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Surface characterization of nanoparticles carrying pH-responsive polymer hair

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ABSTRACT

The surface of near-monodisperse colloidal polystyrene (PS) latex particles carrying pH-responsive poly[2-(diethylamino)ethyl methacrylate] (PDEA) polymer chains as a steric stabilizer has been extensively characterized in dry and wet states. X-ray photoelectron spectroscopy and contact angle measurement studies confirm that PDEA chains are located on the PS latex particle surface. Transmission electron microscopy (TEM) studies reveal that the sterically stabilized PS particles have a core-shell morphology and wet atomic force microscopy data confirm that the pH-responsive PDEA component covers the PS latex core and the thickness of the protonated steric polymer is estimated to be approximately 15 nm. The PS latex particles can be easily dispersed in acidic aqueous media (pH 3.0) whilst they flocculate in basic aqueous media (pH 10.0) due to the pH-responsive PDEA hair. This dispersion–flocculation cycle of the PS latex is fully reversible.

1. Introduction

'Hairy particles' are defined as the particles whose surface is covered with grafted linear polymer chains that have a high affinity with the dispersing media. There has been an increasing interest in stimuli-responsive 'hairy particles' because of their possible applications in various fields, such as catalyst supports [1], smart particulate emulsifiers [2], foam and liquid marble stabilizers [3,4], templates for nanocapsules [5] and novel electrical and optical devices [6]. Several methods have been proposed for the synthesis of such particles: (i) graft polymerization of monomer from the surfaces of core particles (so-called 'grafting from') [7]; (ii) reaction of pre-formed polymers with a functional chain end group onto core particles (so-called 'grafting to') [8]; (iii) synthesis of the polymer latex in the presence of a media-philic macromonomer which can act directly as a colloidal stabilizer [9]; and (iv) self-assembly of block copolymers [10]. Recently, we have demonstrated that sterically stabilized polystyrene (PS) latex particles carrying poly[2-(diethylamino)ethyl methacrylate] (PDEA) chains (PDEA-PS particles) can be synthesized by the dispersion polymerization of styrene using a PDEA-based macro-azoinitiator as an 'inistab' (initiator and colloidal stabilizer) [11]. The changing solubility of the PDEA at its pK_a (pH = 7.3) [12] due to protonation/deprotonation successfully gave the latex a pH-responsive stability in aqueous solution.

Considering the wide variety of application areas mentioned above and that surface of the hairy particles play an important role in their applications, it is crucial to understand the detailed surface characteristics of these latex particles. In the case of the pH-functional particles like the PDEA-PS latex, in particular, in situ surface characterization in aqueous solutions is essential to understand their pH-responsive colloidal behaviors that the particles are expected to have, and to optimize their functions for specific applications. There have been, however, only a limited number of studies on the surface characterization of such stimuli-responsive hairy particles [1b,2b,6,7b]. By contrast, there have been considerably more studies on the characterization of these types of particles in a form of dispersion.

Herein, we describe the extensive surface characterization of the PDEA-PS latex particles. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and elemental analysis were used for the characterization in terms of surface chemistry, particle size and

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chemical compositions. Furthermore, the latex particles have been characterized in situ in terms of surface chemistry and colloidal stability using atomic force microscopy (AFM), contact angle measurement, optical microscopy, laser diffraction method and turbidity measurement.

2. Experimental section

2.1. Materials

Chemicals used for synthesis of PDEA-based macroazoinitiator are the same with those used in our previous study [11]. PS homopolymer (average molecular weight, 45,000), α,α′-azobisisobutyronitrile (AIBN), 2-(diethylamino)ethyl methacrylate (DEA, 99%), styrene, toluene and 2-propanol (IPA: purity, 99%) were purchased from Sigma–Aldrich. Milli-Q water (Millipore Corp., MA, USA) with a specific resistance of 18.2×10^6 Ω cm was used.

2.2. Synthesis of PS latex particles carrying PDEA hair

Sterically stabilized PDEA-PS latex particles were synthesized by the dispersion polymerization of styrene using a PDEA-based macroazoinitiator (degree of polymerization, 50) as an inistab in IPA according to a previously reported protocol [11]. The PDEA macroazoinitiator was synthesized by atom transfer radical polymerization of DEA using 2,2′-azobis[2-methyl-*N*-(2-(2-bromoisobutyryloxy)ethyl) propionamide] as an initiator in IPA at 25 °C and was purified by passing through a silica column.

The PDEA macroazoinitiator (0.47 g; 0.5 mol% based on styrene) and styrene monomer (0.50 g) were added to IPA (5.0 mL) in a flat-bottomed 15 mL vial containing a magnetic stirrer bar. This reaction mixture was vigorously stirred at room temperature until the macroazoinitiator and monomer had dissolved completely. N_2 bubbling was conducted for the mixture for 30 min in order to remove dissolved oxygen. The polymerization commenced put the reaction vessel in an oil bath (80 °C). The reaction was allowed to proceed for 48 h with continuous stirring at 500 rpm under a nitrogen atmosphere. The latex obtained was purified by repeated centrifugation–redispersion cycles with pure IPA (typically 20,000 rpm for 10–30 min) using a centrifuge (Beckman coulter Allegra 64R centrifuge ALV03E06 with a Beckman F1202 rotor). PDEA homopolymer was prepared by free radical solution polymerization of DEA (5.0 g) using AIBN (0.10 g) as a free radical initiator in toluene (10 g).

2.3. Characterization of the PS latex particles with PDEA hair

2.3.1. Scanning electron microscopy (SEM)

The centrifugally washed latex dispersion droplets were dried on an aluminum stub and sputter-coated with gold (SC-701 Quick Coater, Elionix, Japan) in order to minimize sample-charging problems. SEM studies were carried out using a Keyence VE-8800 SEM operated at 5 kV.

2.3.2. Transmission electron microscopy (TEM)

TEM studies were made on diluted dispersion dried onto carbon-coated copper grids using a JEM-2000EX electron microscope (JEOL Ltd., Tokyo, Japan) operating at 120 kV and 70 pA.

2.3.3. Chemical composition

CHN elemental microanalyses were carried out using a CHN-Corder MT-5 (Yanaco, Japan). The PDEA loading of the PDEA-PS particles were determined by comparing its nitrogen content to that of the PDEA homopolymer prepared by the free radical solution polymerization.

2.3.4. X-ray photoelectron spectroscopy (XPS) study

A dried drop-cast film of the sample suspension was mounted onto XPS sample stubs using a conducting tape. XPS measurements were carried out using an AXIS-NOVA spectrometer (Kratos Analytical Ltd.) with a monochromated AlKα X-ray gun. The resolution pass energies were fixed at 160 and 40 eV for wide and narrow scans, respectively. Quantification of the atomic% composition was obtained from the high resolution spectra using the manufacture's sensitivity factors. Spectra were aligned to the hydrocarbon component of the C1s peak set at 284.8 eV.

2.3.5. Contact angle measurements

Contact angles for water droplets (10 μL) placed on pressed pellet made of dried PDEA-PS particles were determined 10 min after setting the water droplet using an Excimer SImage02 apparatus at 25 °C. The pellet was prepared at a pressure of 6.03×10^8 Pa.

2.3.6. Percentage transmittance measurements

%T Values of the aqueous dispersion of the PDEA-PS latex particles were recorded using a Shimadzu UV-1600 spectrophotometer with a 1.0 cm path length quartz cuvette at various pH values. The measurements were conducted in the upper part of the sample: precipitated polymer in the aqueous media settled to the bottom of the quartz cuvette, which leads to high %T values.

2.3.7. Particle size analysis by laser diffraction method

A Malvern Mastersizer 2000 instrument equipped with a small volume Hydro 2000SM sample dispersion unit (ca. 150 mL including flow cell and tubing), a He–Ne laser operating at 633 nm and a solid-state blue laser source operating at 466 nm were used to monitor the size of the latex particles. The stirring rate was adjusted to 2000 rpm. The raw data were analyzed using a Malvern software. The mean particle diameter was taken to be the volume mean diameter ($D_{4/3}$), and the 'span' was taken as a measurement of the width of the particle size distribution. This parameter is calculated using span $= (D(0.9) - D(0.1))/D(0.5)$, where $D(0.9)$ is the diameter for which 90% of the particles are below this size, $D(0.5)$ is the diameter for which 50% of the particles are below this size (also known as the mass median diameter), and $D(0.1)$ is the diameter for which only 10% of the particles are smaller than this size. Particle size can be measured from 0.02 to 2000 μm.

2.3.8. Optical microscopy

IPA medium of the PS dispersion was replaced with water media with pH values of 3 and 10 by dialysis. A drop of the diluted latex was placed on a microscope slide and observed using an optical microscope (Shimadzu Motic BA200) fitted with a digital system (Shimadzu Moticam 2000).

2.3.9. AFM measurements

Wet (in situ) imaging of the PS latex particles covered with a PDEA-rich shell layer was performed with a Veeco Nanoscope IV AFM system. A cantilever with SiO_2 tip whose nominal spring constant of 0.58 N m^{-1} was used for these measurements and was cleaned using a UV-O_3 cleaner prior to use. Ten times diluted sample suspension was introduced to an AFM liquid cell at pH 3.5 (adjusted by HCl) and in situ AFM imaging (tapping mode) was performed on a freshly cleaved mica surface. Then the supernatant was replaced by a pH 3.5 aqueous solution (2 mL) to remove any non-adsorbing or weakly adsorbed PS latex particles. A pH change was made via an alkaline rinse at pH 9 (4 mL, adjusted by KOH) in the AFM liquid systems and again in situ AFM measurements were performed at this pH.

In addition to the AFM imaging, interaction forces were also measured between the cantilever tip and the particle surface. For the force measurements, a PDEA-PS particle layer was made onto a fleshly cleaved mica surface by dropping a solution of the particle in IPA on the surface and drying it. Then, pH-adjusted electrolyte solutions were introduced into the AFM liquid cell to measure the interaction forces. The apparent separation distance between the surfaces was determined by simply assuming the constant compliance region of the force (the region where cantilever deflection versus sample-position curve gives straight line) to be zero distance [13]. It should be noted, therefore, that zero distances determined by this method are not directly measured zero distances but indicate only the point of hard-wall contact where the any layer no longer compresses under the cantilever tip. In the present case, the separation distances given should be considered as a relative distance from an ill-defined zero position, the point of hard-wall contact.

3. Results and discussions

3.1. Synthesis of PDEA-PS latex particles

PDEA homopolymer is a weak polybase that is soluble in aqueous media below pH 7 because of protonation of their tertiary amine groups. At pH 8 or above, PDEA homopolymer has very low or zero charge density, which results in precipitation in basic aqueous media. The PDEA-based polymers have been used for latex particles [14], microgels [15] and shell cross-linked micelles [16]. A number-average molecular weight of the PDEA-based macroazoinitiator used in this study was determined to be 15,300 and 19, 400 by gel permeation chromatography (GPC) and ^{1}H nuclear magnetic resonance (NMR), respectively. The narrow molecular weight distribution (M_w/M_n, 1.12 determined by GPC) of obtained initiator indicated successful atom transfer radical polymerization and the preservation of the azo functionality. It is clear that there is a good agreement between the target number-average molecular weight calculated from the monomer/initiator molar ratio and those determined experimentally from GPC and ^{1}H NMR studies.

The dispersion polymerization using the PDEA macroazoinitiator was conducted at an initiation rate of polymerization of 5.9×10^{12} mL^{-1}s^{-1}, where sufficient initiator radicals are generated in the dispersion polymerization system [11,17]. The formation of the PS latex particles consists of two stages: (1) the formation of PDEA-*block*-PS copolymers through the thermal decomposition of the azo group and free radical polymerization of styrene and (2) self-assembly of the PDEA-*block*-PS copolymers. As polymerization proceeds and PS reaches a critical chain length, PDEA-*block*-PS copolymers are precipitated in the polymerization medium: PS is not soluble in IPA medium and the block copolymer chains self-assemble to form particles. Since the PDEA component is soluble in IPA, it should operate as a steric stabilizer to disperse and stabilize the PS particles in the IPA medium of the dispersion polymerization system. The conversion of styrene reaction was determined to be over 90% gravimetrically. Milky white PDEA-PS latex particles were obtained after the polymerization, which are colloidally stable at least for 2 years (see Fig. 1a). Laser diffraction studies after centrifugal washing with IPA indicated that a $D_{4/3}$ of the PDEA-PS particles was 118 ± 41 nm (span = 0.916) and confirmed the PDEA-PS latex particles disperse readily in IPA even after repeated centrifugation–redispersion cycles. A typical SEM image of the PS latex is shown in Fig. 1b, which indicates the production of near-monodisperse spherical nanoparticles. A number-average diameter and coefficient of variation (C_v) value was estimated to be 117 nm (D_w/D_n, 1.03) and 10% from the SEM image, respectively (over 100 particles were counted). The diameter determined by laser diffraction was consistent with that determined from the SEM image. Elemental analysis indicates that both PDEA macroazoinitiator and PDEA homopolymers have almost the same atomic ratios and they accord well with those calculated from the chemical structure, respectively (Table 1). Percentage mass of PDEA loading in the PDEA-PS particles was determined to be 24.0% by comparing its nitrogen content to that of the PDEA homopolymer ($N = 7.55\%$) synthesized by free radical polymerization (Table 1).

Table 1
Elemental analysis results of PDEA$_{50}$-PS particles, PDEA homopolymer, PDEA$_{50}$ macroazoinitiator and PS homopolymer.

Sample	C%	H%	N%
PDEA$_{50}$-PS particles	85.10	8.29	1.81
PDEA homopolymer	64.53	10.35	7.55
PDEA$_{50}$ macroazoinitiator	64.07	10.29	7.60
PS homopolymer	92.29	7.82	–

3.2. XPS studies

In order to confirm the existence of PDEA on the PS latex particle surface, XPS studies were carried out. XPS is an established spectroscopic technique for assessing the surface compositions of colloidal particles. Fig. 2 shows the XPS survey spectra of (a) the PDEA-PS particles, (b) the PDEA homopolymer (prepared by solution polymerization) and (c) the PS homopolymer. Three elements were detected from the two samples of the PDEA-PS particles and the PDEA homopolymer, namely oxygen, carbon and nitrogen. The O1s signal, observed in the PDEA-PS latex and PDEA homopolymer, was absent in the PS homopolymer reference spectrum. The O1s core-line spectrum confirms that this signal is due to the two oxygen atoms (C=O and C–O) of the methacrylic ester groups on the grafted PDEA stabilizer (Fig. 3). Given that the XPS sampling

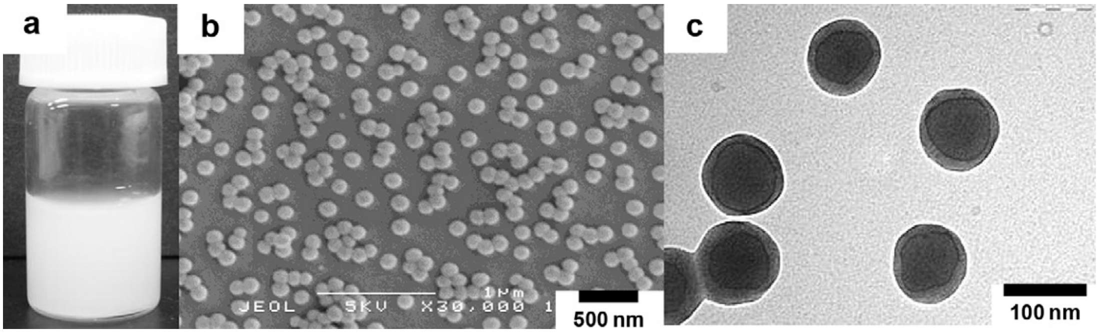

Fig. 1. (a) Digital camera image of PDEA$_{50}$-PS latex particles dispersed in IPA medium, (b) SEM and (c) TEM images of PDEA$_{50}$-PS particles.

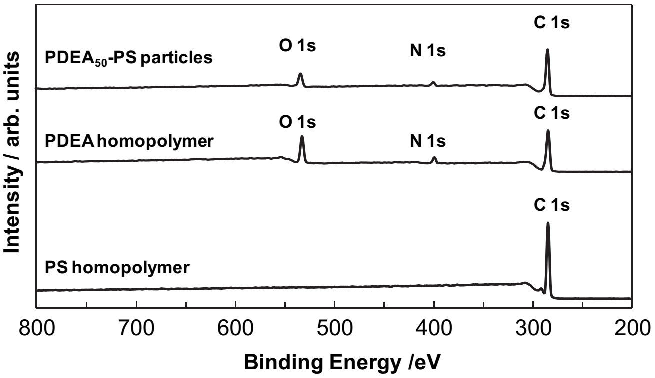

Fig. 2. XPS survey spectra obtained for PDEA_{50}-PS particles, PDEA homopolymer and PS homopolymer.

depth is typically only in the range of 2–5 nm, these observations provide good evidence that the grafted PDEA stabilizer is present at the surface of the PDEA-PS latex particles, as expected. Moreover, the intensity of the N1s signal obtained for the PDEA-PS latex can be compared to that of the PDEA homopolymer in order to estimate a surface existence percentage of approximately 61% for the PDEA stabilizer chains on the latex surface (Table 2). High resolution C1s XPS spectra of the PDEA-PS latexes, PDEA homopolymer and PS homopolymer are shown in Fig. 3. In the C1s core-line spectra of PDEA-PS particles and PDEA homopolymer, two components due to the two carbon atoms (C=O and C–O) of the methacrylic ester groups were observed in addition to that due to carbon atom (C–C) of main polymer backbone. This is a direct evidence for the expected PDEA-rich hair morphology. Recently it was demonstrated that silica can be successfully deposited onto the PDEA-PS latex particles by a biomineralization reaction between the DEA units and tetramethoxysilane at neutral pH. After calcination, hollow silica particles were obtained, which also indicates the PDEA-rich surface [5]. A ‘shake-up’ satellite at approximately 290–293 eV is clearly visible in the spectra of the PDEA-PS latex and PS homopolymer. This feature has been previously assigned to a π–π^* transition for the aromatic rings of the PS component [18]. This result indicates that PS component exists within the depth of 5 nm from the surface (Table 2).

Table 2
Quantitative surface composition of PDEA_{50}-PS particles, PDEA homopolymer and PS homopolymer determined by XPS.

XPS sample	Atom%			Mass%		
	C	N	O	C	N	O
PDEA_{50}-PS particles	85.65	3.82	10.52	82.25	4.28	13.46
PDEA homopolymer	76.64	6.25	17.11	71.82	6.83	21.35
PS homopolymer	99.81	–	0.19	99.75	–	0.25

3.3. TEM studies

A typical TEM image is shown in Fig. 1c. The core-shell morphology of the PS latex particles is verified visually from the TEM image: taking into account that IPA is a good solvent for PDEA and not for PS, the PDEA should form the shell and PS should form the core. A number-average shell thickness was measured to be 12 nm (C_v, 32%), which is thicker than the mean square end-to-end distance for the PDEA with a polymerization degree of 50 (1.3 nm). Two possible models can be proposed for explanation of the thicker shell layer of these latex particles. One model is a fully-extended PDEA hair layer which completely hides the PS core. The length for the fully-extended PDEA ($n = 50$) was calculated to be 12.5 nm, assuming that the C–C bond length is 0.154 nm and the C–C chains form a planar zigzag conformation with a bond angle of 109.28°. This length accords well with the shell thickness observed in the TEM image. We believe, however, this model is not realistic for the present system, taking it into the account that the square root of the molecular area of the soft PDEA chain occupied at the PS core surface (2.1 nm) is comparable to the mean square end-to-end distance (1.3 nm) for the PDEA ($n = 50$) [11]. The square root of occupied molecular area and the mean square end-to-end distance were calculated using a PS density of 1.05, assuming that all the PDEA chains are covalently bonded at the PS particle surfaces and that the PS core has a D_n of 83 nm (determined from the TEM images). In addition, the shell has uneven thickness between 6 and 21 nm and this maximum thickness is much larger than fully-extended PDEA length, 12.5 nm ($n = 50$). It has been previously reported that PS-*b*-poly(methyl methacrylate) copolymer localized at the interface between the two immiscible PS and poly(methyl

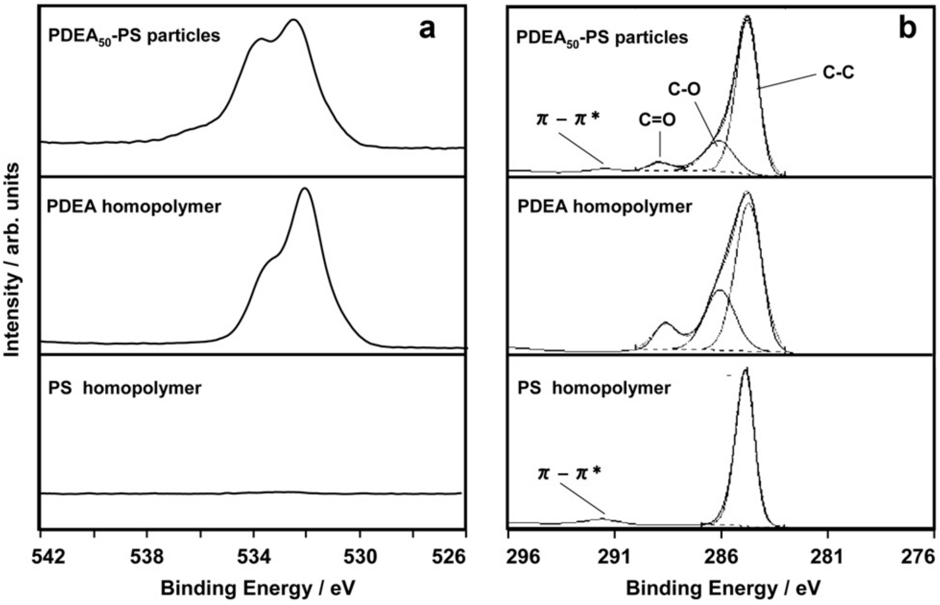

Fig. 3. XPS spectra obtained for PDEA_{50}-PS particles, PDEA homopolymer and PS homopolymer: Core-level (a) O1s and (b) C1s spectra.

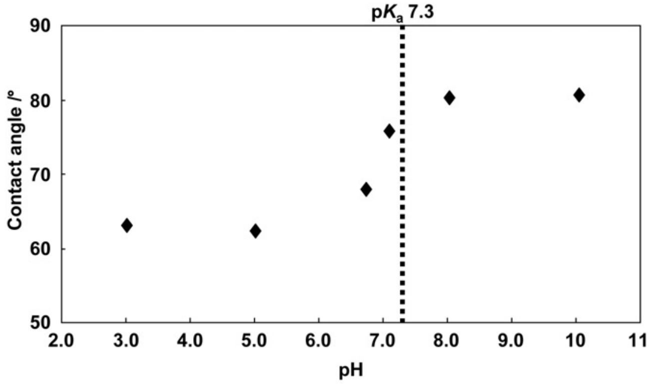

Fig. 4. The effect of pH on the contact angle of a water droplet placed on a pellet prepared by pelletization of dried PDEA$_{50}$-PS latex powder.

methacrylate) homopolymers, an interfacial region with a thickness of approximately 20 nm is formed in which both the PS and poly(methyl methacrylate) components coexist [19]. Considering PS-*b*-PDEA copolymers are expected to be located at the interface between immiscible PS and IPA in this case, it is reasonable to think that the shell may consist of a PDEA-rich polymer layer that also includes some PS component. XPS measurements on the PDEA-PS particles indicated the existence of some PS within a surface depth of 5 nm, which also supports the second model. Consequently we might infer that a PDEA-rich shell layer model is a more realistic representation of this system.

3.4. Contact angle measurements

The static contact angle for a sessile water drop on a pressed pellet of the PDEA-PS particles was measured at different pH values (Fig. 4). Above pH 8.0, the contact angles measured through water were 80°, which indicates that the surface is relatively hydrophobic due to the non-protonated PDEA surface chains. On the other hand, contact angles were reduced to approximately 60° below pH 5.0. This reduction of the contact angle can be explained by the protonation of the PDEA polymer chains which will increase the hydrophilic character for the latex surface.

3.5. AFM studies

Fig. 5 shows the wet (in situ) tapping mode AFM images obtained either (a) at pH 3.5 or (b) at pH 9. One can clearly see circular objects in these AFM images, even after rinsing by pH 3.5 and pH 9 aqueous solutions (Fig. 5b). This suggests that the PS latex particles covered by the PDEA-rich hair are strongly adsorbed to the pristine mica surface. It should be recalled here that the original size of the latex particles is approximately 120 nm in diameter (after drying, see Fig. 1). One may notice that the diameter of circular objects observed in Fig. 5 is somewhat larger than the original latex diameter; however, we must consider the effects of drying in the case of SEM measurements as well as an apparent overestimation as a result of AFM tip convolution. We note that the section analysis of these AFM images suggests the height of the circular objects in the range of 80–140 nm, being broadly consistent with the original latex diameter. Unfortunately, it is hard to see any significant differences in the surface morphologies (size and height of the observed objects) between the two AFM images, within the resolution of our experimental setup.

Typical force-distance data obtained between the AFM probe tip and the PDEA-PS particle surface at pH 3.0 and 10.0 are given in Fig. 6a and b, respectively. At pH 3.0, a monotonically repulsive force

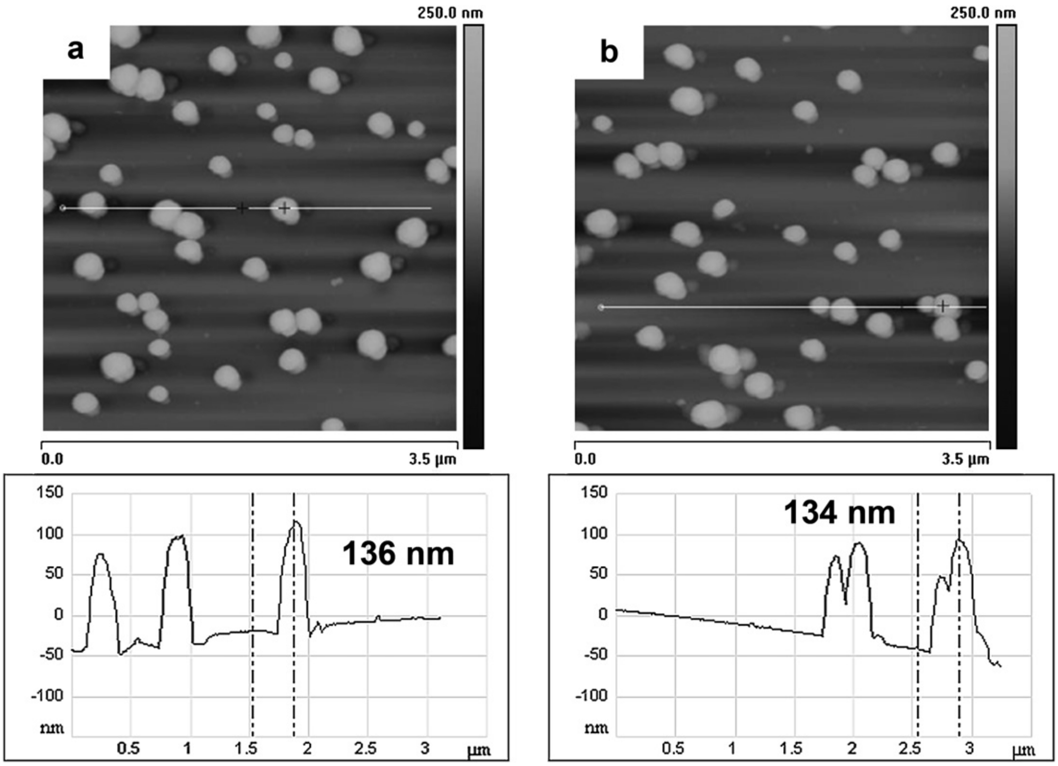

Fig. 5. Wet (in situ) tapping mode AFM images of PS latex particles covered by PDEA-rich hair brushes, measured in (a) pH 3.5 and (b) pH 9 solutions. Cross sectional data are also shown for each figure.

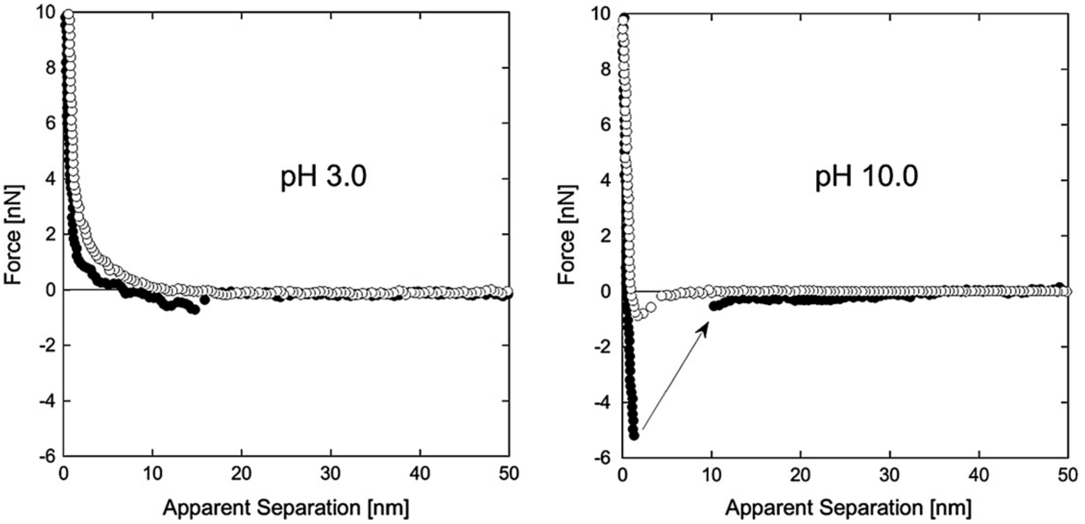

Fig. 6. Force curves between PDEA$_{50}$-PS particle and probe tip obtained in 10 mM KCl solutions with various pH. Open and closed symbols represent data on approaching and retracting of the surfaces, respectively.

was observed in both approaching and retracting force curves, and the range of the forces was seen to be ca. 15 nm. At this pH, the charge of the tip surface, which is made of SiO_2, is thought to be very low since pH 3 is close to the isoelectric point of SiO_2, although zeta potential of the latex surface is around +40 mV [11]. Our preliminary experiment showed that no electrostatic repulsion could be detected between similarly charged surfaces using this probe because the tip radius was very small and this made the interaction force too weak to be detected. These facts suggest that the observed repulsion is steric in nature, rather than electrostatic. It is worth noticing here that the apparent range of the repulsion is in reasonable agreement with the number-average of the shell layer thickness observed with TEM shown in Fig. 1c, although the range of the repulsive force does not necessarily give the exact thickness of the layer. As mentioned in the 'TEM' section, the shell layer of the particle is suggested to consist of a PDEA-rich polymer layer on the core PS particle rather than being fully-extended PDEA chains. This coincidence indicates that the shell layer is rather soft in nature in the aqueous solution at this pH. Such a property of the layer is attributable to the protonation of the PDEA and this protonation could induce PDEA-rich hydrated shell to become flexible. On the other hand, no repulsive force was observed in the force data at pH 10.0. Instead, the force data indicated a short-range attractive force in the approaching curve and an adhesion force in the retracting one. This transformation of the force curve by pH clearly indicates a structural change of the shell layer with pH: the protonated PDEA-rich shell layer at lower pH collapses to a more rigid dehydrated layer at high pH by the deprotonation of the PDEA molecules.

3.6. pH-Responsive colloidal stability of the PDEA-PS latex particles

3.6.1. Percentage transmittance measurements results

It has been confirmed that the PS latex particles carry pH-responsive PDEA polymer chains, and as a result the latex can be

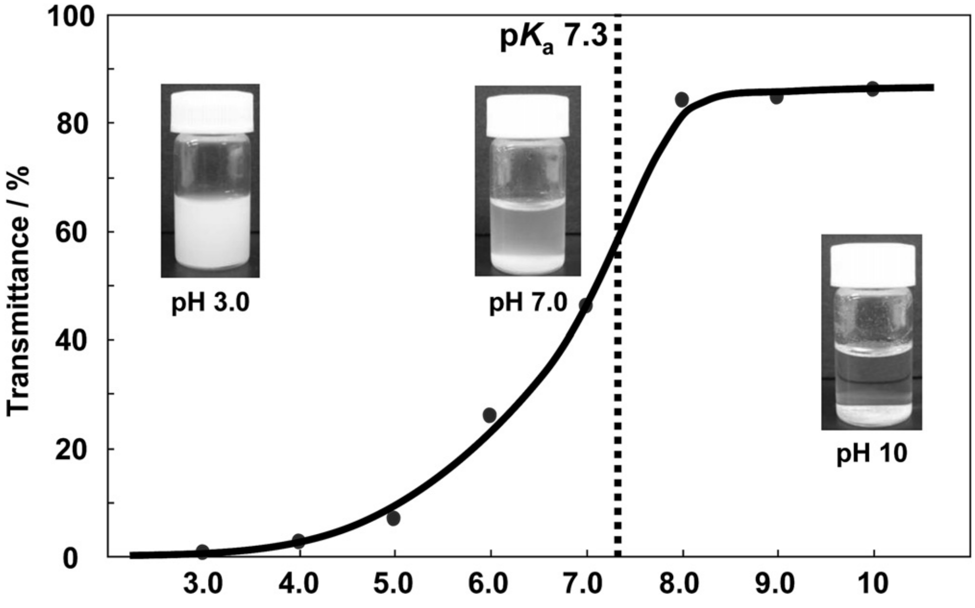

Fig. 7. Percent transmittance (%T) at 545 nm for PDEA$_{50}$-PS particles dispersed in aqueous media at 1.0 wt% as a function of pH.

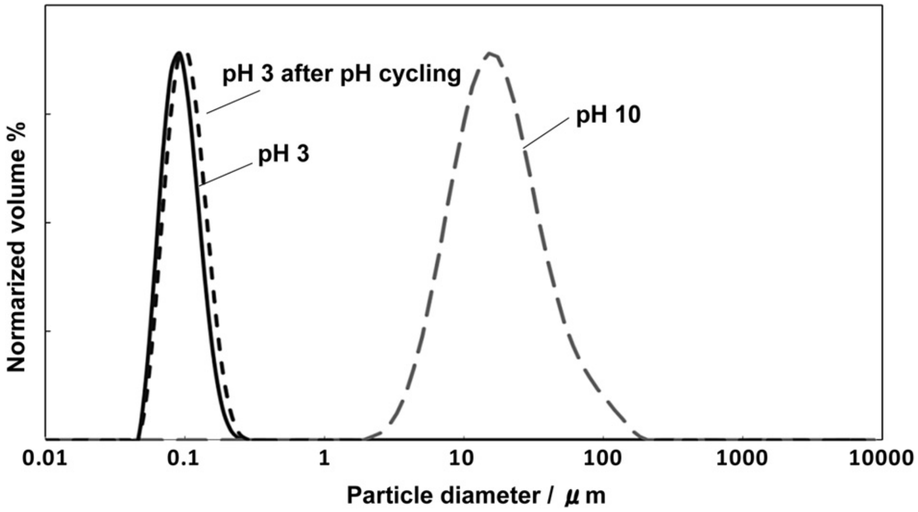

Fig. 8. Laser diffraction particle size distribution curves obtained for $PDEA_{50}$-PS latex particles at pH 3 and pH 10. The dotted curve shown around 0.1 μm was obtained after pH cycling (from pH 3 to 10 and back to pH 3).

dispersed or flocculated with changes in pH. Transmission values (%T) for an aqueous dispersion of PDEA-PS latex particles (0.2 wt%) were measured at various pH values, see Fig. 7. %T values were less than 10% at all pH < 5.0: PDEA is soluble in acidic aqueous media and can work as an effective steric stabilizer, which leads to a stable colloidal dispersion. Increasing the pH above pH 5.0 led to a gradual increase in %T values up to approximately pH 8.0. The PDEA has a pK_a value of 7.3 and the PDEA steric stabilizer should be around 1 and 10% deprotonated at pH 5.3 and 6.3, respectively. Therefore, we expect the PDEA-PS latex to lose stability gradually as the pH is increased. Dynamic scattering data indicated that hydrodynamic diameter of the latex particles increased slightly above pH 5.0, suggesting some flocculation of the latex particles was occuring. This is consistent with the increase in %T as the pH increases. Above pH 8.0, a constant value of %T (approximately 85%) was seen. This is consistent with the aggregation and settling of the PDEA-PS latex, and this feature can be confirmed by direct visual inspection.

3.6.2. Laser diffraction data

Laser diffraction is an established technique for sizing nanometer to millimeter-sized particles and was used in order to characterize the dispersion state of the latexes. Particle sizes and their distributions obtained for dilute aqueous suspensions of the PDEA-PS latex particles at acidic and basic media are shown in Fig. 8. The particle size was measured to be 104 ± 32 nm at pH 3 with the narrow particle size distributions (span, 0.798), suggesting a high degree of dispersion of the PDEA-PS latex particles. On the other hand, at pH 10 the PS particles were obviously flocculated, since there is a significant increase in the apparent particle diameter (25.3 μm) and diameter distribution (span is over 20). The laser diffraction results are in good agreement with those obtained by optical microscopy studies (Fig. 9): Colloidally stable nanoparticles at pH 3.0 could not be observed due to resolution limit for optical microscopy (∼approximately 1 μm) whilst micron-sized flocs could be observed at pH 10. These results confirmed that the PDEA hair exists on the surface of the PS latex particles: the hair is protonated and is solvated in the acidic aqueous media and works as an effective colloidal stabilizer, and is deprotonated and is precipitated in the basic media. Adjusting pH back to 3 from 10 led to redispersion of the PDEA-PS latex particles: the diameter and the span were measured to be 113 ± 36 nm and 0.843, respectively, which are almost the same values with those measured before addition of base. This result indicates PDEA on the surface of the particles was re-protonated and the particles regained the colloidal stability. This dispersion–flocculation cycle was reversible.

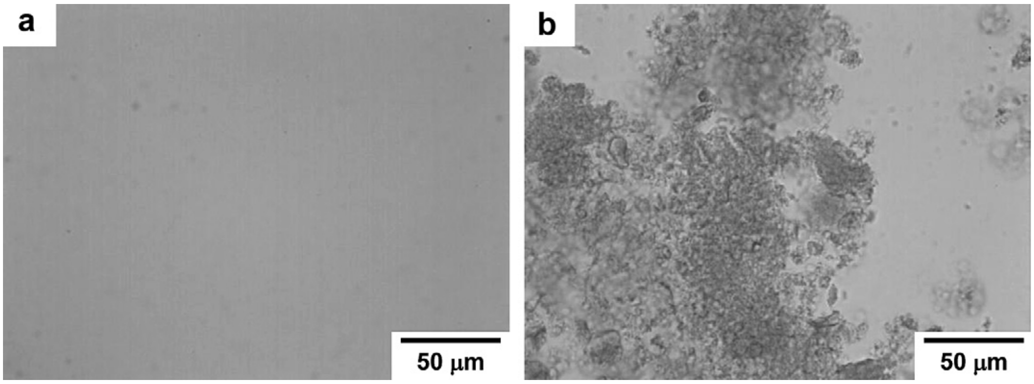

Fig. 9. Optical microscope images of $PDEA_{50}$-PS latex particles dispersed in aqueous media at (a) pH 3 and (b) pH 10.

4. Conclusion

Surface of the near-monodisperse PDEA-PS colloidal particles has been extensively characterized. The XPS and contact angle measurement studies provided direct and strong evidence for the existence of PDEA on the surface of the particles. TEM studies reveal that the PS particles had a core-shell morphology and it is expected that the shell consists of PDEA-rich component hairs. Wet AFM studies also confirmed that the PDEA component covered the PS latex core and the thickness of the hydrated hairy shell was estimated to be approximately 15 nm. The force curves measured between the latex surface and the AFM tip indicated that the PDEA component was protonated and cationically charged at pH 3.0 and was non-protonated at pH 10.0 and this protonation–deprotonation cycle of the PDEA-rich hair was reversible. The PDEA-PS latex particles were colloidally stable below pH 7.0 and aggregated above pH 8.0, which was confirmed by the optical microscopy and the laser diffraction studies. The PS latex particles can be dispersed in acidic aqueous media (pH 3.0) and can be flocculated in basic aqueous media (pH 10.0), which means that the PS particles have PDEA-rich hair. The hair was protonated and was solvated in the acidic aqueous media, and was deprotonated and was precipitated in the basic aqueous media. This dispersion–flocculation cycle of the PS latex was reversible.

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Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.polymer.2010.10.041.

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