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The Polyelectrolyte Brush: Implications from Simulation Results on Polyelectrolytes in Solution

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ABSTRACT: Simulation results as well as experimental data indicate that full stretching of flexible polyelectrolytes will not occur for experimentally realizable solution conditions. Using density-dependent swelling exponents $\nu(\phi)$ as suggested by Stevens and Kremer (SK) from the results of a MD simulation study of fully ionized polyelectrolyte chains in solution without added salt, we present an Alexander–de Gennes-like scaling picture for the behavior of charged brushes. The brush height is found to become dependent on the grafting density as soon as internal stretching is incomplete, i.e., at $\nu(\phi) < 1$. Due to SK the maximum stretching occurring below a characteristic saturation density is given by $\nu_s = 0.90$. For polyelectrolyte brushes, however, even this maximum internal stretching cannot be reached because end-grafted chains do not overlap at the saturation density. Density-independent behavior with $\nu_{sr} = 0.80$ should be seen when the short length scale regime, predicted by SK, is reached at high grafting densities. At intermediate grafting densities the stretching exponent is continuously increased with reduced density. For the particular grafting technique used in the experiment, the grafting density itself becomes dependent on the chain length N. Hence, there appears a modified overall chain length dependence of the brush height.

The behavior of polymers tethered by one end to a solid surface has been extensively studied experimentally, theoretically, and by simulation studies during the past several years. Most of the work has been done on uncharged polymer brushes. Their structure and dynamics as well as the interaction between two such layers are rather well understood now, at least in the case of good solvent conditions (see, e.g., ref 1 and references therein). At high grafting densities, the chains become stretched normal to the surface and the average brush height h scales with the chain length N and the grafting density d^{-2}, where d is the distance between grafting points, as

$$h \cong aN\left(\frac{a}{d}\right)^{2/3} \tag{1}$$

with a being the Kuhn length. Recently, the study of polymer brushes has been extended to tethered polyelectrolyte chains. Due to the long-range electrostatic interaction, the chains are more strongly stretched and polyelectrolyte brushes exhibit a much more complex behavior than that known from neutral ones. There are a few theoretical studies on the scaling behavior of tethered charged chains.[2–8] As pointed out by Pincus,[2] the stretching of the brush is essentially caused by the osmotic pressure of the counterions. In the strong charging limit the counterions are mainly trapped inside the brush, preserving local electroneutrality. In this case, the equilibrium brush height was found to be[2,4]

$$h \cong aNf \tag{2}$$

where f is the degree of ionization. Note that eq 2 shows neither a dependence on the grafting density nor a dependence on the strength of the electrostatic interaction measured by the Bjerrum length $\lambda_B = e^2/4\pi\epsilon\epsilon_0 kT$.

To obtain a complete diagram of states of tethered polyelectrolyte chains in the (d,f) plane, not only the height of polyelectrolyte brushes but also their intrinsic structure have been studied at different grafting and charge density as well as for different solvent quality.[4–8] Several theoretical approaches have been used to succeed in this task. However, all the studies are done within the framework of some mean field treatments or, if scaling approaches are used, they are based on the assumptions (i) that inside the blob of dimension ξ the chain scales like a neutral one, i.e.,

$$\xi \cong ag^{\nu} \tag{3}$$

with

$$\nu = \begin{cases} 1/3, & \text{poor solvent} \\ 1/2, & \theta\text{–solvent} \\ 3/5, & \text{good solvent} \end{cases} \tag{4}$$

where g is the number of segments in a blob, and/or (ii) that the elastic energy of charged chains obeys the relation of Gaussian ones $E_{el} \cong kTR^2/Na^2$, where $R > N^{1/2}a$ is the end-to-end length of the stretched chain.

From simulation studies of polyelectrolyte chains it is known that the electrostatic interaction not only causes higher chain stiffness but also influences chain length dependencies resulting in a stronger swelling as in a good solvent.[9–12] Recently, Stevens and Kremer[13] reported results of molecular dynamics simulations on a system of completely ionized chains under good solvent conditions at varying monomer density ρ and without added salt. The macroions as well as the counterions have been explicitly taken into account in this study. The results indicate the importance of correlations between fluctuations in the counterion density and configurational fluctuations of the macroions. A quite surprising feature, not corresponding to any of the existing theoretical models,[14–16] is a density-independent regime with the exponent $\nu_{sl} = 0.80$ obtained at short length scales $N < N_c$. Therefore, in the picture for the structure of flexible linear polyelectrolytes suggested by Stevens and Kremer, the chains are predicted to be composed of segments that are stretched beyond the neutral good solvent value but are not rodlike. The range of the short length scale regime depends on the relation between the intrinsic chain stiffness and the Coulomb strength. Setting $a = 1.1\lambda_B$, this stretched blob regime extends up to six bond lengths.[13] Current simulation results indicate no sensitive depen-

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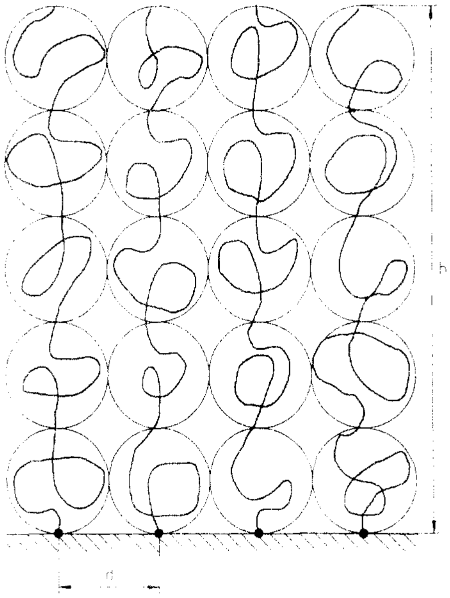

Figure 1. Blob picture of a flat, tethered polymer layer assuming uniform stretching of the chains. h is the average layer thickness (brush height) and d is the average spacing between grafting points.

dence of N_c on the relation between the segment size a and the Bjerrum length λ_B over a considerably wide range of parameters.[17] Thus, $N_c = 6$ seems to be a characteristic value for strongly charged, flexible polyelectrolytes. According to Stevens and Kremer, short-wavelength fluctuations due to small kinks in the chain will eventually cause the short length scale exponent to be 0.8 instead of 1. The chain composed of these segments exhibits a density-dependent structure. With decreasing density the stretching exponent obtained at length scales $N > N_c$ varies continuously from about $\nu = 0.60$ to about $\nu = 0.90$. At high densities, the electrostatic interaction is screened out and excluded volume behavior is recovered for good solvent chains. On the other hand, a reduction in the density reduces the screening by the counterions and the chains are increasingly stretched at longer length scales. However, following the simulation results[13] at very dilute concentrations, there occurs a saturation density ρ_s. A further reduction in the density does not influence the effective screening. Due to the simulation, there still occur strong fluctuations that are directly related to charge density fluctuations of the counterions. Thus, the chains never exhibit rodlike behavior, a result which agrees with recent experimental data.[18,19] Following Stevens and Kremer,[13] the saturation density with $\nu_s \approx 0.90$ is reached when the average counterion spacing roughly equals the coil extension in the stretched state, i.e.,

$$\rho_s^{-1/3} \approx \langle R^2 \rangle_s^{1/2} \cong aN^{\nu_s} \qquad (5)$$

In the following, we will use these results on the behavior of the stretching exponent ν to discuss polyelectrolyte brush properties on the basis of an Alexander–de Gennes-like scaling treatment.[20,21] Within this scaling scheme, the brush height can be evaluated by following the line suggested by Figure 1. The crucial parameter is d, the average distance between attachment points. The brush is built up from blobs with a diameter ξ equal to d. The chain sequences inside the blobs obey the scaling relation which a free, nongrafted chain would follow, i.e., $\xi = ag^{\nu}$. On the other hand, at sufficiently high grafting densities the stretching forces are assumed to be strong enough that the chains can be described as a linear sequence of N/g blobs. Then, the overall height of the brush can be expressed as

$$h \cong \xi\left(\frac{N}{g}\right) \cong Na\left(\frac{a}{d}\right)^{1/\nu-1} \qquad (6)$$

Assuming uniform stretching of the chains along their length leading to a step function behavior of the monomer density in the direction perpendicular to the grafting surface, the monomer density inside the brush is given by

$$\rho = \frac{N}{d^2 h} \qquad (7)$$

Using eq 6 the corresponding segment volume fraction $\phi = a^3\rho$ becomes

$$\phi = \left(\frac{a}{d}\right)^{3-1/\nu} \qquad (8)$$

So, for a discussion of the grafting density dependencies of polyelectrolyte brushes the crucial question is what are the right exponents of a free polyelectrolyte chain in solution. First let us note that at $\nu = 1$, i.e., in the case of fully internal (i.e., inside the blobs) stretching, one obtains the Pincus result given in eq 2. From eq 6 it is evident that only in this case the brush height becomes independent of the grafting density. Simulation results[9–13] as well as experimental data[18,19] indicate, however, that under reasonable conditions complete stretching of polyelectrolyte chains is not likely to occur. To take advantage of the simulation results of Stevens and Kremer, we restrict the consideration to the strong charging limit with complete ionization ($f = 1$). So, due to the density-dependent exponents $\nu(\phi)$, the picture becomes more complicated. A universal behavior can only be expected at high grafting densities when the behavior of the chain sequences inside the blobs will be governed by the density-independent short length scale regime with $\nu(\phi) = \nu_{sl} = 0.80$. In this case eq 6 yields

$$h \cong Na\left(\frac{a}{d}\right)^{0.25} \qquad (9)$$

The density-independent short length scale regime is expected to occur at $d < d_c$ where the upper limiting distance between grafting points is related to N_c by

$$d_c \cong aN_c^{\nu_{sl}} \qquad (10)$$

which gives a lower limiting value of the segment volume fraction inside the brush

$$\phi_c \cong N_c^{1-3\nu_{sl}} \qquad (11)$$

Using the threshold value $N_c = 6$, one obtains a value of the order of $\phi_c = O(10^{-1})$. Setting $a = 1.1\lambda_B$, the relation used in the simulation, eq 10, yields the estimation $d_c \approx 33$ Å. In first experimental studies on polyelectrolyte brushes, the distance between grafting points was estimated to be 90–100 Å.[22,23] Hence, at very high grafting densities the short length scale regime seems to be an attainable limit.

To see whether the density is high enough to observe highly screened behavior, i.e., the excluded volume one for good solvent chains, let us consider the Debye length at the limiting density of the short length scale regime given in eq 11. As confirmed by simulation results, the highly screened limit can be expected when the Debye length $\lambda_D = (1/4\pi\lambda_B c)^{1/2}$ becomes the smallest length scale in the system. Considering fully ionized chains without added salt, the ion concentration c is equal to the monomer concentration ρ. Using the estimation of the critical density to realize the short length scale regime $\rho_c \sim 10^{-1}/a^3$ given above, the Debye length becomes in the high-density limit

$$\lambda_D \sim a\left(\frac{10a}{4\pi\lambda_B}\right)^{1/2} \tag{12}$$

Since the square root expression gives a value of the order of 1, the Debye length λ_D can be less as well as larger than the contour length between charges a depending on the particular system parameter. Hence, by increasing d to above d_c, it is possible that one returns to the highly screened regime and the chains become internally more flexible over length scales $l > aN_c^{\nu_{sl}}$. For good solvent chains, the grafting dependence of the brush height h is then governed by the relation of neutral chains given in eq 1. With growing d, however, screening is continuously decreased due to the reduced counterion density. The chains again will be more stretched and the grafting density dependence of the brush height h becomes weaker.

A question which immediately arises is whether the maximum internal stretching with $\nu_s = 0.90$ can be reached in brushes or not. Following eq 6 in this case the brush height is predicted to scale as

$$h \cong Na\left(\frac{a}{d}\right)^{0.11} \tag{13}$$

As mentioned above, the saturation density is obtained when we have, on average, one counterion per chain $\rho_s^{-1/3} \approx aN^{0.9}$. Using eq 7 the lower saturation spacing between grafting points becomes

$$d_s \cong aN^{3\nu_s^2/(3\nu_s-1)} \approx aN^{1.4} \tag{14}$$

which exceeds the total chain length $L = aN$ in any case. Thus, there is no overlapping in this limit and the grafted chains remain in the "mushroom" regime. Hence, not only does complete internal stretching not occur in polyelectrolyte brushes but also the maximum chain stretching obtained for free polyelectrolyte chains in solution cannot be reached in brushes. Roughly speaking, the monomer density necessary for forming a brush is connected with a counterion density which is large enough to screen considerably the electrostatic interaction. Within this simple scaling picture, the minimum density for brush formation ρ_m is determined by the condition $d^2 \cong \langle R^2(N)\rangle_{\rho_m}$ that yields

$$\rho_m \cong \frac{N}{\langle R^2(N)\rangle_{\rho_m}{}^{3/2}} \cong \frac{1}{a^3}N^{1-3\nu(\rho_m)} \tag{15}$$

Thus, the minimum density for a polyelectrolyte brush is more than N times larger than the saturation density of free polyelectrolyte chains in solution which is about $1/(a^3N^{2.7})$.[13] On average, there is not one counterion per chain length but more than $N^{1/3}$. Hence, for sufficiently large chains, there is always considerable screening which prevents high internal stretching unless the grafting density is large enough to enter the short length scale regime.

So far the grafting density has been considered to be independent of the chain length. For particular grafting processes, however, such an assumption may be wrong. A simple way to form a polyelectrolyte brush is, e.g., to anchor hydrophilic–hydrophobic diblock copolymers[22-24] when all the electrostatic interaction is suppressed by adding low molecular salt ions and then "washing out" all the additional salt ions. Then, in a very crude picture the grafting density is governed by the chain length and the solvent quality relating to a quasi-neutral chain

$$d = \langle R^2(N)\rangle^{1/2}_{\text{salted}} \cong aN^{\nu_0} \tag{16}$$

with ν_0 beign given by eq 4.[25] Hence, in the case of the particular anchoring process eq 6 yields the following effective dependence of the brush height on the chain length N

$$h \cong aN^{\nu_b} \tag{17}$$

with an overall brush stretching exponent

$$\nu_b = 1 - \nu_0\frac{1-\nu(\phi)}{\nu(\phi)} \tag{18}$$

Due to eq 8 the segment density becomes

$$\phi \cong N^{-\nu_0(3\nu(\phi)-1)/\nu(\phi)} \tag{19}$$

Naturally, brush formation is caused by the additional swelling of charged chains when screening is reduced, i.e., by the difference between $\nu(\phi)$ and ν_0. The number of blobs N/g, or the brush height h relative to the coil dimension of the quasi-neutral chain R_0, becomes

$$\frac{N}{g} \cong \frac{h}{R_0} \cong N^{1-\nu_0/\nu(\phi)} \tag{20}$$

The condition for short length scale behavior $d < d_c$, where d_c is determined by eq 10, yields the relation $N < N^*$ for reaching this regime, with an upper limit of the chain length

$$N^* \cong N_c^{\nu_{sl}/\nu_0} \tag{21}$$

For grafting of poor solvent chains, Θ chains, and good solvent chains, respectively, with $N_c = 6$, eq 21 yields $N^* \approx 75$, 20, and 10, which corresponds, e.g., for poly(styrenesulfonate) (PSS), with a monomer length $a_0 \sim 2.5$ Å to a number of monomers $N_0^* \approx 230$, 60, and 30. Note that recent experimental data indicate chain stretching already during the grafting process.[23] Thus, due to higher grafting densities the short length scale regime seems to be attainable also with chains longer than the limits given above.[25] According to eq 21 a factor of 1/2 in the grafting distance d results in a factor of $2^{1/\nu_0}$ in N^*, which equals 4, e.g., for Θ chains.

Evidently, the poorer the solvent conditions during the anchoring process, the higher the grafting densities and the stronger the brush effect that can be obtained within this grafting procedure. For polyelectrolytes, the solvent quality can be tuned by adding additional salt. For example, PSS behaves like a neutral polymer in a good solvent at an aqueous sodium chloride concentration of 0.15 M at 25 °C[26] and has a Θ point at 4.2 M at 25 °C.[27] Recent adsorption studies on PSS-based diblock copolymers have been carried out at a concentration of 1 M. At this concentration the polyelectrolyte chains should exhibit conformational properties similar to those of neutral chains in moderate-to-good solvent conditions.[23] To get a better feeling about what can happen in the behavior of polyelectrolyte brushes when the chain length is increased, we evaluate the dimensionless density ϕ according to eq 19 for several particular values of $\nu(\phi)$ at varying N. Grafting

Table 1. Behavior of Brush Parameters with Growing Chain Length for Chains Anchored at Good Solvent Conditions (ν_0 = 3/5) by a Chain Length Controlled Grafting Process (See Text) Assuming the Behavior Inside the Blobs To Be Governed by Different Swelling Exponents $\nu(\phi)$[a]

N	N_0	d/a	g_{sl}	$\phi_{LL}(\mu = 0.9)$	$\phi_{LJ}(\mu = 0.8)$	$\phi_{LJ}(\nu = 0.7)$	$\phi_{LJ}(\nu = 0.6)$	$\phi_{s,LJ}$
8	25	3.5	$\boxed{4.8}$	7.3×10^{-2}	8.7×10^{-2}	1.1×10^{-1}	1.5×10^{-1}	2.8×10^{-3}
16	50	5.3	8.0	3.4×10^{-2}	4.2×10^{-2}	5.7×10^{-2}	8.4×10^{-2}	4.3×10^{-4}
32	100	8.0		1.5×10^{-2}	2.0×10^{-2}	3.0×10^{-2}	4.8×10^{-2}	6.6×10^{-5}
64	200	12.1		6.7×10^{-3}	9.8×10^{-3}	1.5×10^{-2}	2.8×10^{-2}	1.0×10^{-5}
128	400	18.4		3.2×10^{-3}	4.7×10^{-3}	8.0×10^{-3}	1.6×10^{-2}	1.6×10^{-6}
256	800	27.9		1.5×10^{-3}	2.3×10^{-3}	4.2×10^{-3}	9.1×10^{-3}	2.4×10^{-7}
512	1600	42.2		6.7×10^{-4}	1.1×10^{-3}	2.2×10^{-3}	5.2×10^{-3}	3.7×10^{-8}
1024	3200	64.0		3.1×10^{-4}	5.3×10^{-4}	1.1×10^{-3}	3.0×10^{-3}	5.7×10^{-9}
2048	6400	97.0		1.4×10^{-4}	2.6×10^{-4}	5.9×10^{-4}	1.7×10^{-3}	8.8×10^{-10}
4096	12800	147.0		6.4×10^{-5}	1.2×10^{-4}	3.1×10^{-4}	9.9×10^{-4}	1.4×10^{-10}
8192	25600	222.9		2.9×10^{-5}	6.0×10^{-5}	1.6×10^{-4}	5.6×10^{-4}	2.1×10^{-11}
16384	51200	337.8		1.3×10^{-5}	2.9×10^{-5}	8.4×10^{-5}	3.3×10^{-4}	3.2×10^{-12}

[a] N is the number of Kuhn segments, N_0 is the corresponding number of PSS monomers, d is the blob diameter according to eq 16 (grafting at the θ point, $\nu_0 = 1/2$), and $g_{sl} = (d/a)^{1/\nu_{sl}}$ is the number of segments inside a blob assuming short length scale behavior ($\nu_{sl} = 0.8$). To compare the densities following from eq 19 with the simulation data, they are expressed in terms of Lennard-Jones units, i.e., $\theta_{LJ} = \phi\sigma^3/a^3$ with $a = 1.1\sigma$. The last row shows the lower saturation density $\phi_s \cong N^{-2.7}$. The regions showing values which are consistent with the simulation results of polyelectrolyte chains in solution are marked.

Table 2. As Table 1 but for Grafting at the Θ-Point (ν_0 = 1/2)

N	N_0	d/a	g_{sl}	$\phi_{LJ}(\nu = 0.9)$	$\phi_{LJ}(\nu = 0.8)$	$\phi_{LJ}(\nu = 0.7)$	$\phi_{LJ}(\nu = 0.6)$	$\phi_{s,LJ}$
8	25	2.8	3.6	1.1×10^{-1}	1.2×10^{-1}	1.5×10^{-1}	1.9×10^{-1}	2.8×10^{-3}
16	50	4.0	5.7	5.7×10^{-2}	6.7×10^{-2}	8.6×10^{-2}	1.2×10^{-1}	4.3×10^{-4}
32	100	5.7	8.8	3.0×10^{-2}	3.6×10^{-2}	5.0×10^{-2}	7.5×10^{-2}	6.6×10^{-5}
64	200	8.0		1.5×10^{-2}	2.0×10^{-2}	2.9×10^{-2}	4.7×10^{-2}	1.0×10^{-5}
128	400	11.3		8.0×10^{-3}	1.1×10^{-2}	1.7×10^{-2}	3.0×10^{-2}	1.6×10^{-6}
256	800	16.0		4.2×10^{-3}	5.8×10^{-3}	9.6×10^{-3}	1.9×10^{-2}	2.4×10^{-7}
512	1600	22.6		2.2×10^{-3}	3.2×10^{-3}	5.6×10^{-3}	1.2×10^{-2}	3.7×10^{-8}
1024	3200	32.0		1.1×10^{-3}	1.7×10^{-3}	3.2×10^{-3}	7.4×10^{-3}	5.7×10^{-9}
2048	6400	45.3		5.9×10^{-4}	9.4×10^{-4}	1.9×10^{-3}	4.7×10^{-3}	8.8×10^{-10}
4096	12800	64.0		3.1×10^{-4}	5.1×10^{-4}	1.1×10^{-3}	2.9×10^{-3}	1.4×10^{-10}
8192	25600	90.5		1.6×10^{-4}	2.8×10^{-4}	6.2×10^{-4}	1.8×10^{-3}	2.1×10^{-11}
16384	51200	128.0		8.4×10^{-5}	1.5×10^{-4}	3.6×10^{-4}	1.2×10^{-3}	3.2×10^{-12}

at the Θ point as well as anchoring good solvent chains is relevant to experimental studies.[23] For both these cases, the results are summarized in Tables 1 and 2, respectively. Comparing the resulting densities with the simulation data[13] on the chain form factor

$$S(\mathbf{q}) = \frac{1}{N}\left|\sum_{j=1}^{N} \exp[i\mathbf{q}\mathbf{R}_j]\right|^2 \tag{22}$$

the spherically averaged form of which scales in the range $2\pi/R < q < 2\pi/a$ as

$$S(q) \cong q^{-1/\nu(\phi)} \tag{23}$$

(Figure 1 in ref 12), one gets some information on the densities which are consistent with the particularly chosen exponents and vice versa which internal swelling or stretching exponents $\nu(\phi)$ can be expected with increasing chain length. The resulting tendencies in the overall brush stretching exponent ν_b are schematically shown in Figure 2. With growing chain lengths there appear three different regions: the short length scale regime, the strong screening regime, and the regime in which the brush properties are governed by partial internal stretching. The most remarkable feature is the significant deviation from an N^1-like scaling behavior at the transition from the short length scale regime to the strong screening regime. However, let us make three comments. (i) Here we use simulation results on polyelectrolytes in a good solvent. These are to date the only available non mean field results at finite density. At the Θ point as well as under poor solvent conditions it is reasonable to expect the chains to become even more compressed in the strong screening regime. Hence, the dip in the brush stretching exponent behavior is expected to appear more pronounced in this case. Assuming that in the strong screening limit polyelectrolyte chains show the same conformational properties as corresponding neutral ones, for non good solvent chains, the simulation results on good solvent chains can be corrected in the strong screening regime. For anchoring at the Θ point, the resulting corrections are also schematically shown in Figure 2. (ii) As discussed above, whether the strong screening regime is well pronounced or not strongly depends on the actual system parameters. If screening is so high that $\nu(\phi)$ is reduced to ν_0, then not only a more marked dip occurs in the brush stretching exponent behavior but according to eqs 17–20 the brush becomes unstable at the corresponding chain lengths. The density in the polyelectrolyte brush is so high that "washing out" of additional salt ions does not considerably reduce screening effects. Hence, the polyelectrolyte chains remain in a "mushroom" or prestretched conformation. (iii) Anchoring the chain at solution conditions better than the poor one, for equivalent chain lengths, one obtains lower monomer concentrations in the polyelectrolyte brush. Thus, the curve indicating the brush behavior in Figure 2 is shifted and the region corresponding to the short length scale regime is reduced. Hence, for good solvent chains the universal short length scale regime appears to be not attainable under reasonable conditions. We remember, however, that rather higher grafting densities have been realized in recent experiments.[23,25]

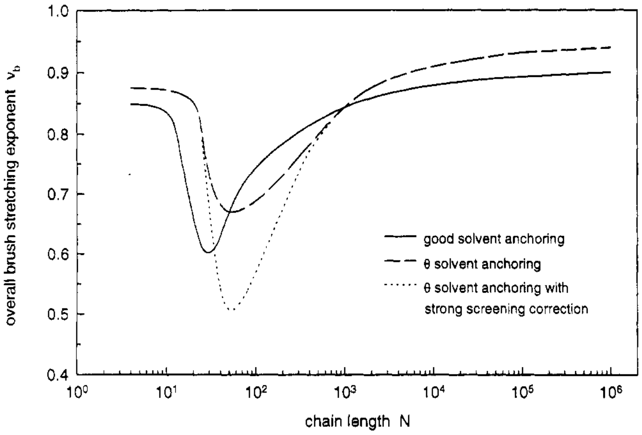

Figure 2. Overall brush stretching exponent ν_b as a function of the chain length N for a chain length controlled grafting process (schematic picture).

So, possibly the short length scale regime can be reached under good solvent conditions, too.

Finally, we note once more the qualitative character of the scaling analysis. Several constant factors have been neglected. Therefore, only some tendencies in the scaling behavior of polyelectrolyte brushes can be discussed. Some peculiarities in the grafting density and/or chain length dependence of the brush height are predicted to appear due to the unusual internal flexibility of polyelectrolyte chains which is governed by density-dependent stretching exponents $\nu(\phi)$. For the case of the particular chain length controlled grafting process used in experimental studies, we discuss an anomaly in the overall stretching exponent ν_b of polyelectrolyte brushes that occurs with growing chain length. Thus studies on polyelectrolyte brushes offer an independent way to check the new polyelectrolyte model suggested by Stevens and Kremer.[13]

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(24) One block is the polyelectrolyte, e.g., poly(styrenesulfonate), and the anchoring unit is a short-chain hydrophobic block, e.g., poly(*tert*-butylstyrene).[22,23]
(25) Note the more complex nature of the real adsorption process. Recent experimental data show that the chains are already stretched during the grafting process.[24] Hence, the saturation grafting density will be determined by the balance between the energy cost associated with chain stretching and the gain in energy due to adsorption at the surface. Thus, the maximum grafting density that can be reached by the particular grafting process is higher than the value indicated by eq 16.
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