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Spherical polyelectrolyte brushes: Comparison between annealed and quenched brushes

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We report on a study of spherical polyelectrolyte brushes that consist of a solid core onto which linear polyelectrolyte chains are chemically grafted. The core particles are made up of solid poly(styrene) and have a radius R of ca. 50 nm. As polyelectrolyte chains the weak polyelectrolyte poly(acrylic acid) or the strong polyelectrolyte poly(styrenesulfonate) was used. These chains were generated directly on the surface of the core particles by a grafting-from technique. Hence, the chains are chemically bound to the surface but can be cleaved off and analyzed separately. The contour length L_c and the number of grafted chains per unit area σ can thus be determined accurately. The thickness L of the brush layer on the surface has been determined by dynamic light scattering. It is measured for different L_c/R as a function of pH, ionic strength, and valency of counterions. Annealed brushes exhibit a transition with increasing pH in which the chains are stretched to nearly full length. This can be traced back to the building up of the osmotic pressure of the counterions. The brush height L decreases considerably with increasing ionic strength, most notably when adding divalent ions. The entire set of L as a function of R, L_c, and σ can be fully explained in terms of a simple two-parameter theory developed by Hariharan *et al.* [Macromolecules **31**, 7514 (1998)].

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I. INTRODUCTION

Polyelectrolyte brushes consist of polyelectrolyte chains attached to planar or curved surfaces. These systems have attracted much attention recently [1] and have been the object of a great number of theoretical studies [2–15]. The thickness of the brush has been shown to result from a balance of the osmotic pressure of the counterions within the brush and the configurational elasticity of the chains. Hence, in the osmotic regime, i.e., at low concentrations of added salt, the chains may be stretched to nearly full length. At high concentrations of added salt the electrostatic forces within the brush are strongly screened (salted brush). In this limit the equilibrium structure of an uncharged brush is recovered. An important point to be considered in these systems is the chemical nature of the charges: If the charges affixed to the polymer chains depend on the pH, the system is classified as an annealed brush. In these systems the fraction of charged monomers may also become a function of the concentration of added salt and of the grafting density. In the case of quenched brushes, however, the chains are charged under arbitrary ionic strength and pH.

Compared to the advanced theoretical understanding of brushes, the number of experimental studies devoted to planar systems is much smaller [16–22] (see also Ref. [1]). This is due to the difficulty of generating a dense polymer layer on a well-defined surface. The experimental studies available so far, however, have corroborated the main predictions of theory [1] and planar brushes seem to be rather well understood by now.

If the polyelectrolyte chains are attached to core particles of colloidal size, spherical polyelectrolyte brushes result that are akin to charged star polymers [23,24]. Such systems represent ideal models for the study of stabilization of colloidal particles by polymeric chains [25]. An additional length scale, namely, the radius R of the core particles, is present that strongly influences the behavior of these systems. If R is small, the systems resemble star polymers. If R is large compared to the contour length L_c of the grafted polymer chains, the resulting polyelectrolyte layer is akin to planar brushes. Such systems can be generated by adsorption of suitable block copolymers consisting of a hydrophobic and a polyelectrolyte block on latex particles [26–28]. Micellization of suitable block copolymers may also lead to spherical particles onto which polyelectrolyte chains are grafted [29–31]. Moreover, well-defined spherical polyelectrolyte brushes can be obtained by photoemulsion polymerization [32,33].

Compared to planar brushes, spherical polyelectrolyte brushes are by far less well understood and the number of experimental studies devoted to these systems is rather small [26–28,33–36]. A comprehensive study of spherical micelles having a charged corona has recently been presented by van der Maarel and co-workers [34–36]. These workers investigated spherical micelles by small-angle neutron scattering (SANS) including contrast variation. Their results demonstrate that the counterions are mainly confined within the brush. In the case of salt-free, fully charged systems the distribution of the counterions follows that of the segments forming the charged block [35]. Addition of salt leads to a marked shrinking of the brush [36] in agreement with independent studies [28,33]. To the authors' best knowledge, however, no systematic study of spherical polyelectrolyte brushes in the presence of divalent counterions has been presented. Moreover, no systematic comparison of quenched and annealed spherical brushes has yet been done.

Here we wish to present an experiment study on spherical polyelectrolyte brushes generated by photoemulsion polymerization [32,33] (see Fig. 1). The systems studied here consist of a solid poly(styrene) (PS) core onto which poly(acrylic acid) (PAA) chains are grafted. In the course of the synthesis of these particles [32] the polyelectrolyte chains are directly polymerized onto the surface. In this way a dense brush is generated on the surface of well-defined, almost monodisperse core particles. The advantages of this synthe-

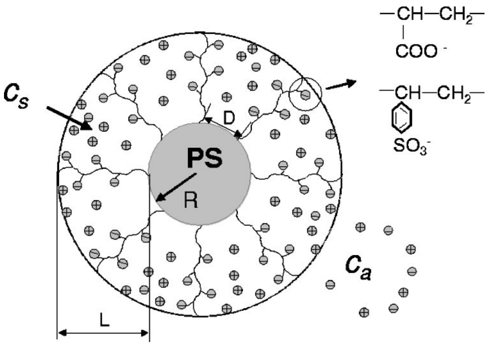

FIG. 1. Schematic representation of the spherical polyelectrolyte brushes investigated herein. Two different types of brush are investigated here: quenched brushes where poly(styrenesulfonate) chains are grafted to the surface, and annealed brushes where poly(acrylic acid) chains are affixed to the surface of the poly(styrene) core particles. The brush thickness L is determined by dynamic light scattering and is a function of the ionic strength c_s within the brush. c_a is the concentration of added salt.

sis are obvious: The radius R and the surface of the core particles is defined down to an experimental uncertainty of ca. 1 nm. The contour length L_c and the grafting density σ (number of grafted chains per nm^2) can be determined accurately and used for a comprehensive comparison of theory and experiment. Moreover, a wide variety of water-soluble monomers can be grafted onto the surface of the PS cores.

Two types of spherical polyelectrolyte brush will be studied (see Fig. 1): (i) annealed brushes bearing a corona of PAA chains, and (ii) particles bearing a quenched brush composed of poly(styrenesulfonic acid) (PSS). As in our previous study [33] we use dynamic light scattering (DLS) to study the overall dimensions of the particles in aqueous solution. DLS is ideally suited to investigate the particles because it gives the outermost diameter, i.e., the longest chains determine the measured hydrodynamic radius R_H. A recent comparison of R_H and radii determined by SANS and small-angle x-ray scattering [37] conducted on uncharged latexes has shown clearly that the overall dimensions are obtained most accurately by DLS.

It needs to be noted that no electrokinetic effects [25] need be invoked. As already discussed above, the charges are confined within the corona of the particles [35]. This can also be shown by direct measurements of the osmotic pressure of the counterions of salt-free solutions of the spherical polyelectrolyte brushes [38]. Here it turned out that only a few percent of the couterions are active, which corroborates the earlier findings of Groenewegen *et al.* [35]. Hence, the measured R_H derived from the diffusion coefficient is directly the outer radius of the particles. The same conclusion was drawn by Vaynberg and Wagner in a recent rheological study of comparable systems [39].

The present study aims at a fundamental understanding of strongly curved brushes. A comprehensive comparison of quenched and annealed spherical polyelectrolyte brushes will be given. For this purpose a corona of either PAA chains (annealed brush) or PSS chains (quenched brush) has been grafted on PS core particles of the same diameter. Hence, all parameters characterizing the particles, namely, R, L_c, and σ, can be kept constant while changing the chemical nature of the attached charges. Since all parameters are known the precise data for R_H deriving from DLS can be directly compared to current theoretical predictions in the literature.

TABLE I. Properties of spherical polyelectrolyte brushes: Quenched brushes.

Latex	R (nm)[a]	L_c (nm)[b]	σ(nm^{-2})[c]	L_c/R
LQ1	105	131	0.041	1.25
LQ2	68	86	0.033	1.26
LQ3	68	108	0.039	1.59
LQ4	68	147	0.037	2.16
LQ5	72	159	0.027	2.21
LQ6	68	165	0.027	2.43
LQ7	54	141	0.031	2.61

[a] Radius of core particles.
[b] Contour length of polyelectrolyte chains.
[c] Grafting density of chains.

II. EXPERIMENT

All particles investigated here were prepared by photo-emulsion polymerization according to Refs. [32,33]. The latexes were purified by extensive ultrafiltration. The contour length L_c of the grafted polymer was determined by cleaving off the chains with a strong base [32]. The entire amount of PSS on the surface was determined by conductometric titration. The amount of grafted chains and their length then yield the grafting density σ. Details of the synthesis and the characterization are presented in Ref. [33]. Table I gives a survey of the data pertaining to all quenched spherical polyelectrolyte brushes under consideration here; Table II gathers all the data for the annealed brushes used here for comparison.

Dynamic light scattering was done using a Peters ALV 4000 light scattering goniometer. DLS measurements at different pH and salt concentrations were done as follows. A given latex was diluted by the appropriate salt solution to

TABLE II. Properties of spherical polyelectrolyte brushes: Annealed brushes.

Latex	R (nm)[a]	L_c (nm)[b]	σ(nm^{-2})[c]	L_c/R
L4	57	42	0.038	0.74
L7	105	123	0.018	1.17
L10	66	86	0.039	1.30
L14	72	134	0.024	1.86
L15	66	134	0.052	2.03
L17	68	150	0.017	2.21
L18	68	153	0.024	2.25
L19	54	131	0.025	2.43
L22	68	233	0.026	3.43
L23	66	228	0.039	3.45

[a] Radius of core particles.
[b] Contour length of polyelectrolyte chains.
[c] Grafting density of chains.

obtain particle concentrations of ca. 2 ppm. Hence, the change of salt concentration of the system on adding the latex can be neglected. Measurements conducted at different pH were done by adding small amounts of NaOH and NaCl to keep the overall salt concentration constant. The pH was measured by use of a microprocessor pH meter (pH 537; WTW, Germany). Water was purified by reverse osmosis (Millipore Milli-RO) and subsequent ion exchange (Millipore Milli-Q).

III. THEORY

A suitable approach to spherical polyelectrolyte brushes is given by the modified Daoud-Cotton [40] model developed by Hariharan *et al.* [13,27] to treat charged systems. In this model the spherical polyelectrolyte brushes are described by a sphere of radius R onto which linear chains are grafted with a grafting density σ. The average distance between the chains is much smaller than the contour length of the chains. The modeling of the chains is in terms of volume filling blobs of cross section ξ that varies linearly with the radial distance from the surface. In a good solvent the blob size ξ and the number of Kuhn segments per blob N_ξ are related to the excluded volume parameter v and the Kuhn length l_K of the chains through [41]

$$\frac{\xi}{l_K} \approx N_\xi^{3/5} \left(\frac{v}{l_K^3} \right)^{1/5}. \tag{1}$$

The layer thickness then follows as [13,27]

$$\left(\frac{L}{R} + 1 \right)^{5/3} = 1 + K \frac{L_c}{R} \left(\frac{\sigma v}{l_K} \right)^{1/3}. \tag{2}$$

Here K is a constant of order unity. Equation (2) hence provides the relation between the brush thickness L and the ratio v/l_K. The limits of the validity of this expression have been discussed in detail by Hariharan *et al.* [13,27]. A prerequisite for application of Eq. (2) is that the blob size ξ is larger than the Debye length within the brush. This condition is well fulfilled for the outer largest blobs at the limits of the sphere that mainly govern the measured hydrodynamic radius R_H.

Equation (2) was shown to provide a good description for experimental data in the case of neutral brushes [26] and for spherical polyelectrolyte brushes in the presence of high concentrations of added salt [33]. For lower ionic strength, however, the Kuhn length l_K and the excluded volume parameter v become explicit functions of the ionic strength. The resulting treatment can be summarized as follows ([13]; see also [33]). The counterions are assumed to remain in the brush. This approximation is well supported by experimental findings [36,38]. Hence, the charges of the polyelectrolyte chains within the brush are exactly balanced by the counterions.

In all cases to be discussed here the polyelectrolyte chains are highly charged, that is, the distance l_c between two charges along the chain is smaller than the Bjerrum length l_B ($=0.714$ nm in H_2O at 25 °C). Hence, the present systems consist of strongly charged brushes. The strong interaction thus inferred will be partially compensated by counterion condensation [42,43]. To a good approximation it can be assumed that condensation takes place until $l_c = l_B$. In the following it will therefore be assumed that only charges separated by a distance l_B will be effective; all other charges are disregarded [13]. From this the local ionic strength c_s (in molar units) within the brush is related to the salt concentration c_a in the system by [13]

$$c_s = \frac{1}{2} \sum_i \frac{n_i z_i^2}{N_L} = c_a \left[1 + \left(\frac{z \overline{\rho_f}}{2 e N_L c_a} \right)^2 \right]^{1/2}, \tag{3}$$

where n_i is the number density of ions of species i, z_i is the valency of the respective ions, N_L is Avogadro's number, e is the unit charge, and $z = z_+ = -z_-$ because we assume a symmetric electrolyte. $\overline{\rho_f}$ is the average charge density within the brush,

$$\overline{\rho_f} = -\sum_i e z_i n_i = \frac{3 e R^2 \sigma L_c}{l_B [(R+L)^3 - R^3]}. \tag{4}$$

Equations (3) and (4) hence provide a relation between the ionic strength within the brush and the experimental quantities L, R, and c_a for strongly curved systems. Although Eq. (4) is an approximation inasmuch as it assumes a uniform distribution of the counterions, it seems to be a good choice for the description of spherical polyelectrolyte brushes [13,33]. A possible reason for the success of this approach is the fact that c_s can become much larger than c_a. It furthermore depends sensitively on the layer thickness L as captured through Eq. (3). Equations (3) and (4) seem to capture the essential effects of the problem at hand.

Having calculated the average ionic strength c_s within the brush, it remains to model the dependence of v and l_K on the local Debye length κ^{-1} which follows from the calculated c_s. As outlined in Ref. [33] different scaling laws connecting the two parameters and κ^{-1} may thus be introduced into Eq. (3) and compared to experimental data [33]. The previous analysis of annealed systems [33] showed that the overall dependence of v/l_K on κ^{-1} could be described best by $v/l_K \sim \kappa^{-3}$ (model 2 of Ref. [33]). As an alternative to this approach this ratio may be obtained directly from experimental data through [13]

$$\left(\frac{v}{l_K l^2} \right)^{1/3} \approx \frac{R}{L_c (l^2 \sigma)^{1/3}} \left[\left(\frac{L}{R} + 1 \right)^{5/3} - 1 \right], \tag{5}$$

where l is the bare Kuhn length of the corresponding polyelectrolyte chain. Here the constant K of Eq. (2) has been equated to unity. The ratio $v/l_K l^2$ should hence be a universal function of κ^{-1} in the range where the electrostatic repulsion between the chains dominates the measured brush thickness L.

IV. RESULTS AND DISCUSSION

A. Dependence of L on pH

The general aim of this work is a comparison of quenched and annealed brushes attached to spherical particles. The an-

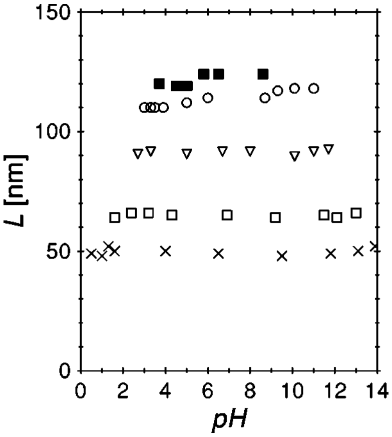

FIG. 2. Dependence of brush thickness L on pH in the solution for a quenched brush. The parameter of the data is the ionic strength in the solution, which was adjusted by adding KCl. Crosses, $1M$; open squares, $0.1M$; triangles, $0.01M$; open circles, $0.001M$; filled squares, $0.0001M$. The latex LQ4 (see Table I) was used.

nealed system results if PAA chains are grafted to the surface whereas a quenched brush follows from grafting PSS chains on PS cores (cf. Fig. 1). In the following the dependence of the brush thickness L on the pH in the solution will be discussed, i.e., charges will be introduced into the brush by titrating the essentially uncharged carboxyl groups of the PAA. The hydrodynamic radius R_H has been determined by DLS for a carefully adjusted pH. The height of the brush layer L then follows as $L = R_H - R$. Since the polydispersity of the PS core particles is very small [33] this procedure leads to L without problems. Moreover, DLS gives very accurate data for R_H and the high dilution obviates the need for extrapolation to vanishing concentration. Hence, the data thus obtained may be analyzed in a quantitative fashion and compared to the above theory.

Figure 2 displays the brush thickness L obtained for particles bearing a quenched brush whereas Fig. 3 gives the result for annealed brushes. The parameter of the different curves is the salt concentration in the solutions, which was adjusted with NaCl (see Sec. II). It must be noted that the pH refers to the entire solution in which a minute amount of particles is dissolved. The few ppm of particles present in the solutions used for the DLS experiment do not shift the pH in a significant manner. Hence, immersing these small amounts of particles in NaCl solutions leads directly to $p\mathrm{H} \approx 7$. Since a change of the pH requires addition of NaOH or HCl and a concomitant increase of the ionic strength, however, the available pH range is more and more restricted when working at low ionic strength.

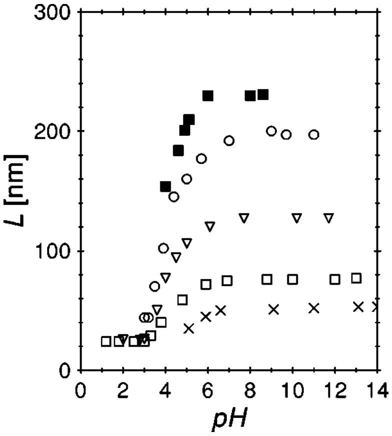

FIG. 3. Dependence of brush thickness L on pH for an annealed brush. The parameter of the data is the ionic strength in the solution, which was adjusted by adding KCl. Crosses, $1M$; open squares, $0.1M$; triangles, $0.01M$; open circles, $0.001M$; filled squares, $0.0001M$. The latex L23 (see Table II) was used.

In the cases of quenched polyelectrolytes, L proves to be independent of the pH for all salinities. The PSS chains are fully dissociated under all circumstances. The slight increase for the lowest salt concentrations under consideration here (see filled squares of Fig. 2) is hardly beyond experimental uncertainty and will not be considered in detail. As expected from previous work [33], however, L is strongly dependent on the concentration of added salt c_a (see Fig. 2) and the entire salt concentration must be kept constant carefully for all pH. The data shown in Fig. 2 may therefore be regarded as a test for the experimental method as well.

Evidently, the titration curve of an annealed spherical brush should be markedly different [20,33]. This is indeed found and Fig. 3 demonstrates that the brush thickness L increases strongly with increasing pH. A low pH the carboxyl groups of the PAA chains are virtually uncharged and the chains are only slightly stretched due to their interaction with neighboring chains. At higher pH charges are gradually introduced and the osmotic pressure of the counterions will swell the brush more and more. The stretching of the chains in the brush becomes more and more pronouced when the the ionic strength in the system is lowered. Here as in the case of quenched systems (see Fig. 2) the pH range in which the transition can be studied is considerably smaller at lower ionic strength, of course. At the lowest salt concentration only a portion of the titration curve is available. All available data demonstrate, however, that there is a strong stretching of the chains at a pH of approximately 5. At low ionic strength the PAA chains are stretched to nearly full length. This can be seen directly from a comparison of the corresponding data for L_c and L (see Fig. 3).

The grafting-from method employed here to generate the spherical polyelectrolyte brushes is a radical polymerization that leads to polydisperse PAA or PSS chains [33]. The analysis shows that the polymerization leads to a most probable distribution with the weight-average molecular weight being approximately twice the number-average molecular weight [33]. It is evident that this polydispersity may smear out the transition shown in Fig. 3. It must be noted, however, that all data referring to the contour length L_c were calculated from the weight-average molecular weight. Since the longest chains govern the measured hydrodynamic radius R_H (see above and Ref. [37]) the discussion of L in comparison to L_c is well founded. Moreover, Fig. 3 demonstrates that L increases by about one order of magnitude on increasing the pH. Compared to this marked stretching of the chains the

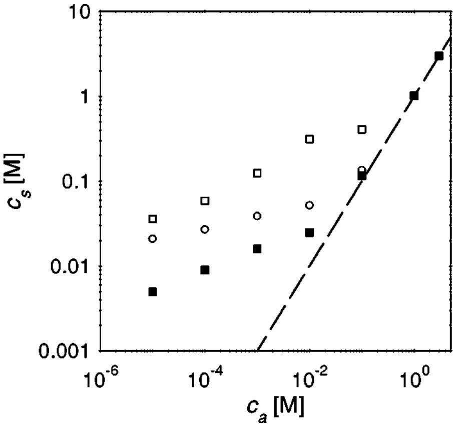

FIG. 4. Local salt concentration c_s within the quenched brushes calculated as a function of the concentration c_a of added salt. The calculation of c_s was done by use of Eq. (3). Open circles, LQ2 in KCl solution; filled squares, LQ6 in KCl solution; open squares, LQ6 in $MgSO_4$ solution. The dashed line shows where $c_s = c_a$. The respective L_c, σ, and R of these systems are gathered in Table I.

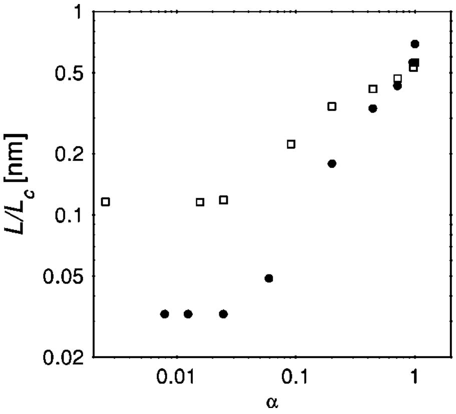

FIG. 5. Plot of the reduced brush thickness L/L_c as a function of the degree of dissociation α. The overall salt concentration c_a adjusted with NaCl is $0.01M$. α was calculated from Eq. (6). Open squares, L23, $R = 66$ nm, $L_c = 228$ nm, $\sigma = 0.039$ nm^{-2}; filled circles, L7, $R = 105$ nm, $L_c = 123$ nm, $\sigma = 0.018$ nm^{-2}. See text for further explanation.

effect of polydispersity is small and may be dismissed in the present discussion.

An important point for the quantitative discussion of these data is the average ionic strength c_s within the brush as opposed to the concentration c_a of added salt. Figure 4 displays the c_s calculated for a quenched brush according to Eq. (3). It is obvious that c_s differs markedly from c_a in the osmotic regime, i.e., when c_a is very small. This difference is more pronounced for thin brushes than for systems with long grafted chains: Fig. 4 shows c_s calculated from c_a for a thin brush (LQ2) and for a thick brush (LQ6). In the latter case the effect of curvature leads to a stronger dilution for the long distances from the surface whereas thin brushes behave nearly as planar systems. The periphery of a thick brush hence experiences essentially the outside conditions but there is a strong difference between c_a and c_s for thin systems. This point will be of considerable importance for subsequent discussions. Moreover, Fig. 4 shows that c_s is much higher in the case of divalent salts, which is directly obvious from inspection of Eq. (3).

The data displayed in Fig. 3 do not allow determination of the degree of dissociation α of the carboxyl groups. The point of inflection indicates only the pH at which the osmotic pressure becomes the dominating effect. A direct determination of α requires optical techniques that have been applied to suitable planar brushes by Currie *et al.* [19]. If the pH within the brush is known exactly, α can be calculated from the dissociation constant K_s of PAA by [19]

$$\alpha = \frac{\mathrm{K}_s}{[H^+] + K_s}, \tag{6}$$

where $[\mathrm{H}^+]$ denotes the local concentration of protons. In general, the concentration of an ionic species c_s inside a brush is different from its outside concentration c_a. The discussion of Fig. 4 has shown, however, that this effect is small for thick brushes if $c_a \approx 0.01$. Hence, Eq. (6) can be applied in this case to a good approximation. The dissociation constant K_s was approximated by $pK_s = 4.6$ for the given ionic strength of 0.01 [44]. Figure 5 shows the reduced brush thickness L/L_c as a function of the calculated α for two different systems. The open squares refer to the same system used in the study of L as a function of pH (see Fig. 3) whereas the filled circles refer to a thin and sparsely grafted brush. The increase of L with increasing α is more pronounced in the case of a low σ than in the case of a dense brush where the mutual interaction leads to significant elongation of the chains already in the neutral state. In the case of lower σ (filled circles in Fig. 5) the increase of L is nearly proportional to α when $\alpha > 0.08$ (exponent ≈ 0.9). This demonstrates the stretching by the osmotic pressure of the counterions. Figure 5 also underscores the strong stretching at full dissociation already discussed above.

B. Dependence of *L* on ionic strength for quenched and annealed brushes

Having discussed the transition within annealed brushes we now turn to a discussion of the fully charged systems. In our previous investigation [33] this state was reached by adjusting at sufficiently high pH values in solutions of annealed spherical brushes. This limits the minimal pH value that can be reached. Quenched systems, however, are independent of the pH (see the discussion of Fig. 2). These systems can be investigated down to the lowest ionic strengths possible that can be attained by immersing the particles in purest water. Figure 6 displays the brush thickness L for two quenched systems as a function of the concentration of added salt. Here we assigned $c_a \approx 10^{-7}$ for solutions in highly purified water.

The data demonstrate that the osmotic regime is indeed reached if the particles are immersed in solutions of monovalent salt of the lowest concentration. Here L is found to be essentially independent of c_a. At higher concentrations of added salt, however, L starts to decrease rapidly. Depending

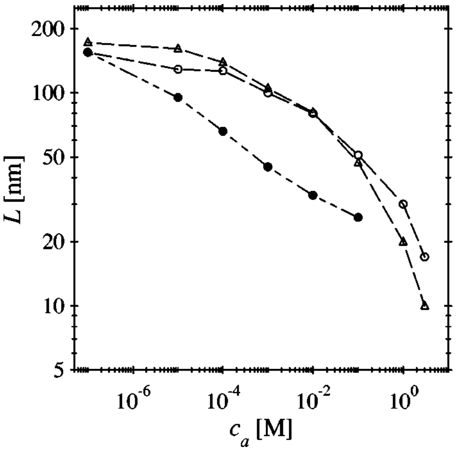

FIG. 6. Dependence of brush thickness L on concentration of added salt for quenched brushes. Triangles, LQ5 in KCl solution, $L_c = 159$ nm, $\sigma = 0.027$ nm^{-2}, $L_c/R = 2.21$ (see Table I); open circles, LQ7 in KCl solution, $L_c = 141$ nm, $\sigma = 0.031$ nm^{-2}, $L_c/R = 2.61$ (see Table I); filled circles, LQ7 in $MgSO_4$ solution.

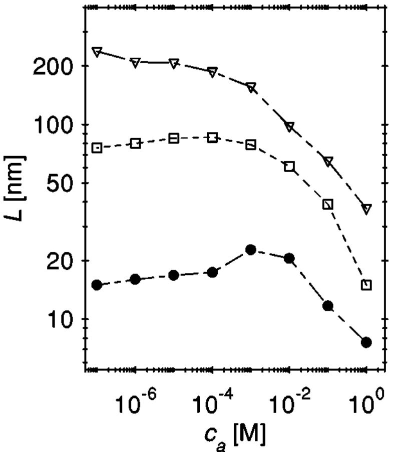

FIG. 7. Dependence of brush thickness L on concentration of added salt for annealed brushes. Triangles, L23 in KCl solution, $L_c = 228$ nm, $\sigma = 0.039$ nm^{-2}, $L_c/R = 3.45$ (see Table II); open squares, L7 in KCl solution, $L_c = 123$ nm, $\sigma = 0.018$ nm^{-2}, $L_c/R = 1.17$ (see Table II); filled circles, L4 in KCl solution; $L_c = 42$ nm, $\sigma = 0.038$ nm^{-2}, $L_c/R = 0.74$ (see Table II).

on the grafting density σ, the curves of L as a function of c_a may even intersect each other. This may be explained by the stronger mutual interaction at higher σ which is followed by a less pronounced shrinking on adding salt. In the presence of the smallest amount of divalent Mg^{2+} ions, there seems to be no truly osmotic regime any longer that extends over an appreciable range of c_a. This again is expected and can be traced back to the much stronger screening by a divalent salt [cf. Eq. (3)].

Figure 6 also points to the fact that the variation of L with c_a cannot be captured in terms of a simple scaling law. This is a general finding for virtually all systems studied so far. A possible reason for this observation may be the fact that the contour length L_c is smaller than or of the same order of magnitude as all other length scales in these systems, such as, e.g., R. It is certainly not a problem of polydispersity of the grafted chains. As already discussed in Sec. IV A the variation of L as a function of the pertinent parameters is much more pronounced than any effect of polydispersity.

A different behavior is expected for annealed brushes. Figure 7 displays the thickness L measured for three different systems as a function of the concentration of added salt c_a. In all cases a monovalent salt (KCl) was used to adjust c_a. Here it must be kept in mind that the particles have been dispersed in either pure water or salt solution and the pH in the system is approximately 7 for all experiments. For thin brushes (filled circles in Fig. 7), however, the discussion of Fig. 4 has demonstrated that the pH within the brush is markedly different if the ionic strength is sufficiently low. Only at high c_a do we have $c_a = c_s$. For the particles bearing chains with the greatest contour length L_c (triangles in Fig. 7), however, the data directly reflect L taken at $p\text{H} \approx 7$ in Fig. 3. The charges are mostly dissociated under these conditions and adding salt leads to a shrinking of the brush as observed in the case of quenched brushes (see the discussion of Fig. 6). In this case a behavior similar to that of quenched brushes is expected and indeed observed.

On the other hand, the pH in the thin brush (filled circles in Fig. 7) must be much smaller for the reasons indicated above. This leads to a smaller degree of dissociation α and hence to a smaller L. When monovalent salt is added, a nonmonotonic variation of L with c_a is seen. This feature was predicted by Birshtein and co-workers [8,11] and finds explanation in a partial replacement of the protons within the brush by salt ions when c_a is raised. The increase of the pH thus effected leads to a higher dissociation of the chains and a concomitant increase of the number of counterions in the brush. The increasing osmotic pressure then will lead to a stretching of the chains. At still higher c_a, however, the higher ionic strength within the brush is followed by the decrease of L already observed for quenched brushes.

To the authors' best knowledge, this is the first observation of the anomalous salt effect predicted some time ago [8,11]. We are not aware of any other experimental observation of this effect. The absence of any extended region in which a scaling law can be applied, however, makes a quantitative comparison with the predictions of Refs. [8,11] difficult. It is evident, however, that the subtle interplay of electrostatic screening and the osmotic stretching of chains is correctly predicted by the theory.

C. Comparison with the modified Daoud-Cotton model

In the following the data obtained for quenched brushes as well as for fully ionized annealed brushes will be compared to the simple model described in Sec. III [13,33]. For a given L_c, σ, and R the layer thickness is related to the ratio of the excluded volume parameter v and the Kuhn length l_K through Eq. (2). First the data taken at high ionic strength will be discussed. The electrostatic interaction of the chains should be fully screened under these conditions and v/l_K is expected to be a constant. Moreover, the ratio of the excluded volume parameter to the cube of the bare Kuhn length, v/l^3, should reflect the solvent power of the salt so-

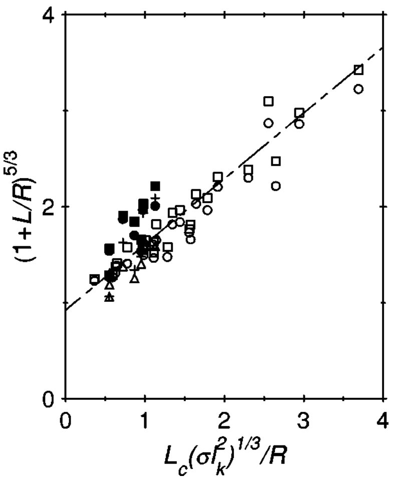

FIG. 8. Plot of the data according to Eq. (2) for high ionic strength. Here it has been assumed that v/l_K is independent of ionic strength and is given by the value of the uncharged chains. The parameter l is the bare Kuhn length of the PAA or PSS chains. Crosses, PSS in $1M$ KCl; triangles, PSS in $3M$ KCl; filled circles, PSS in $0.1M$ $MgSO_4$; filled squares, PSS in $0.01M$ $MgSO_4$; hollow circles, PAA ($pH\approx 9$) in $3M$ KCl; hollow squares, PAA (pH ≈ 9) in $1M$ KCl. See text for further explanation.

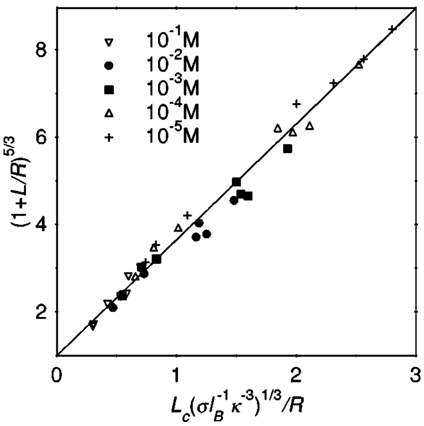

FIG. 9. Plot of the brush thickness L according to Eq. (2) with the assumption that $v/l_K \sim \kappa^{-3}$ (model 2 of Ref. [33]). See text for further explanation.

lutions for the polyelectrolyte chains under consideration here. Figure 8 shows the results. Given the various sources of error, a linear relationship is found that underscores the validity of Eq. (2). From the slope it follows that $v/l^3 \approx 0.3$, which is an entirely reasonable value. It must be kept in mind that the rather concentrated salt solutions are rather poor solvents for PAA and PSS [45]. Hence, the modified Daoud-Cotton model [Eq. (2)] captures the interplay of the curvature, grafting density, and contour length in these systems.

We next turn to the data obtained for quenched brushes at low ionic strength. Now v as well as l_K depends explicitly on the ionic strength within the brush, c_s. This concentration must be calculated by use of Eq. (3). The comparison of theory and experiment is therefore a test of two models at the same time. In particular, the error in the various parameters (L_c, σ, R) propagates throughout both calculations. Despite these problems the model given in Sec. III is highly predictive. The only parameter that specifies the chemical nature of the polyelectrolyte chains is l, the bare Kuhn length of the PAA or PSS chains.

Figure 9 displays a plot according to Eq. (2) for data obtained at low ionic strength from the quenched systems, i.e., from particles that bear PSS chains on their surface. Here the Debye length κ^{-1} has been calculated directly from c_s (see the discussion of Fig. 4). From Fig. 9 it is evident that $v/l_K \sim \kappa^{-3}$. This has already been found in the previous study of annealed spherical polyelectrolyte brushes in which different relations of v/l_K and κ^{-1} were discussed. The best fit was achieved by model 2 of Ref. [33], which assumes $v/l_K \sim \kappa^{-3}$ (see the discussion of Fig. 8 of Ref. [33]). We reiterate that the present discussion relates only v/l_K to experimental values; no conclusions can be drawn with regard to the dependence of v or of l_K on κ^{-1}, of course. It can thus be concluded that the present comparison corroborates the previous result obtained on annealed brushes at high pH [33].

An even more sensitive test of the simple two-parameter model may be achieved by a plot according to Eq. (5). Here v/l_K has been scaled by l^{-2} to compare data deriving from PAA and from PSS chains. The two chains are characterized by different bare Kuhn lengths l (PAA, $l = 1.5$ nm [45]; PSS, $l = 4.0$ nm [45]). Figure 10 displays a plot of 10 sets of

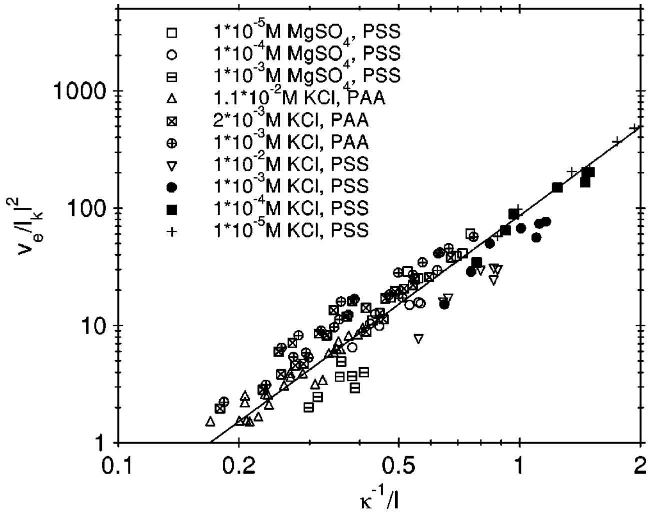

FIG. 10. The ratio v/l_K obtained from experimental data according to Eq. (5). The data shown here comprise both the quenched systems (brush of PSS chains) and the annealed systems (brush consisting of PAA chains). In the latter case the data refer to sufficiently high pH to render the *PAA* chains fully charged. To ensure a meaingful comparison of the two systems all data have been scaled by the reciprocal square of the bare Kuhn length l of the respective polyelectrolyte chains. Both monovalent counterions (particles dispersed in KCl solutions) and divalent counterions (particles dispersed in $MgSO_4$ solutions) were used. As the independent variable the Debye length κ^{-1} within the brush was used. κ^{-1} was calculated from c_s, the ionic strength within the brush obtained from Eq. (3). (See also the discussion of Fig. 4.) The line shows the fit of $v/l_K \sim \kappa^{-3}$ to all data displayed here.

data obtained under different salt concentrations and valencies of the added salt. Only data obtained at lower ionic strength are presented, where v/l_K is expected to be mainly determined by κ^{-1}. Each data point refers to a system characterized by a given L_c, σ, and R. Since the ratio L_c/R determines c_s through Eq. (3), different κ^{-1} are obtained for the same c_a. Hence, the entire comparison is highly sensitive toward the parameters introduced into the calculation of v/l_K and of κ^{-1}.

Figure 10 demonstrates that within the limits of error all data follow a master curve given by $v/l_K \sim \kappa^{-3}$ (the line in Fig. 10). Also, the data obtained in the presence of the divalent counterions Mg^{2+} seem to be well described by this relation. It is thus evident that Eq. (5) together with Eq. (3) provides a valid description of all data obtained at ionic strength low enough to render the electrostatic repulsion between the grafted chains the dominant effect.

V. CONCLUSION

A quantitative analysis of spherical polyelectrolyte brushes has been presented. The particles investigated here consist of a solid poly(styrene) core (diameter ≈ 100 nm) onto which an annealed brush [poly(acrylic acid) chains] or a quenched brush [poly(styrenesulfonic acid) chains] has been grafted. The dependence of the brush thickness L on pH and on the concentration of added salt c_a has been studied. In the case of annealed polyelectrolyte brushes the transition from nearly neutral to the fully charged system can be studied by change of the pH. Depending on salt concentration, a rather sharp stretching transition is seen. All data pertaining to the fully charged state can be described in terms of a modified Daoud-Cotton model [13] that captures the effects of curvature, grafting density, contour length of the grafted chains, and concentration of added salt. Moreover, the ratio v/l_K was found to be a universal function of the Debye length within the brush κ. Hence, data at lower ionic strength can be described by $v/l_K \sim \kappa^{-3}$ as shown in Fig. 10.

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[1] F. Dubreuil and P. Guenon, Eur. Phys. J. E **5**, 59 (2001).
[2] P. Pincus, Macromolecules **24**, 2912 (1991).
[3] O.V. Borisov, T.M. Birshtein, and E.B. Zhulina, J. Phys. II **1**, 521 (1991).
[4] G. J. Fleer, M. A. Cohen Stuart, J. M. H. M. Scheutjens, T. Cosgrove, and B. Vincent *Polymers at Interfaces* (Chapman and Hall, London, 1993).
[5] E.B. Zhulina, O.V. Borisov, and T.M. Birshtein, J. Phys. II **2**, 63 (1992).
[6] J.F. Argiller and M. Tirell, Theor. Chim. Acta **82**, 343 (1992).
[7] O.V. Borisov, E.B. Zhulina, and T.M. Birshtein, Macromolecules **27**, 4795 (1994).
[8] E.B. Zhulina, T.M. Birshtein, and O.V. Borisov, Macromolecules **28**, 1491 (1995).
[9] F. von Goeler, and M. Muthukumar, Macromolecules **28**, 6608 (1995).
[10] Yu.V. Lyatskaya, F.A.M. Leermakers, G.J. Fleer, E.B. Zhulina, and T.M. Birshtein, Macromolecules **28**, 3562 (1995).
[11] T.M. Birshtein and E.B. Zhulina, Ber. Bunsenges. Phys. Chem. **100**, 929 (1996).
[12] E.B. Zhulina and O.V. Borisov, Macromolecules **29**, 2626 (1996).
[13] R. Hariharan, C. Biver, and W.B. Russel, Macromolecules **31**, 7514 (1998).
[14] E.B. Zhulina, O.V. Borisov, and T.M. Birshtein, Macromolecules **32**, 8189 (1999).
[15] E.B. Zhulina, J. Klein Wolterink, and O.V. Borisov, Macromolecules **33**, 4945 (2000).
[16] H. Ahrens, S. Förster, and C.A. Helm, Macromolecules **30**, 8447 (1997).
[17] H. Ahrens, S. Förster, and C.A. Helm, Phys. Rev. Lett. **81**, 4172 (1998).
[18] S.W. An, P.N. Thirtle, R.K. Thomas, F.L. Baines, N.C. Billingsham, S.P. Armes, and J. penfold, Macromolecules **32**, 2731 (1999).
[19] E.P.K. Currie, A.B. Sieval, M. Avena, H. Zuilhof, E.J.R. Sudhölter, and M.A. Cohen Stuart, Langmuir **15**, 7116 (1999).
[20] M. Biesalski, J. Rühe, and D. Johannsmann, J. Chem. Phys. **111**, 7029 (1999).
[21] Y. Tran, P. Auroy, and L.-T. Lee, Macromolecules **32**, 8951 (1999).
[22] Y. Tran and P. Auroy, Eur. Phys. J. E **5**, 65 (2001).
[23] O.V. Borisov and E.B. Zhulina, Eur. Phys. J. E **4**, 205 (1998).
[24] J. Klein Wolterink, F.A.M. Leermakers, G.J. Fleer, L.K. Koopal, E.B. Zhulina, and O.V. Borisov, Macromolecules **32**, 2365 (1999).
[25] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, 1989).
[26] C. Biver, R. Hariharan, J. Mays, and W.B. Russel, Macromolecules **30**, 1787 (1997).
[27] R. Hariharan, C. Biver, J. Mays, and W.B. Russel, Macromolecules **31**, 7506 (1998).
[28] R.D. Wesley, T. Cosgrove, L. Thomson, S.P. Armes, N.C. Billingham, and F.L. Baines, Langmuir **16**, 4467 (2000).
[29] M. Moffit, K. Khougaz, and A. Eisenberg, Acc. Chem. Res. **29**, 95 (1996).
[30] N.S. Cameron, M.K. Corbierre, and A. Eisenberg, Can. J. Chem. **77**, 1311 (1999).
[31] F. Muller, M. Delsanti, L. Auvray, J. Yang, Y.J. Chen, J.W. Mays, B. Deme, M. Tirell, and F. Guenon, Eur. Phys. J. E **3**, 45 (2000).
[32] X. Guo, A. Weiss, and M. Ballauff, Macromolecules **32**, 6043 (1999).
[33] X. Guo and M. Ballauff, Langmuir **16**, 8719 (2000).

[34] W. Groenewegen, S.U. Egelhaaf, A. Lapp, and J.R.C. van der Maarel, Macromolecules **33**, 3283 (2000).
[35] W. Groenewegen, A. Lapp, S.U. Egelhaaf, and J.R.C. van der Maarel, Macromolecules **33**, 4080 (2000).
[36] J.R.C. van der Maarel, W. Groenewegen, S.U. Egelhaaf, A. Lapp, Langmuir **16**, 7510 (2000).
[37] S. Seelenmeyer, I. Deike, S. Rosenfeldt, Ch. Norhausen, N. Dingenouts, M. Ballauff, T. Narayanan, and P. Lindner, J. Chem. Phys. **114**, 10471 (2001).
[38] B. Das, X. Guo, and M. Ballauff (unpublished).
[39] K.A. Vaynberg and N.J. Wagner, J. Rheol. **45**, 451 (2001).
[40] M. Daoud and J.P. Cotton, J. Phys. (Paris) **43**, 531 (1982).
[41] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
[42] G. Manning, Annu. Rev. Phys. Chem. **23**, 117 (1972).
[43] See the discussion of this point by M. Deserno, Ch. Holm, J. Blaul, M. Ballauff, and M. Rehahn, Eur. Phys. J. E **5**, 97 (2001).
[44] J. Blaakmeer, M.R. Boehmer, M.A.C. Cohen Stuart, and G.J. Fleer, Macromolecules **23**, 2301 (1990).
[45] *Polymer Handbook*, edited by J. Brandrup and E. H. Immergut (Wiley, New York, 1989).