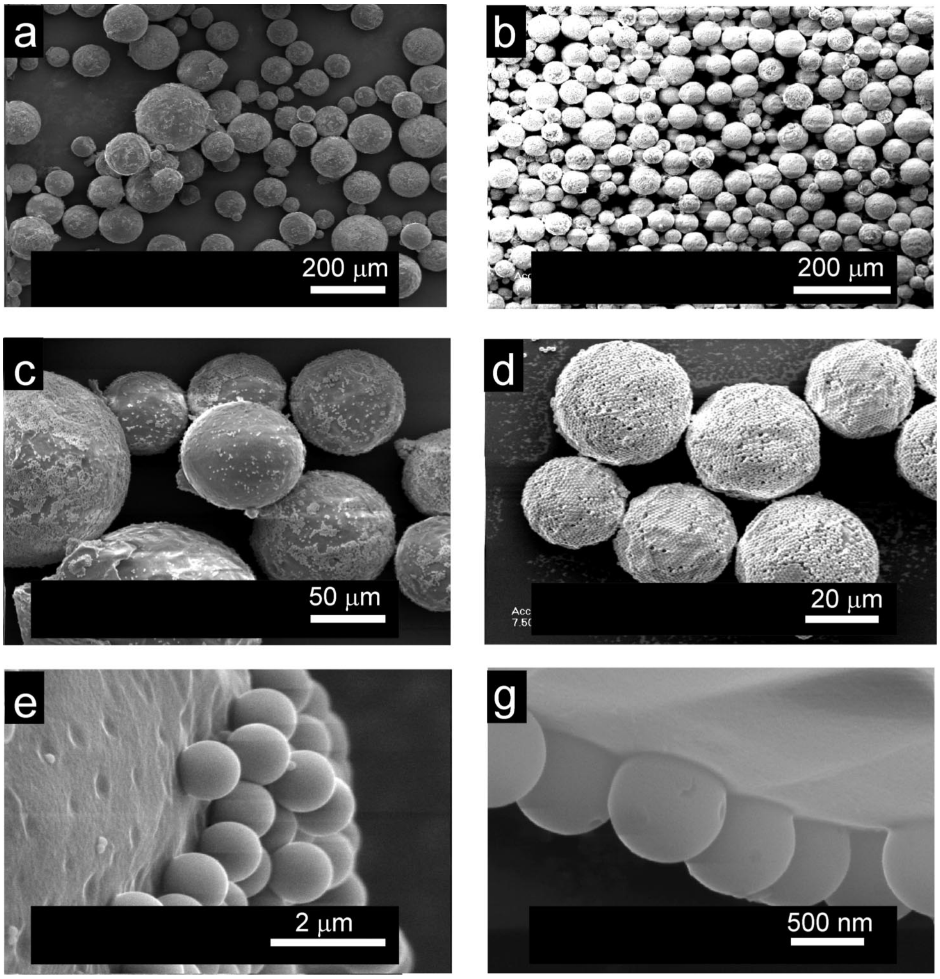

Figure 1. ESEM microphotographs of wax colloidosomes coated by native (a, c, e) and APS-modified (b, d, g) silica particles. In images a, c, and e is demonstrated that very few particles stick on top of the colloidosomes monolayer owing to imperfect washing or detachment of particles during the ESEM sample preparation. Panels b, d, and g show that once silica particles were modified by 2 wt % APS, they became more close packed and better ordered on the wax surface.

the substrates. The error of the mean contact angle values, calculated as the standard deviation, did not exceed 2° and 3°. All contact angle measurements were carried out at 24 ± 0.5 °C and relative humidity of 40 ± 3% which were kept constant. The static contact angles, measured on smooth silicon surfaces coated with the silane, were used to calculate the solid surface tension γ_{sv} according to the equation-of-state approach (EQS).[46]

Null Ellipsometry. The thickness of silane, initiator, and polymer layers in the dry state was measured at $\lambda = 632.8$ nm and an angle of incidence of 70° with a null ellipsometer in a polarizer compensator−sample analyzer (Multiscope, Optrel Berlin) as described elsewhere.[47]

Results and Discussion

Preliminary Functionalization of Particles: Colloidosomes Preparation. The Janus beads with two polymers grafted to the opposite sides of micrometer-sized silica particles were fabricated by using the toposelective modification approach, proposed by Granick and co-workers.[6,8] The original method suggested by the authors is based on the preparation of a large amount of wax colloidosomes coated with native inorganic silica particles and sequential modification of both sides of the silica particles with different silanes. We modified this method and used 3-aminopropyltriethoxysilane (APS)-coated particles to form colloidosomes (Figure 1). Further, one side of the particles was coated by ATRP initiator groups which were used to grow polymer chains. Then, carboxy-terminated second polymer was grafted to opposite side of the particles, which has free amino groups.

Use of APS-modified silica particles gives certain advantages compared to native silica particles with respect to yield and quality of JPs. To demonstrate this, we prepared wax colloidosomes coated with APS-modified silica particles and native ones. We found that the native silica particles were slightly immersed into wax (∼10 wt % of their diameter) and formed imperfect shell around wax droplet (Figure 1a,c,e). We achieved striking improvement of quality of silica wax colloidosomes if the silica beads were preliminary modified by moderately hydrophobic APS (Figure 1b,d,g). The APS-modified particles formed dense, partially hexagonally packed shell around wax (Figure 1d) and were immersed in wax up to 20−25% of their diameter. This improvement could be explained considering surface energies of materials used. The APS-modified silica particles have a lower value of surface free energy ($\gamma_{APS} = 49$ mJ/m^2) compared to that of unmodified ones ($\gamma_{SiO2} = 72$ mJ/m^2) and, therefore, possess higher affinity to the hydrophobic wax ($\gamma_{WAX} = 32$ mJ/m^2).[48]

The ATRP-initiator groups were immobilized on the exposed side of the APS-modified (SiO_2/APS) particles assembled around wax colloidosomes using the standard carbodiimide-activated reaction between carboxylic and amino groups (Figure 2). After the functionalization, wax was dissolved yielding silica particles, which are amino and ATRP-initiator (SiO_2/APS/In) functionalized at opposite sides. We found that the isoelectric point (IEP)

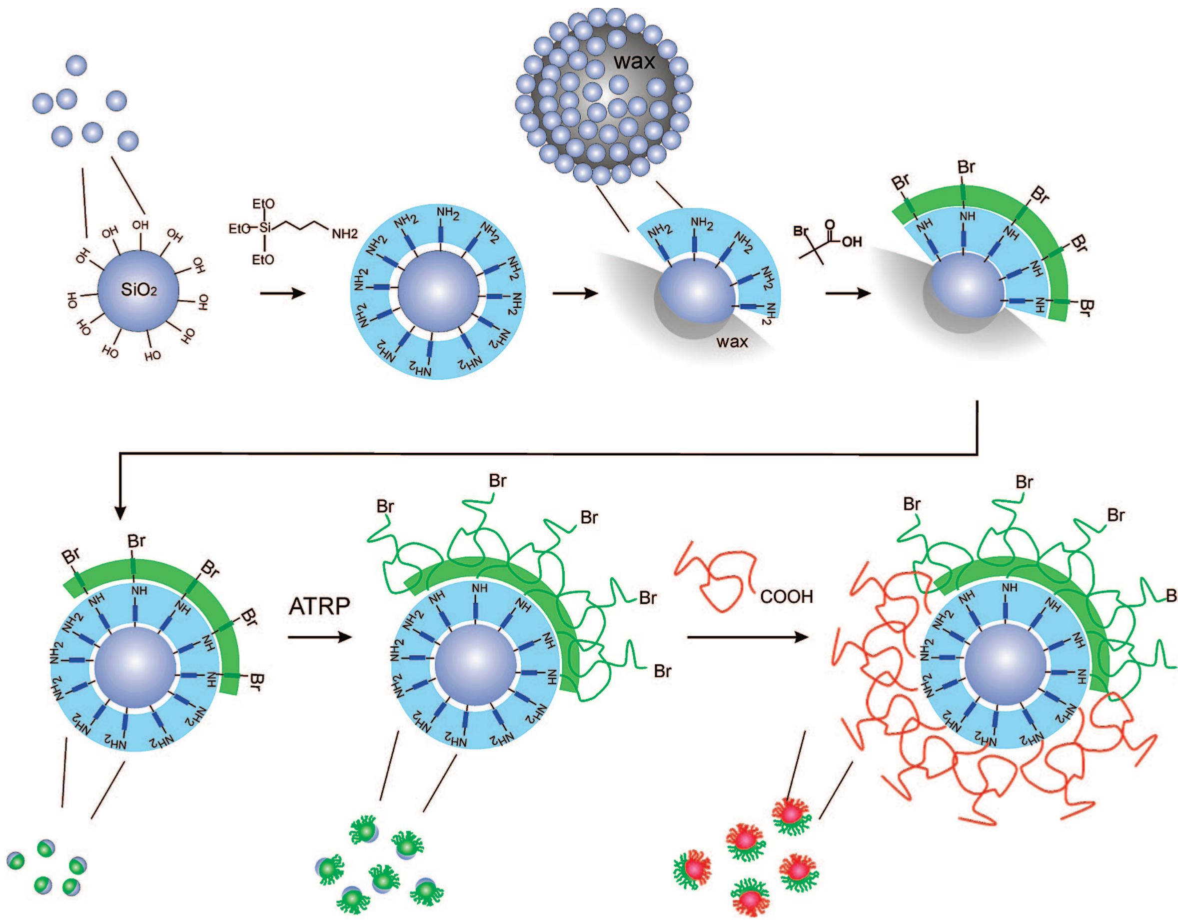

Figure 2. Scheme of the synthesis of bicomponent Janus particles by “grafting from” and “grafting to” approaches. The bare silica particles are coated by APS, assembled around wax colloidosomes and selectively modified by ATRP initiator at one side (upper panel). The first polymer (PtBA or PNIPAAm) is grafted by surface-initiated ATRP. The carboxyl-terminated second polymer (P2VP) is grafted to free amino groups on silica particles by the “grafting to” approach.

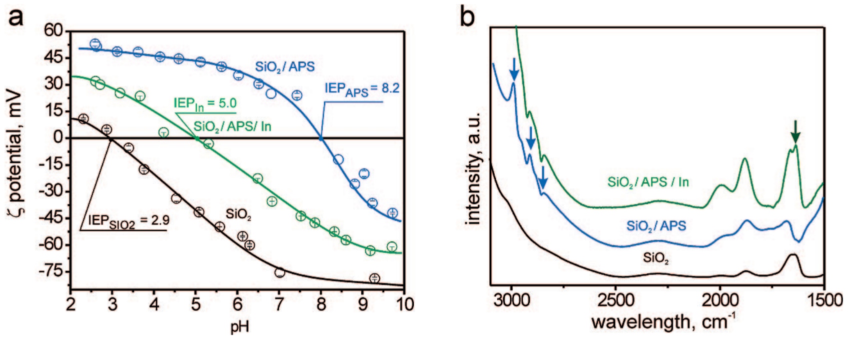

Figure 3. Properties of silica particles at different steps of modification. (a) ζ potential and (b) FTIR spectra of bare silica particle (black lines, open symbols), silica particle fully covered by APS (red lines, open symbols) and half-APS/half-ATRP-initiator coated ones (blue lines, open symbols). Characteristic bands of native SiO_2, APS-modified (SiO_2/APS) and ATRP-initiator (SiO_2/APS/In) functionalized are shown in FTIR spectra (b) by black, blue, and green arrows, respectively.

shifted from pH = 2.9 for unmodified (SiO_2) to pH = 8.2 for APS-modified (SiO_2/APS) and then down to pH = 5.0 for APS−Br−In silica particles (Figure 3a). Furthermore, the appearance of characteristic bands of APS residues (at 2700−3000 cm^{-1}) and bromoisobutyrate residue (1630 cm^{-1}) in the FTIR spectra of the particles (Figure 3b) proves the success of each step of modification.

Grafting of Stimuli-Responsive Polymers. We demonstrated grafting of first polymer on the example of surface-initiated ATRP of tBA and NIPAAm with small addition (2 wt %) of fluorescein *o*-acrylate. The role of fluorescein *o*-acrylate (fluorescent emission in the green wavelength range) was to make the synthesized polymer brushes detectable by fluorescence microscopy. On the example of grafting of tBA, it was shown that after the polymerization the FTIR-ATR spectra of the particles represent characteristic bands of the poly(*tert*-butyl acrylate) at 1740 cm^{-1} (Figure 4b, green line, data shown only for PtBA). Moreover, we accurately controlled the changes in ζ potential values and especially IEP of Janus beads after growing first polymer from the surface (Figure 4a). The isoelectric point was found to be at pH = 5.0 for the PtBA-decorated (Figure 4a, green line) and at pH = 6.9 for PNIPAAm-modified (data not presented here) Janus beads, respectively.

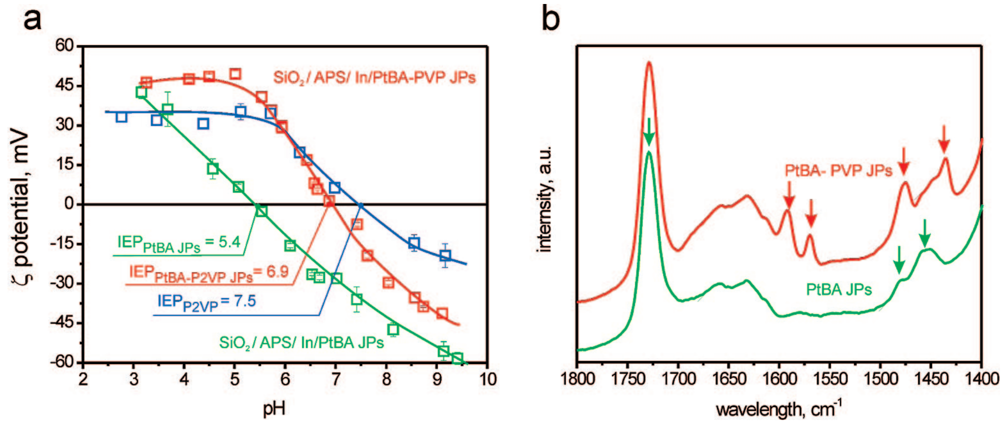

Figure 4. Properties of PtBA and PtBA−P2VP Janus particles. (a) ζ potential and (b) FTIR spectra of monofunctional PtBA JPs (green lines, open symbols), PtBA−P2VP JPs (red lines, open symbols) and reference P2VP-completely covered silica particles (not Janus ones). Characteristic bands of PtBA and P2VP initiator are shown in FTIR spectra (b) by green and red arrows, respectively.

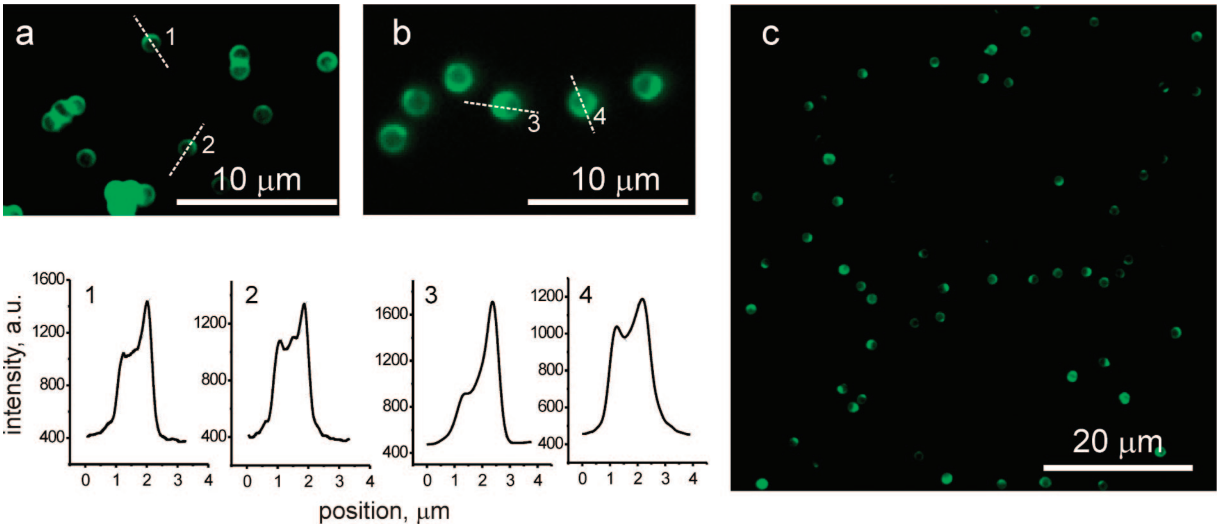

Figure 5. Fluorescence images of PtBA (a) and PNIPAAm (b, c) monofunctional JPs. Images were obtained using FITC (green fluorescence) filter sets. Intensity profiles (bottom) are given for the numbered particles in the images a and b.

Using fluorescence microscopy investigations, we verified the Janus character of the obtained particles. In particular, we found that one side of the monofunctional polymeric particles decorated with either PtBA or PNIPAAm was always brighter than the other one (Figure 5). The uncovered side of the particles appeared slightly fluorescent because of the transparency of the silica particles and multiple reflections as well as scattering of the light emitted by the fluorophore.

Diffuse reflection IR spectroscopy and TGA investigations were performed for determination of grafted amount of PtBA or PNIPAAm on silica particles. It was found that both methods were very consistent and indicated that mass fraction of PtBA was in order of 5−6 wt %.[49] Surface density of grafted polymer chains and height of polymer layer in dry state were estimated considering that 75% of particles surface was covered by ATRP-initiator as could be assumed from the structure of colloidosomes (Figure 2). The distance between grafting points was found to be smaller than the height of polymer layer which allowed us to conclude that the PtBA layer is in brush regime.[50]

The second polymer—carboxy-terminated copolymer of 2-vinylpyridine with a small addition of red-fluorescent rhodamine comonomer (see Experimental Section)—was grafted onto unoccupied amino functional part of PtBA Janus beads using the "grafting to" approach in melt.[43,51] The grafting of the poly(2-vinylpyridine) (P2VP) was proved by FTIR, TGA, electrokinetic, and fluorescence microscopy measurements as well. First, the total amount of grafted polymers increased after grafting of P2VP: PtBA−P2VP JPs contained 8.4 wt % of polymer which was more than that in PtBA JPs. Second, isoelectric point (IEP) shifted closer to the IEP of P2VP (Figure 4a). Third, FTIR spectra of bicomponent PtBA−P2VP JPs contain characteristic bands of both polymers: PtBA (1740 cm^{-1}) and P2VP (1590/1570 cm^{-1}). Finally, fluorescence microscopy (Figure 6) and SEM images (Figure 7) confirmed the Janus character of the obtained particles. From fluorescent microscopy investigations we found that while one side of the particles possess more green-fluorescent (Figure 6c), the other one is more red-fluorescent, demonstrating that the polymers were grafted to the opposite sides of the particles (Figure 6c). Figure 6c shows a combination of "green" and "red" fluorescent signals produced by the grafted polymers. Because of the scattering of the light emitted by the fluorophores on the edges of transparent silica particles, the contrast between these signals is reduced. On the other hand, the sharp contrast can be expected only in the case when the particles are oriented in the manner that border between the sides is oriented vertically. If the particles are inclined, the border between the areas with different polymers cannot be clearly distinguished.

Moreover, SEM revealed different morphology of PtBA- and P2VP-modifed sides of the JPs. Interestingly to note, the PtBA-decorated part possesses raspberry structures and appears as rougher than the P2VP-coated one (Figure 7).

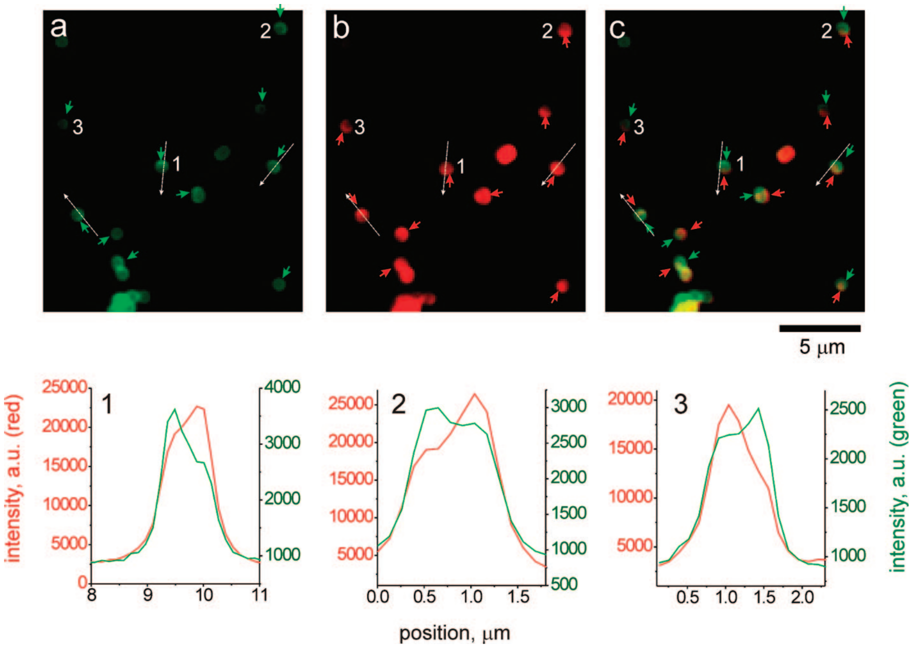

Figure 6. Fluorescence microscopy images of PtBA-PVP JPs obtained using FITC (a, green) and TRITC (b, red) filter sets. Image (c) is a color combination obtained from the images (a) and (b). Intensity profiles are given for numbered particles in images (a) and (b).

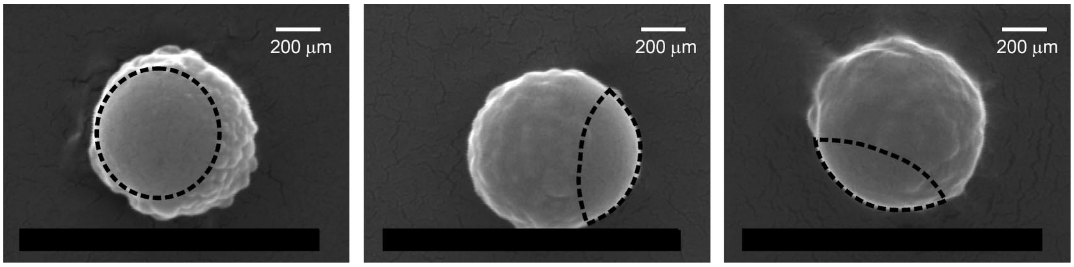

Figure 7. ESEM images of the PtBA−P2VP Janus particles. The P2VP-modified area is enclosed by a dashed line.

Using diffuse IR spectroscopy, we estimated the grafted amount of both polymers in obtained PtBA−P2VP JPs (Table 1) from calibration curves. We found that grafted amount of PtBA calculated did not change after grafting of the P2VP, indicating that the grafting of PtBA was robust (Table 1). We note that in the case of the rhodamine-labeled P2VP, exact determination of weight loss from TGA experiments was hardly possible because the thickness of the polymer layer produced by the "grafting to" procedure was rather small. Therefore, the grafting density of the rhodamine-labeled P2VP was evaluated using a reference sample where the P2VP was grafted onto flat silica wafer using exactly the same experimental procedure. The thickness of the grafted P2VP film was measured by means of null-ellipsometry experiments and was used for evaluation of the grafting density and (Γ) and distance between grafting sites (D)[47] (Table 1). In particular, we found that the distance between grafting points of P2VP was found to be smaller than the height of the P2VP layer which allows us to conclude that the P2VP layer is in the brush regime as well.

Stimuli-Responsive Properties of JPs. Finally, PtBA−P2VP JPs were hydrolyzed in acidic media yielding mixed polyelectrolyte poly(acrylic acid) (PAA)−poly(2-vinylpyridine) (P2VP) JPs. Next, responsive properties of bicomponent JPs decorated with two different polyelectrolytes PAA and P2VP to pH changes were investigated by means of in situ ζ potential and size measurements (Figure 8a,b). As was previously noted,[52] the swollen chains of PAA themselves dissociate and create an ionized meshwork in part penetrated by the flowing solution. Thereby, the exact determination of a discrete shear plane potential is certainly questionable for this system. Therefore, all discussion about electrokinetic properties of PAA-grafted layers should be described in term of the apparent ζ potential.

We observed a very interesting pH-dependent aggregation of bicomponent PAA−P2VP Janus particles. Depending on the hydrodynamic diameter of the JPs, three different regimes were distinguished (Figure 8a,b).

Regime I ($2 < \text{pH} < 5$): The Janus particles form large aggregates of about 4−10 μm in diameter, which could not be redispersed by sonification in ultrasonic bath.[53] In this regime, PAA ($\text{iep}^{\text{PAA}} = 2.3$) and P2VP ($\text{iep}^{\text{PVP}} = 7.3$, Figure 4a) chains are charged negatively and positively, respectively.[41] Thereby, the charges of polymers are compensated when the JPs are aggregated and the aggregates appear to be uncharged. We believe that the electrostatic attraction between the oppositely charged sides on the particles cause formation of massive aggregates. Similar behavior we observed in fluorescent microscopy images and photographs made for the same dispersions (Figure 8c,d).

Regime II ($5.5 < \text{pH} < 7.5$): The singular particles are observed in solution (Figure 8b). The dispersion is stable, and no coagulation and precipitation were observed (Figure 8c,d). In this regime, PAA and P2VP (Figure 4a) are negatively charged and almost uncharged, respectively.[41] However, since PAA covers 75% of the particle surface, the charge and therefore the stability of the particles are determined by the properties of PAA. Thereby, JPs are electrostatically and sterically stabilized.[54,55]

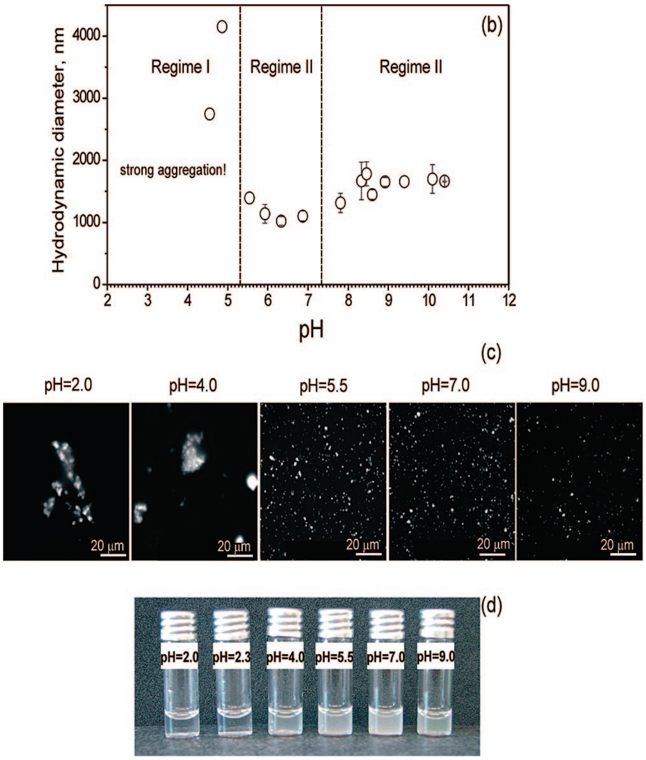

Figure 8. Stimuli-responsive behavior of mixed oppositely charged polyelectrolyte PAA−P2VP Janus particles: ζ potential (a), hydrodynamic diameter (b), fluorescence microscopy images (c), and photographs (d) of PAA−P2VP JPs dispersions at different pH values. All fluorescent microscopy investigations were performed in real dispersions.

Regime III (7.5 < pH < 9.2): Further increase of pH value up to 9.2 led to the formation of small aggregates composed almost of 2 JPs (Figure 8b). Dispersion of JPs at pH = 9.2 found to be less stable (Figure 8d). At the same time, the apparent value of ζ potential of JPs decreased from ζ = −50 mV down to ζ = −40 mV when pH increased from pH = 7.5 up to pH = 9.2, respectively (Figure 8 a,b). Observed decrease of the charge could be explained by an increase of electrolyte concentration in the system upon higher pH values during the titration. The negative charges on PAA chains are therefore partially screened by charged ions. As a result, electrostatic repulsions are reduced and particles are slightly aggregated.

Conclusions

In summary, we presented a new versatile concept for design of stimuli-responsive bicomponent Janus particles decorated by polymers with different polarity and charge. To synthesize responsive Janus particles, we applied sequentially "grafting from" and "grafting to" approaches. The first polymer was grafted on one side of silica particles using the surface-initiated ATRP, "grafting from" method. The second polymer was immobilized using the "grafting to" procedure in melt by reaction of reactive terminating carboxylic group and functional groups on the other side of the particle surface. It was demonstrated that the synthesized Janus particles possess a sharp interface between the constituent phases. The obtained bicomponent Janus particles are stimuli-responsive and changes in pH resulted in the formation of hierarchically structured aggregates from JPs. We believe that switchable Janus particles decorated with two sorts of responsive polymers can be used for controlled stabilization of emulsions and regulation of the molecular transport at interface between immiscible liquids.

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