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Synthesis of Spherical Polyelectrolyte Brushes by Photoemulsion Polymerization

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ABSTRACT: The synthesis and characterization of latex particles consisting of a poly(styrene) (PS) core and a shell of linear poly(acrylic acid) (PAA) chains are described. The particles have been synthesized by photoemulsion polymerization of acrylic acid on PS core particles containing a thin shell of the photoinitiator 2-[*p*-(2-hydroxy-2-methylpropiophenone)]−ethylene glycol−methacrylate (HMEM). The particles thus obtained have a defined core−shell morphology with a narrow size distribution. The dependence of the hydrodynamic radius of the fully dissociated PAA chains on the ionic strength is in qualitative accord with recent theoretical predictions.

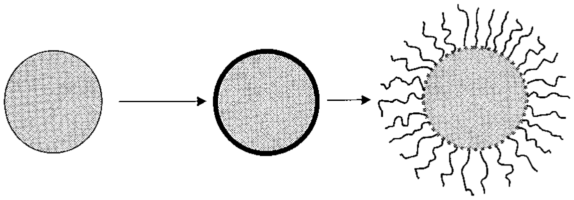
Introduction

If linear polyelectrolyte chains consisting of for example poly(acrylic acid) (PAA) are affixed to latex particles, spherical brushes result which are important systems for a number of reasons. On one hand, adsorbed or chemically bound polyelectrolytes lead to an electrosteric stabilization of latex particles which is operative even at elevated concentrations of added salt.[1] On the other hand, spherical polyelectrolyte brushes present an interesting theoretical problem which has been studied by a number of groups recently.[1−9] An excellent survey of the pertinent literature may be found in ref 8. Addressing the effect of curvature in terms of the Daoud−Cotton model,[10] Russel and co-workers[7−9] made a number of detailed predictions concerning the effect of electrostatic interaction and chain stretching on the thickness of the polyelectrolyte layer.

While the theory of spherical polyelectrolyte brushes seems to be well developed by now, only a few experimental studies are available so far. In most cases the polyelectrolyte brush has been made through adsorption of amphiphilic block copolymers consisting of a hydrophobic and a polyelectrolyte block onto spherical particles or on defined surfaces. (See ref 7 and further citations given therein.) It is obvious that the amount of adsorbed block copolymer is related to the ionic strength and the curvature of the particles.[7] Moreover, the surface coverage can only be varied in a restricted fashion. Another route is given by the use of macromolecular surfactants during emulsion polymerization.[11,12] This approach leads to electrostatically stabilized latex particles, but the amount and the grafting density of the surface layer can only be adjusted within certain limits.

Testing the various theoretical predictions would require stable latex particles consisting of a well-defined core and a surface layer of chemically fixed linear polyelectrolyte chains. To vary the grafting density within wide limits, the chains should be generated by a polymerization directly on the surface of the core particles. Recently, Rühe and co-workers[13−15] have demonstrated that high grafting densities can be achieved through use of radical initiators attached chemically to the surface. In particular, Rühe et al. could demonstrate that photoinitiators chemically attached to surfaces allow to obtain planar brushes with defined structure.[15] These synthetic routes give the opportunity to achieve stable layers of densely grafted polymers on model surfaces that would not be accessible by any other method.

Scheme 1. Schematic Representation of the Synthesis of Defined Polyelectrolyte Brushes[a]



[a] In the first step a poly(styrene) latex is generated which is covered by a thin layer of the photoinitiator HMEM in the second step. Photoinitiation in the presence of water-soluble monomers as for example acrylic acid leads in the third step to polyelectrolyte chains grafted onto the surface of the core particles.

In this paper we present a novel method for the synthesis of well-defined latex particles having a poly(styrene) (PS) core and a shell of PAA chains. The synthesis of these particles proceeds in three steps (Scheme 1): In the first step PS latex was prepared by a conventional emulsion polymerization. A seeded emulsion polymerization covers in the second step these cores with a thin layer of the photoinitiator 2-[*p*-(2-hydroxy-2-methylpropiophenone)]−ethylene glycol−methacrylate (HMEM) **2**. The polymer formed by HMEM on the surface during the second step acts as an photoinitiator in the third step by radiation of the covered particles with UV light. HMEM splits into two radicals[16] according to Scheme 2.

The third emulsion polymerization is done in the presence of a water-soluble monomer such as for example acrylic acid (AA). Here the radicals formed by photolysis of the HMEM groups on the surface will start the radical polymerization of the water-soluble monomer. Hence, linear polymer chains will be generated by a grafting-from technique shown schematically in Scheme

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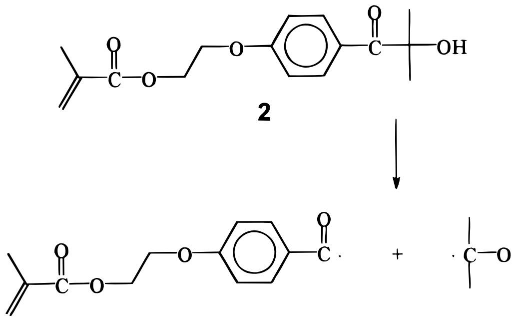
Scheme 2. Photoinitiator HMEM and Its Decomposition into Radicals during Photoinitiation



1. Since only one end of the photoinitiator is affixed to the surface, half of the amount of added monomer is expected to be grafted onto the surface.

The advantages of this method of synthesis are at hand: The geometry of the core particles is well-defined and can be investigated prior to the third emulsion polymerization. The "grafting-from" technique[13−15] furthermore allows to adjust the grafting density within wide limits not accessible by adsorption of block copolymers.

Up to now, photoinitiation has been used only in a few instances for the preparation of colloidal particles (cf. e.g. refs 17−19). It has been applied to transparent systems, but the strong turbidity in latex suspensions presents no principal difficulty: The strong scattering of light in colloid dispersions is elastic, and light is not absorbed. Hence, photopolymerization may be used for strongly scattering suspensions as well. Using initiators located on the surface of the particles, photoemulsion polymerization may be used to synthesize defined spherical brushes of colloidal dimensions.

Experimental Section

Materials. All solvents were analytical grade and used as received. Styrene (BASF) and acrylic acid (Fluka) were distilled under a reduced pressure to remove the inhibitor and stored at 4 °C until use. $K_2S_2O_8$ (KPS) (Fluka), SDS (Fluka), 2-hydroxy-4′-hydroxyethoxy-2-methylpropiophenone **1** (Irgacure 2959, Ciba), and methacryloyl chloride (Fluka) were used without further purification. The water used in emulsion polymerization was purified by reverse osmosis (Millipore MilliRO) and subsequent ion exchange (Millipore Milli-Q).

^{1}H NMR spectra were recorded at room temperature in acetone-d_6 using a Bruker AC 400 spectrometer. Tetramethylsilane (TMS) served as an internal standard. The size of the particles and their size distribution were determined by use of a Brookhaven DCP-disk centrifuge and by transmission electron microscopy (TEM, Hitachi 700). Dynamic light scattering (DLS) was performed using a Peters ALV 4000 light scattering goniometer.

Synthesis of 2-[*p*-(2-Hydroxy-2-methylpropiophenone)]−Ethylene Glycol−Methacrylate 2. Compound **2** was prepared by a Schotten−Baumann reaction of 11.89 g of 2-hydroxy-4′-hydroxyethoxy-2-methylpropiophenone **1** and 5.39 g of methacryloyl chloride in 100 mL of acetone using 10 mL of pyridine as base. The resulting product was carefully washed with water. Further purification was achieved through chromatography on silica gel (Silica gel 60, Fluka) using acetone as eluent. The overall yield was 40%.

^{1}H NMR (CD_3COCD_3): δ 1.53 (s, 3 H, $-C(CH_3)-$), 1.93 (s, 3 H, $=C(CH_3)$)), 2.89 (s,1 H, OH), 4.45, 4.54 (t, 4 H, CH_2CH_2), 5.69, 6.10 (d, 2 H, CH_2), 7.70, 8.28 (m, 4 H, C_6H_4).

Synthesis of Core Latex (Step I + II). The first two steps depicted in Figure 1 were done as follows: The PS core latexes were synthesized using a conventional emulsion polymerization. Hence, in typical run 150 g of styrene was polymerized in 540 mL of H_2O using 1.5 g of SDS as surfactant and 0.31 g of KPS as initiator. After 1 h a thin shell of HMEM was generated by adding 8.48 g of **2** dissolved in 20 mL of acetone. To achieve a well-defined core−shell morphology in this step, **2** was added under starved conditions (0.05 mL/min). After the last addition the latex was cooled to room temperature and purified by extensive serum replacement against pure water.

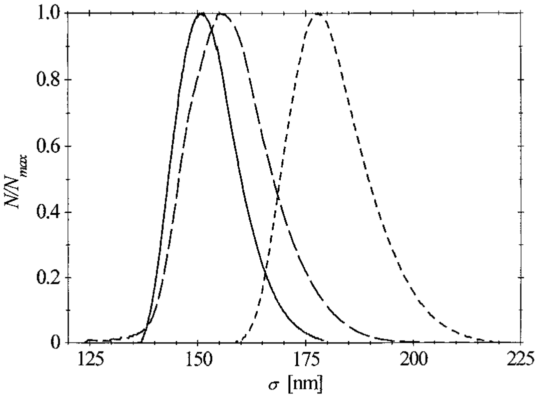


Figure 1. Buildup of the core−shell structure during the three steps depicted in Scheme 1: size distributions of the PS core (solid line), of the PS/HMEM latex (long dashed line), and of the spherical polyelectrolyte brush (short-dashed line). The size distributions have been determined by disk centrifugation.

Synthesis of Core−Shell Particles by Photopolymerization (Step III). A 650 mL aliquot of a core latex modified by a thin shell of **2** and diluted to 2.5 wt % was charged in a UV reactor (TQ 150; Heraeus, 650 cm^3 volume, range of wavelengths 200−600 nm). Acrylic acid was added, and the whole reactor degassed by repeated evacuation and subsequent addition of nitrogen. The amount of AA used in these runs varied between 10 and 100 mol % of the PS cores. Photopolymerization was done by use of UV/vis radiation at a temperature of 25 °C. Vigorous stirring ensured homogeneous conditions during the photopolymerization. Small samples were drawn repeatedly to follow the extent of reaction. After completion of the emulsion polymerization the latex was purified exhaustively by serum replacement using pure water until the conductance of the eluate did not change anymore. Conductometric titration was used to determine the amount of attached PAA chains after serum replacement.

Results and Discussion

The synthesis of well-defined spherical brushes by the method devised here requires the generation of closed shells in each step of the procedure shown in Scheme 1. The buildup of the various layers during the two seeded emulsion polymerizations can be easily monitored by dynamic light scattering and by disk centrifugation. It can be shown that the amount of **2** added in the second step of the synthesis must lead to a shell of 1−2 nm, which is observed indeed. Using starved conditions in this step ensures formation of a closed shell; a quick addition of **2** in this step may lead to more complicated morphologies. The PS/HMEM latexes had diameters ranging between 100 and 160 nm and were narrowly distributed. As an typical example, Figure 1 displays a comparison of the distributions obtained by disk centrifugation at the three steps (cf. Scheme 1).

Having shown that the second step leads to a well-defined PS/HMEM core−shell latex, we now turn to the discussion of the third step in which the shell of PAA chains is generated. Figure 2 displays the increase of the thickness Δ of the surface layer determined by DLS. Small amounts of sample were drawn during photopolymerization and dispersed in pure water. The de-

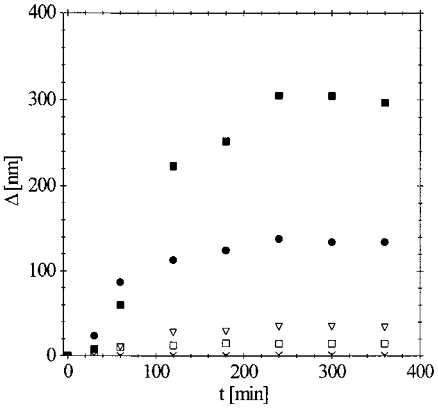


Figure 2. Thickness Δ of the polyelectrolyte layer as a function of reaction time *t*. Δ has been determined by dynamic light scattering. (×) Without HMEM layer; (□) 10% AA; (▽) 30% AA; (●) 50% AA; (■) 100% AA.

pendence of Δ was monitored from these samples by DLS as a function of time. The parameter is the amount of AA used in the third step.

The rapid increase of the hydrodynamic diameter of the particles is directly evident. Experiments using latex particles without a shell of photoinitiator demonstrated that polymerization proceeds only in the presence of the HMEM layer on the surface; without HMEM no change of hydrodynamic diameter of the particles resulted. Moreover, the PAA chains are affixed to the surface of the core particles. This can be easily shown by titration of the core–shell latex before and after exhaustive serum replacement. After removing the free PAA by serum replacement, titration demonstrates that the amount of PAA chains on the surface of the particles ranges between 41 and 48% of the total amount of AA used in the third step. Hence, only half of the AA has been polymerized by radicals generated by HMEM on the surface; the other half has been polymerized in solution as expected (cf. Scheme 2).

It is thus evident that photoemulsion polymerization may be used for the generation of well-defined core–shell particles despite the fact that the core latex presents a turbid system. As mentioned above, the strong light scattering in these latexes is practically elastic. The scattered light thus may start the photoinitiator as well, and the strong turbidity presents no general obstacle for photoinitiation in latex systems.

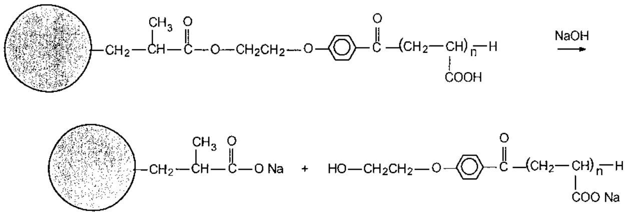
The analysis of the size distribution after serum replacement furthermore demonstrated that the polydispersity of the particles has not been changed in the third step. Only if large amounts of AA are used in the photoemulsion polymerization, disk centrifugation indicates the formation of larger particles. This may be traced back to the recombination of two growing radicals located on different spheres. This leads to the formation of doublets or multiplets of latex particles.

In this context it must be noted that the spherical brushes may fill the entire volume of the latex and hence touch each other despite the fact that the volume fraction ϕ_c of the core particles in the system is low. To put this into a more quantitative form, an effective volume fraction of the core–shell particles may be defined through

$$\phi_{\text{eff}} = \phi_c\left(\frac{\sigma_c + 2\Delta}{\sigma_c}\right)^3 \qquad (1)$$

where σ_c denotes the diameter of the core particles. Because of the strong increase of the thickness Δ in the course of the polymerization, ϕ_{eff} thus defined may quickly exceed 60% and the coronae of the particles will overlap extensively. To avoid possible cross-linking at this stage, the reaction has been stopped at conversions in which $\phi_{\text{eff}} < 25\%$.

Scheme 3. Cleavage of the Polyelectrolyte Chains Affixed to the Surface of the Latex Particles



Since the ester bond of the photoinitiator **2** may be cleaved by a strong aqueous base, the PAA chains may be removed from the surface of the particles and analyzed separately (see Scheme 3). Hence, a small amount of latex was heated to 120 °C in 2 M aqueous NaOH for 10 days. Because of the loss of the steric stabilization by the PAA chains, the latex coagulated slowly during this process. The amount of PAA in the supernatant serum was determined gravimetrically (after precipitation from 2 M aqueous HCl and drying). In some case the amount was measured photometrically by means of UV spectroscopy. Measurements of the intrinsic viscosity $[\eta]$ in 2 M NaOH by 25 °C then allowed to determine the molecular weight of the PAA chains ($K = 4.22 \times 10^{-2}$ mL/g, $\alpha = 0.64$, ref 20). From these measurements the average molecular weight of ca. 56400 g/mol could be determined. From measurement of dynamic light scattering the thickness of shell Δ was determined to 59 nm in the case of this system (in 10^{-3} M NaOH at 25 °C).

For the above system the area per chain may be estimated to 43 nm^2. This figure follows directly from the amount of PAA chains on the surface of the particles determined by titration and the average molecular weight of these chains (see above). The linear distance between two grafted points follows as ca. $\sqrt{43} \approx 6.6$ nm. Hence, each chain occupies an area on the surface of the particles with a radius of ca. 3–4 nm. This figure may be compared with the hydrodynamic radius of the sodium salt of the poly(acrylic acid). Hence, for 0.05 M NaBr solution the above molecular weight corresponds to a hydrodynamic radius of ca. 10 nm whereas in 0.005 M NaBr a value of ca. 15 nm follows. Both data have be calculated from the Mark–Houwink relations gathered in ref 20. The considerable crowding of the chains on the surface is directly evident from this comparison. It must therefore lead to a concomitant stretching. This may provide an explanation for the increase of Δ with conversion seen in Figure 2: The average contour length of the chains generated on the surface should not vary considerably during the photopolymerization on the surface because the extent of reaction has been kept small. The increase of Δ as a function of time may therefore be due to the increased crowding of the chains on the surface followed by a concomitant stretching.

The dependence of Δ on the salt concentration C_s has recently been discussed by Hariharan et al.[8] in terms of scaling laws stating that $\Delta \propto C_s^{-m}$. Modifying the Daoud–Cotton model[10] of spherical brushes, they predicted an exponent $m = -{}^1/_{10}$ for strongly curved

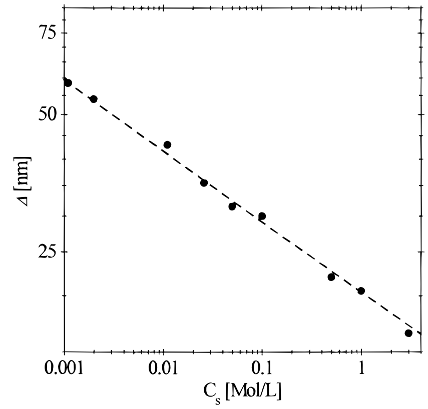


Figure 3. Thickness Δ of the polyelectrolyte layer as a function of salt concentration C_s in solution. The dashed line gives the resulting scaling law with $m = -0.155$.

surfaces which was close to their experimental result ($m = -0.11$). For particles with large diameters they predicted $m = -{}^1/_6$. To compare our system with these predictions, the hydrodynamic radius was measured for a spherical brush with a core radius of 56.5 nm as a function of salt concentration C_s. The particles were transformed into the fully dissociated form by addition of small amounts of 10^{-3} M NaOH until a pH of 11 was reached. Subsequently, the salt concentration was adjusted between 10^{-3} and 3 M by diluting the latex with KCl solutions of respective concentration. Figure 3 displays the thickness Δ obtained as a function of C_s.

The data thus obtained follow the scaling law, and the exponent m is given by $m = -0.155$. This is more closely to $m = -{}^1/_6$ and considerably greater than $m = -0.11$ found experimentally by Hariharan et al.[8] A more elaborate comparison, however, requires further data obtained from particles with different core radii. An investigation of this point is under way.

Conclusion

The synthesis of spherical polyelectrolyte brushes by photoemulsion polymerization has been described. The PAA chains are affixed on the surface by a grafting from techniques which leads to particles with well-defined morphology and narrow size distribution. The swelling of the polyelectrolyte brush on the surface in salt solution follows a scaling law. The exponent $m = -0.155$ found here is located between the limits of a recent prediction by Hariharan et al.[8]

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