

A novel photoreactor for the production of electrosterically
stabilised colloidal particles at larger scales

*Marc Schrinner, Björn Haupt, Alexander Wittemann**

Physikalische Chemie I, University of Bayreuth, Universitätsstr. 30, D-95440 Bayreuth, Germany

*Corresponding author

E-mail: Alexander.Wittemann@uni-bayreuth.de. Telephone: +49 921 55 2776, Fax +49 921 55 2780.

ABSTRACT

A novel photoreactor to facilitate electrosteric stabilization of colloidal polymer particles is presented. Anionic and cationic polystyrene particles having a diameter of ca. 100 nm and bearing a thin layer of photoinitiator are used as seed colloids. Anionic and cationic chains of weak or strong polyelectrolytes are grafted onto the surface of these particles. The polyelectrolyte chains are densely tethered onto the surface of the polymer particles. For this purpose, a commercial photoreactor setup developed for water and liquid waste treatment has been adapted. Compared to the photoreactor used earlier for photoemulsion polymerization, the new reactor largely shortens the reaction times and improves the reproducibility of the reaction. This is achieved by the higher UV power and controlled radiation times and power.

KEYWORDS

colloidal particles; polyelectrolyte brush; polymer latex; emulsion polymerization; photopolymerization; electrosteric stabilization; suspension; grafting from

INTRODUCTION

Colloidal suspensions have found an almost unlimited broad range of technical applications in paper, leather, textile and construction industry but also in medicine and pharmacy.¹ Amongst others, they serve as coatings, inks, paints, lubricants, adhesives and foams.¹ The modification of the surface of colloidal particles is of wide interest to provide specific interactions among the particles or towards the external environment. In particular, the large interfacial area of colloidal particles requires sufficient stabilization to prevent phase separation and coagulation.²

Stable colloidal suspensions can be achieved by incorporating ionic groups onto the particles or adsorbing surfactant molecules.³ However, electrostatic stabilization is only operative at low ionic strength. A second kind of stabilization is achieved by either adsorbing or grafting polymer chains onto the surface of colloidal particles.^{4, 5, 6} Non-ionic steric stabilization allows stabilization at high concentrations of added salt, which is required in many technical applications.¹ Combining both, electrostatic and steric stabilization, is a very effective way to stabilize colloidal suspensions.^{7, 8} The so-called electrosteric stabilization is provided by dense polyelectrolyte brushes grafted onto the surface of the colloidal particles.^{9, 10, 11}

Polyelectrolyte brushes can be created by physisorption of polyelectrolytes or copolymers bearing one polyelectrolyte block onto the surface.^{12, 13, 14} A stronger attachment to the surface is provided by chemically grafted polyelectrolytes.¹⁵ Two techniques have been applied to synthesize surface grafted polymer brushes: Preformed polymers of a desired end functionality are reacted with functional groups on the surface.¹⁰ Due to the steric hindrance among the preformed polymers, a limited grafting density is attained by this “grafted to” method. This is avoided by surfaces bearing initiator functionalities, which are suitable for the brush synthesis from the surface.¹⁰ Biesalski and R  he used this “grafting from” method to synthesize polyacid brushes on planar surfaces.¹⁶ Ballauff and coworkers prepared spherical polyelectrolyte brushes (SPB) consisting of either weak or strong polyelectrolytes onto the surface of polymer particles by free radical polymerization (Fig. 1).^{17, 18, 19} This technique is termed photoemulsion polymerization. It has been shown that these colloidal particles stabilised by polyelectrolyte brushes are

stable even at high amounts of added salt and over a wide pH range.^{20, 21} Moreover, the SPB have already found various possible technological applications as carrier for proteins²²⁻²⁴, catalytically active metal nanoparticles^{18, 25} and retention agents²⁶ for papermaking.

This wide range of applications created a high demand for SPB to further explore the properties of the material. Thus, we were looking for a technique, which facilitates the process of photoemulsion polymerization. We assigned the reaction described in Ref.¹⁷ to a commercial UV reactor system (aqua concept Laboclean LC Forschungsreaktor, Karlsruhe, Germany), which has been designed for water and liquid waste treatment, i.e. applications, that involve large throughputs or poor transmission (Fig. 2b). After adaptation to the present purpose, this novel reactor largely improves the efficiency of the photoemulsion polymerization by reduced reaction times, larger scales and reproducible reaction conditions. A detailed study on the formation of polyelectrolyte brushes onto model latexes using the novel UV reactor is presented.

EXPERIMENTAL

Materials: Purification of styrene (BASF, Ludwigshafen, Germany) was accomplished by washing with 10 wt-% NaOH solution to remove the inhibitor followed by distillation under reduced pressure. Acrylic acid (AA, Sigma-Aldrich, Buchs, Switzerland) was distilled under reduced pressure to remove the inhibitor. Sodium styrene sulfonate (NaSS), N,N-dimethylaminoethyl methacrylate (DMAEMA), potassium persulfate (KPS), sodium dodecylsulfate (SDS), cetyltrimethylammonium bromide (CTAB), α,α' -azodiisobutyramidine dihydrochloride (V-50) and methacrylic acid hydrochloride were purchased from Sigma-Aldrich (Buchs, Switzerland) in analytical grade and used without further purification. 2-aminoethylmethacrylate hydrochloride (AEMH) was obtained from Polysciences (Heidelberg, Germany) and Irgacure 2959 was provided by courtesy of Ciba Specialty Chemicals (Lampertheim, Germany). Deionized water obtained from a reverse osmosis water purification system (Academic A10, Millipore, Schwalbach, Germany) was used throughout the entire studies. All other chemicals and solvents were of analytical grade and were used as received.

Synthesis of HMEM and EDMB: The photoinitiator (HMEM) was prepared by a Schotten-Baumann reaction of Irgacure 2959 and methacrylic acid hydrochloride as described in Ref.¹⁷. Purification was achieved by column chromatography on silica gel. The purity of the product was verified through NMR spectroscopy (AC 250, Bruker, Karlsruhe, Germany). EDMB (N-ethyl-N,N-dimethylaminoethyl methacrylate bromide) serving as monomer in the synthesis of the cationic brushes was prepared, purified and characterized as described in Ref.²⁷.

Synthesis of the PS core: The synthesis of anionic and cationic PS latex particles bearing a thin layer of photoinitiator was accomplished by emulsion polymerization using a 3 L double-jacket glass reactor (Büchi Glass, Uster, Switzerland) which was heated through a thermostat (R400 Lauda, Lauda-Königshofen, Germany). In a typical synthesis batch of anionic PS particles, 521 g of freshly distilled styrene was added to a solution of 7.28 g of SDS in 2.17 L of water. The mixture was deoxygenated by several vacuum/nitrogen purge cycles and brought gradually to 80 °C under N₂ atmosphere and continuous stirring (320 rpm). The polymerization was initiated by addition of 2.04 g KPS dissolved in 50 mL of water. After 1 h, the turbid suspension was cooled to 70 °C. A solution of 29.16 g HMEM dissolved in 22.4 ml of acetone was added dropwise (0.2 mL/min) to the suspension and the reaction was continued for a further 5 h.

The preparation of the cationic PS particles was performed along the same lines. Briefly, 208 g of styrene were added to a solution of 2.65 g CTAB in 846 mL of water. After several vacuum/nitrogen purge cycles the reaction mixture was heating to 80 °C. 20 minutes after addition of the initiator (0.87 g V-50 dissolved in 100 mL of water), the suspension was cooled to 70 °C and 11.6 g of HMEM dissolved in 12.2 mL acetone were added (0.2 mL/min). The reaction was carried out under nitrogen atmosphere and continuous stirring (300 rpm) for 6 h.

All PS-co-HMEM latexes were filtrated through glass wool and purified by exhaustive ultrafiltration (cellulose nitrate membrane, pore diameter 50 nm, Schleicher & Schuell, Dassel, Germany) against water prior to the grafting of the brushes.

Grafting of the polyelectrolyte brushes: The photopolymerization was carried out in a high performance UV reactor setup (aqua concept Laboclean LC Forschungsreaktor, Karlsruhe, Germany) consisting of a UV radiation chamber, circulation pump and a 3000 mL reservoir with condenser (Fig. 2b). The spectrum of the light emitted by the Hg medium pressure lamp comprises a number of wavelengths in the range of 200 to 600 nm. The emission in the UV range between 200 and 300 nm is reinforced. The broadband spectrum the lamp offers makes the device suitable for many applications such as disinfection, curing of paints and lacquers and other photochemical tasks. Here this setup is used for the buildup of polyelectrolyte brushes on the surface of PS latexes. Briefly, 50 g PS-co-HMEM particles suspended in 2 L of water were placed into the reservoir. External cooling by water recirculation (UWK 140/TP2, Thermo Haake, Karlsruhe, Germany) kept the temperature of the suspension below 32 °C. The desired amount of water-soluble monomer (AA, NaSS, AEMH or EDMB) was added and the reaction mixture was deoxygenated by several vacuum/nitrogen purge cycles. Every five minutes, minute amounts of the suspensions were taken to study the increase in brush thickness during the 30 minutes of UV irradiation.

UV power of the photoreactor: The UV power of the Hg medium pressure lamp was determined every 10 operating hours. The rate of the UV induced decomposition of hydrogen peroxide was used as a measure for the UV power. Briefly, 3000 mL of 0.2 M hydrogen peroxide solution were irradiated for 15 min under permanent external cooling at 8 °C. In regular intervals minute samples were taken. The concentration of hydrogen peroxide in the samples was determined by cerimetric titration with 0.002 M Ce(IV) solution and ferroin as indicator. The rate of the decomposition of hydrogen peroxide normalized to the output power of the lamp of 500 W was in the range of 2.1 mol H₂O₂ per kWh.

Methods: Cryogenic transmission electron microscopy (cryo-TEM) specimens were prepared by vitrification of thin liquid films of the suspensions supported by a copper grid (600 mesh, Science Services, Munich, Germany) in liquid ethane. The specimen were inserted into a cryo-transfer holder (CT3500, Gatan, Munich, Germany) and transferred to a Zeiss EM922 EFTEM (Zeiss NTS GmbH, Oberkochen, Germany) operating at an accelerating voltage of 200 kV. Images were recorded digitally

by a CCD camera (UltraScan 1000, Gatan) and processed with a digital imaging system (Digital Micrograph 3.9, Gatan). More detailed information can be found in Ref.¹⁹.

The distributions of the core particle sizes were recorded on a disc centrifuge (BI-DCP, Brookhaven Instruments Corporation, Holtsville, USA) and by transmission electron microscopy (TEM, H7, Hitachi High-Technologies, Krefeld, Germany). Dynamic light scattering (DLS) measurements were performed on an ALV-4000 (ALV, Langen, Germany) light scattering goniometer equipped with a He-Ne laser (uniphase 1145P-3083, Manteca, USA) which provides a wavelength of 632.8 nm, and an ALV-5000 Multiple Tau Digital Correlator (ALV). Hydrodynamic radii were obtained by a cumulant analysis²⁸ from the correlation functions.

Conductometric titration (Cond 197i, WTW, Weilheim, Germany) was employed to determine the total mass of polymer that has been attached to the polystyrene particles during photoemulsion polymerization (see Table 1). This method was based on the change in the electric conductance during acid-base titration or precipitation of hardly soluble silver salts. Minute amounts of the suspension were purified by exhaustive ultrafiltration against water. The carboxylic groups of the PAA brushes were titrated against standard solutions of sodium hydroxide. The amount of cationic polymers was determined by titration of the bromine or chloride counterions against a standard solution of 0.1 M AgNO₃. The results were verified by elementary analysis (Vario EL III, elementar Analysengeräte, Hanau, Germany). The amount of PSS chains was quantified gravimetrically. To that end, the amount of solid present in the suspension was determined before and after exhaustive ultrafiltration against water. The loss of solid during purification gives the amount of free PSS chains or unreacted monomers. Hence, the mass of tethered PSS chains is obtained as the difference between the mass of added NaSS and the mass of the removed solid.

To determine the molecular weight of the tethered chains, the grafted chains were cleaved off from the polystyrene particles. The anchoring groups of the attached polyelectrolyte chains contain an ester bond which stems from the former photoinitiator (Fig. 3). These ester bonds were hydrolysed in presence of strong aqueous bases. To that end, the SPB particles were suspended in 2 M NaOH and kept at 120 °C

for 14 days. Such a rather harsh treatment was necessary since negative coions such as the hydroxide ions are expelled from anionic brushes.²⁹ The latex particles were separated from the cleaved polyelectrolyte chains by filtration through a cellulose nitrate membrane of 50 nm pore size (Schleicher & Schuell) after neutralisation with hydrochloric acid. The removal of the large amount of added salt was accomplished by exhaustive ultrafiltration (regenerated cellulose membrane, MWCO 5,000, Millipore) against deionized water. The completeness of the purification was monitored through the conductance of the filtrate. The purified polyelectrolyte chains were freeze-dried and analyzed using a Viscotek (Weingarten, Germany) triple-detection size-exclusion chromatography (SEC) system.

RESULTS AND DISCUSSION

The objective of the present study is to demonstrate the suitability of a novel UV reactor for photoemulsion polymerization. The reaction itself was carried out along the lines given in Ref.¹⁷. Figure 3 gives a schematic view on the individual stages of the synthesis of latex particles bearing densely packed polyelectrolyte brushes. Briefly, a narrow-dispersed PS latex is prepared by emulsion polymerization.³⁰ In the stage of particle growth a copolymerizable photoinitiator is added to the PS seed particles under starved conditions.²⁰ Here HMEM was used as a model photoinitiator. Other photoinitiators that are polymerizable could be used as well.³¹ HMEM is a vinyl monomer (Fig. 3) itself, but it is less hydrophobic than styrene. Thus, a thin shell of photoinitiator is formed onto the surface of the latex particles as the result of the copolymerization of styrene and the polymerizable photoinitiator. In the final step a water-soluble monomer is added and the suspension is irradiated by UV light. Radicals formed on the surface of the latex particles initiate the polymerization of the water-soluble monomer which results in polymer brushes covalently attached to the latex particles (Fig. 3). One would expect that the strong turbidity of the PS latex might present a severe limitation for a photoreaction. However, the turbidity is even essential for the photopolymerization. This was explained by multiple elastic scattering of the UV light within the suspension which allows the photoreaction to take place.²⁰

The decomposition of the photoinitiator moieties on the surface of the latex particles gives not only rise to surface-bound radicals but also to free radicals in solution (Fig. 3). The free polymer chains in solution thus obtained are removed from the suspension by ultrafiltration against water. This is necessary to obtain a well-defined model system for the studies described below.

Preparation of PS particles bearing photoinitiator moieties:

Both anionic and cationic polyelectrolyte brushes should be attached onto PS latex particles to probe the versatility of the photoemulsion polymerization as a tool to stabilize latex particles (Fig. 1). Thus, the PS particles that serve as carrier for the brushes and the monomer used to form the tethered chains must be like-charged. Otherwise electrostatic interactions among the PS particles and the growing polyelectrolyte chains would result in coagulation of the suspension. Thus, anionic and cationic PS latexes were synthesized following the procedure described above. The amounts of surfactant and initiator were chosen to obtain particles with diameters near 100 nm. The ionic nature of the initiator (KPS or V-50) leads to ionic groups on the surface of the PS particles which give the particles sufficient electrostatic stability prior to the grafting of the polyelectrolyte layer. The emulsion polymerization is carried out in a batch process at 80 °C until most of the styrene has reacted. Then the copolymerizable photoinitiator HMEM was added under starved conditions at 70 °C. At this stage of the reaction the PS particles are still swollen with styrene. Copolymerization of styrene and HMEM yielded a thin solid layer of photoinitiator onto the latex particles. Morphological studies by small angle X-ray scattering (SAXS) indicated that the thickness of the photoinitiator layer is in the order of two nanometers.¹⁵ Thus, a well-defined thin photoinitiator layer was obtained by this procedure. The size distribution of the PS particles was determined using an analytical disc centrifuge. The average diameter of the particles was in the order of 100 nm (Table 1). The polydispersity in particle size expressed as the weight-average diameter divided through the number-average diameter was less than 1.02. Since the PS particles are quite uniform in size, they are suitable seed particles for the built-up of well-defined core shell particles during the photoreaction.

Synthesis of the Spherical Polyelectrolyte Brushes: Photoemulsion polymerization:

The UV lamp of the photoreactor used in Ref.¹⁷ was directly immersed into the suspension (Fig. 2a). Thus the volume was fixed by the size of the reaction vessel (650 mL) circumventing the UV module. In the present setup the reaction mixture circulates continuously from the reservoir into the UV radiation chamber and via a condenser back into the reservoir (Fig. 2b). The circulation of the suspension guarantees a highly turbulent flow and prevents the formation of deposits in the reactor. The electronic performance of the UV module allows for repetitious accuracy of the irradiation time and power. At regular intervals the power of the UV lamp was determined through the UV induced decomposition of hydrogen peroxide. To ensure comparable reaction conditions the anionic and cationic brushes were prepared under similar UV powers of ca. 2.1 mol of decomposed H₂O₂ per kWh.

The PS-co-HMEM latex particles were used as seeds to conduct polymerization in the suspension of the particles comprising a water-soluble monomer. The content of seed particles was fixed to 2.5 wt.-%. The highest concentration of monomer used in the experiments was 0.15 M. These concentration limits helped to prevent the recombination of growing polyelectrolyte chains attached to different latex particles and thus the formation of a network of cross linked particles. The formation of individual particles of well-defined core-shell morphology under these premises becomes evident in the cryo-TEM images (Fig. 3).

Minute samples of the suspensions were taken during the photoemulsion polymerization to study the formation of the polyelectrolyte brushes onto the latex particles. DLS is well-suited to study the thickness of SPB.²⁰ The hydrodynamic thickness of the brush layer is obtained by subtraction of the hydrodynamic radius of the SPB at a given reaction time from the radius of the seed particles. Figure 4a contains data for the built-up of PAA brushes. The formation of the brush layer starts right after the UV radiation is started. A rapid increase of the brush thickness is obtained during the first minutes of irradiation. The reaction is completed after only 20 minutes of polymerization, i.e. maxima of the brush thickness and of the monomer conversion are attained. However, 240 min were necessary to come at the

same stage of the polymerization with the setup used by Guo *et al.* (cf. Fig. 2 of Ref. ¹⁷). Hence, the new reactor largely shortens the reaction times, which is mainly achieved by the increase of the UV power from 150 to 500 W.

The thickness of the brush layer L is governed by the osmotic pressure of the counterions of the polyelectrolyte chains.^{20,32} The absolute number of counterions within the brush increases with the contour length L_c and grafting density σ of the polyelectrolyte chains. The brush thickness shown in Fig. 4a is governed by two opposing phenomena. In principle, the brush thickness should increase with the content of photoinitiator moieties as higher grafting densities increase the concentration of counterions entrapped within the brush. On the other hand, the monomer-to-initiator ratio decreases as the total amount of monomer is kept constant in all experiments. Moreover, since DLS radii are dominated by the longest chains of the brush, the polydispersity of the tethered chains has an additional impact on the brush height. This is discussed in conjunction with Fig. 5. Thus, an exact interpretation of the brush heights shown in Fig. 4a as the function of photoinitiator moieties and monomer concentration is rather difficult. However, if the photoinitiator content of the seed particles is kept constant, a lower monomer concentration yields a lower brush height as expected (see system PAA2 vs PAA5 in Fig. 4a).

The total conversion of acrylic acid was determined through the content of solid in the suspension. To this end, the samples of the suspension taken during the photoreaction were subdivided into amounts of 2 g. The volatile monomer and water was removed under reduced pressure at 80 °C. The conversion of acrylic acid was obtained as the difference between the total content of solid and the content of added seed particles (2.5 wt-%) divided by the initial content of acrylic acid. The percentage of consumed acrylic acid comprises both PAA chains attached to the latex particles and free PAA chains in solution.

The monomer conversion (Fig. 4b) shows the same characteristics as the brush thickness L with reaction time t (Fig. 4a). The consumption of acrylic acid proceeds very fast at the earlier stages of the irradiation and a plateau value is attained after 15 minutes. The plateau consumption increased with the content of photoinitiator of the seed latex. A higher percentage of consumed monomer is also obtained if

less monomer is added (not shown). For all five reactions studied the monomer consumption did not exceed 80 %. Hence, the reaction is terminated without full consumption of acrylic acid. This does not mean that an excess of monomer was added since a higher brush thickness was obtained at higher monomer concentration (Fig. 4a). In fact, the mechanisms that terminate the growing of the chains on the seed particles should bring about incomplete conversion of monomer. These mechanisms are not known in detail. Such mechanisms might involve recombination with free chain radicals grown in solution or short-chain radicals. The latter ones could be formed by side reactions during photoirradiation.³¹

Since the photoinitiator is decomposed into surface-bound radicals and free radicals in solution, free polyelectrolyte chains are formed during the photopolymerization. The free chains were removed by exhaustive ultrafiltration against water. This purification step was used to determine the composition of the PSS brushes, i.e. the mass ratio of polystyrene to grafted polyelectrolyte (m_{PS}/m_{PEL}). For this purpose the content of solid in the suspension before and after the removal of unbound PSS chains was determined. The difference between the mass of sodium styrene sulfonate added to the seed latex and the mass of free PSS chains is the mass of PSS attached to the latex particles. The relative experimental error of m_{PS}/m_{PEL} is 5 % based on the relative error of the solid content of 0.4 % and taking weighing errors and mass losses during synthesis and purification into account.

A different approach was applied for the brushes composed of PAA since the molar mass of acrylic acid is lower than the one of sodium styrene sulfonate. m_{PS}/m_{PEL} was determined by conductometric titration of the carboxyl groups. The relative experimental error is 4 %. The mass ratio m_{PS}/m_{PEL} obtained for the PAA and PSS brushes are summarized in Table 1. Between 29 % and 52 % of the total monomer is consumed to build up the polyelectrolyte brush. This percentage increases with the HMEM content of the seed latex and decreases with the initial monomer concentration. Division of this percentage by the total fraction of monomer consumed during the photoemulsion polymerization gives the ratio of PAA tethered to latex particles to free PAA (Table 1). Depending on the experiment,

between 1.1 and 1.8 chains of PAA were grafted to the seed particles with respect to one free chain. One would expect a one-to-one ratio since the photoinitiator is decomposed into two radicals. However, recombination of free chain radicals with tethered chain radicals decreases the amount of free chains.

More specific information on the grafted polyelectrolyte chains is obtained through cleavage of the chains from the latex particles and characterization of the cleaved chains by SEC. We restricted such an analysis to selected samples (Table 1) since a large amount of the suspension is consumed to obtain a reasonable quantity of cleaved polyelectrolyte. The former photoinitiator moieties which serve now as anchor groups of the polyelectrolyte chains bear an ester group (Fig. 3). The hydrolysis was achieved over 15 days in presence of 2 M NaOH at 120 °C.¹⁷ The cationic chains comprising ester bonds in their monomer units (Fig. 3) were hereby converted into PAA chains. The average molecular weight and the polydispersity of the cleaved polyelectrolyte chains were obtained by SEC (Fig. 5). Polydispersity is defined as the weight-average molecular weight M_w divided by the number-average molecular weight M_n . The M_w/M_n values of the grafted polyelectrolyte chains are in the range of 2, as expected for a radical polymerization (Table 1).

Fig. 5 contains the molecular weight distributions of PAA cleaved from two different SPB. The grafting density σ is the same for both systems. The PAA chains cleaved from PAA3 show a quite narrow-dispersed molecular weight distribution for a radical polymerization. The distribution of the PAA chains of PAA2 exhibits a shoulder at higher molecular weights. This is explained by a recombination of free chain radicals with chain radicals grafted to the latex particles as already discussed above. Since chain termination is brought forth by radicals of low molecular weight as well, the shoulder at higher molecular weight might be less distinctive in some experiments. The brush thickness was determined by DLS. Since DLS radii are mainly governed by the longest chains of the brush layer²⁰, PAA2 exhibits a higher brush thickness than PAA3 due to the fraction of PAA chains of higher molecular weight (Fig. 5).

From the number-average molecular weight M_n , the contour length L_c is obtained as the product of the number of monomer repeat units and the distance of 2 C-C bonds of 0.25 nm. The grafting density σ could be calculated as well since the average molecular weight M_n and the total mass of polyelectrolyte chains per particle expressed in m_{PS}/m_{PEL} are known. The grafting densities obtained were in the range of 0.13 polyelectrolyte chains per nm^2 surface of the latex particles, i.e. 4000 polyelectrolyte chains were covalently attached per latex particle of 100 nm diameter. The distance between two grafting points is 3 nm. Since the photoemulsion polymerization allows coating latex particles with a densely packed polyelectrolyte layer, dispersions of the resulting particles are electrostatically stabilized in an efficient manner. Much work has been devoted to the stabilizing nature of polyelectrolyte brushes.^{7, 9, 32, 33, 34} This effect can be directly measured using a surface force apparatus.³⁵ The cryo-TEM images demonstrate that the polyelectrolyte chains are strongly stretched (Fig. 3). This is demonstrated in more detail in Ref. ¹⁹. The fact that the tethered chains are strongly stretched together with the thickness of the densely packed layer of several tens of nanometers gives the particles sufficient stabilization since aggregation among particles would demand a compression of the brush layer.

The novel photoreactor was designed for lab-scale experiments. As mentioned above it allows the fabrication of up to 100 g SPB in just 30 min. This amount could be further increased by using a larger reservoir. Such a quantity should be enough for most experimental studies. Larger UV reactors based on the same principle as the high performance lab-reactor are commercially available which provide flow rates from 5 up to 1000 m^3/h (aqua concept, Karlsruhe, Germany). Hence, such reactors would allow the electrostatic stabilization of several tons of particles per day for industrial applications. The production of the precursor latex particles does not present a limiting step for industrial applications since these particles can be made by emulsion polymerization which is a standard technique for the production of such particles.¹ The seed particles with sizes from 50 nm up to 300 nm can be made from all monomers such as styrene, vinyl acetate, vinyl chloride or acrylates that undergo radical polymerization, and which are hardly soluble in water.^{1, 30} Moreover, the need for a photoinitiator that is copolymerizable should

not present an obstacle as well since such compounds are used in the coating industry for solvent-free lacquers.³¹ In the present study, the photoinitiator HMEM was obtained through a one step chemical modification of such an photoinitiator (Irgacure 2959, Ciba Specialty Chemicals, Lampertheim, Germany). Other copolymerizable photoinitiators that are poorly soluble in water such as benzoin acrylate can be used as well.³¹ Hence, the photopolymerization presents a versatile technique since the chemical composition and dimensions of the particles can be adjusted in a wide range.

CONCLUSION

In conclusion, affixing long polyelectrolyte chains to polymer particles by photoemulsion polymerization opens new perspectives for stabilized polymer suspensions. In principle, chains of any water-soluble vinyl monomer can be attached to colloidal particles bearing photoinitiator moieties. Hence, the technique presents a versatile tool to stabilize colloidal particles but also allows specific surface functionalization. The novel photoreactor helps to further explore the potential of this technique since a better control of the photoreaction is achieved, along with shorter irradiation times. Moreover, the flow-through UV module enables large-scale reaction processing. This renders the technique promising for industrial applications that involve stabilized colloids.

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TABLES

Table 1: Parameters of the model latexes used in the present study. The nomenclature of the SPB refers to the type of tethered polyelectrolytes (PAA1-5: poly(acrylic acid); PSS1-2: poly(styrene sulfonate); PAEMH1: poly(2-aminoethylmethacrylate hydrochloride); PDMAEMA1: poly(N,N-dimethylaminoethyl methacrylate); PEDMB1: poly(N-ethyl-N,N-dimethylaminoethyl methacrylate bromide)).

SPB	R^a	L_c^b	L_{water}^c	M_n^d	M_w^e	PDI^f	m_{PS}/m_{PEI}^g	$\sigma[\text{nm}^{-2}]^h$
PAA1	50	-	75	-	-	-	12.7	-
PAA2	50	79	75	13600	30000	2.2	8.1	0.13
PAA3	50	51	62	11300	20000	1.7	9.4	0.13
PAA4	50	-	112	-	-	-	9.2	-
PAA5	56	-	17	-	-	-	12.0	-
PSS1	56	-	65	-	-	-	2.7	-
PSS2	56	-	120	-	-	-	2.1	-
PAEMH1	45	68	54	16000	31000	1.9	8.5	0.11
PDMAEMA1	45	89	85	12700	25000	2.0	11.3	0.14
PEDMB1	45	75	68	15000	35000	2.3	9.7	0.13

a) radius of the PS core; b) contour length of the grafted polyelectrolyte chains; c) brush thickness in water; d) number-average molecular weight and e) weight-average molecular weight of the polyelectrolyte chains; f) polydispersity index (M_w/M_n); g) mass composition m_{PS}/m_{PEI} of the SPB where m_{PS} and m_{PEI} are the masses of the PS core and polyelectrolyte shell, respectively; h) grafting density (number of chains per core surface).

FIGURE CAPTIONS

Figure 1. The SPB consist of solid polystyrene particles of ca. 100 nm diameter bearing a dense layer of tethered anionic (A) or cationic polyelectrolytes (B). If chains of weak polyelectrolytes such as PAA and PAEMH are attached, the degree of charges of the SPB depends strongly on the pH, and as a consequence the electrostatic stabilization of the particles is influenced by the external pH. However, if chains of the strong polyelectrolytes PSS and PEDMB are bound, the amount of charges onto the SPB does not depend on the pH.

Figure 2. Photoreactor systems used to conduct photoemulsion polymerization: The schematic representation on the left shows the reactor used by Guo *et al.*¹⁷ A medium pressure mercury lamp (TQ 150 Z3, Heraeus Noblelight, Hanau, Germany; range of wave lengths 200-600 nm, power consumption 150 W) surrounded by a cooling quartz tube was directly placed in a 650 ml reactor glass vessel. The right-hand illustration gives a schematic rendition of the UV reactor (aqua concept Laboclean LC Forschungsreaktor, Karlsruhe, Germany) used in the present study. The suspension circulates continuously from a reservoir (here: 3000 ml) into a UV radiation chamber (power consumption reduced to 500 W) and via a condenser back into the reservoir. This setup allows for variable batch sizes that only depend on the size of the reservoir. Continuous circulation of the suspension allows for a highly turbulent flow and prevents the formation of deposits. Moreover, the electronic performance of the UV module enables a repetitious accuracy of the UV irradiation.

Figure 3. Preparation of latex particles stabilized with long polyelectrolyte chains: At first polystyrene spheres were prepared by emulsion polymerization. The PS particles were coated with a thin layer of a polymerizable photoinitiator at a given conversion of styrene. The seed particles were extensively purified by ultrafiltration against water. Water-soluble monomers such as acrylic acid or styrene sulfonate were added. UV irradiation of the suspension led to surface-bound radicals and free radicals in solution. Both types of radicals initiated the polymerization of the water-soluble monomer. Hence, both polyelectrolyte chains anchored onto the PS seed particles and free chains in solution were obtained. The free chains in solution were removed by exhaustive ultrafiltration. Cryo-TEM micrographs demonstrate that well-defined core-shell particles can be made by this technique.

Figure 4. (A) Hydrodynamic thickness L of brushes composed of PAA as the function of the reaction time t . Parameter is the amount of photoinitiator used in the synthesis of the PS-co-HMEM seed (squares: PAA1 0.5 mol% HMEM; down triangles: PAA4 1.0 mol% HMEM; up triangles: PAA3 2.0 mol% HMEM; circles: PAA2 4.0 mol% HMEM in respect of the content of styrene units of the core

particles). The amount of acrylic acid was the same (40 mol% in regard to the content of styrene units of the core). Latex PAA5 (diamonds) was prepared using the same PS-co-HMEM seed as for PAA2. The lower brush thickness results from the lower amount of acrylic acid added (25 mol%). (B) Conversion of acrylic acid during the photoemulsion polymerization. An increasing amount of HMEM leads to a higher total conversion of monomer (squares: PAA1 0.5 mol% HMEM; down triangles: PAA4 1.0 mol% HMEM; up triangles: PAA3 2.0 mol% HMEM; circles: PAA2 4.0 mol% HMEM in respect of the content of styrene units of the core particles). Both experiments, namely the increase in particle size measured by DLS and the monomer conversion, clearly indicate that the formation of the brush is completed after a reaction time of 30 min.

Figure 5. Molecular weight distributions (MWD) of sodium polyacrylate chains cleaved from PAA2 (dashed line) and PAA3 (solid line). The average molecular weights and polydispersity indices are gathered in Table 1. The polydispersities close to 2 are typical for a free radical polymerisation.