Structure and Dynamics of Hairy Spherical Colloids in a Matrix of Nonentangled Linear Chains

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ABSTRACT: We describe the structure and dynamical behavior of a homogeneous mixture of hairy nanospheres, i.e., polyorganosiloxane microgels grafted with polystyrene chains, and linear polystyrene chains. Previously, it has been found that such mixtures are only homogeneous if the molecular weight of the polymer hairs is at least as large as that of the linear matrix chains. Otherwise, the depletion mechanism typical for most colloid−polymer mixtures leads to a phase separation. It indicates that the length of the polymer hairs with respect to the length of the matrix chains has an important effect on structure and dynamics of the colloid−polymer blends. Here we demonstrate that if the chains are much shorter than the hairs, the colloidal hair corona is strongly swollen by the matrix polymer, leading to a long-range soft interparticle repulsion ("wet brush"). If hairs and chains are comparable in length, the corona shows much less volume swelling, leading to a short-range repulsive potential similar to hard-sphere systems ("dry brush"). As a consequence, wet brush mixtures exhibit a liquid−solid transition, as identified by dynamic mechanical measurements, at much lower particle weight fraction in comparison to dry brush systems. These studies are compared with our recent work on copolymer micelles with corona and matrix chains of much higher molecular weight.

Introduction

Polymer brush surfaces are very important in the field of colloid stabilization. Standard colloidal particles usually are entropically incompatible with linear polymer chains and show a macroscopic phase separation[1−3] known as depletion demixing.[1] On the other hand, colloids with polymeric surfaces ("colloidal brushes") are highly compatible with linear chains, as has been shown for example during recent investigations of the dynamics of copolymer micelles in a homopolymer matrix.[4−7] Therefore, these colloidal brushes provide a potential route for the preparation of homogeneous polymer−colloid blends, with colloidal particles used for example as mechanical reinforcing agent or as pigment carriers in photoreactive polymer films. In contrast to their relevance, the studies of colloidal brushes in a melt of linear polymer chains found in the literature so far are very limited. An overview of recent theoretical and experimental work on this topic is given in the article by Martin and Wang.[8]

In this context, the influence of the molecular weight of the linear polymer chains on the structure of the colloidal brush plays an important role. In the case of a matrix of very low molecular weight, the brush is strongly swollen by the matrix chains ("wet brush"). On the other hand, if the molecular weight of the linear matrix chains is comparable to that of the brush chains, the brush is supposed to show no swelling but completely expels the matrix chains ("dry brush"). With decreasing molecular weight of the matrix chains, the density of the brush decreases while its thickness increases. This creates an interaction pair potential of two neighboring brushes ranging from short-range strongly repulsive (dry brush) to long-range soft repulsive (wet brush). Leibler and Pincus[9] presented calculations of the interaction pair potential between AB copolymer micelles swollen with A homopolymer chains in dependence of the molecular weight of the copolymer and homopolymer chains, respectively. They also roughly predicted the transition regime from a disordered liquidlike to an ordered crystalline arrangement of micelles as a function of the swelling ratio by using hard-sphere colloids[10] as a reference system. More recently, Martin and Wang determined the density profile of a planar brush with high grafting density in dependence of the molecular weight of the polymer matrix chains in the regime from wet to dry brush by self-consistent-field calculations (Figure 5 in ref 8, polymerization degree $N_{\mathrm{brush}} = 400$, grafting density 0.1 chains per unit area, polymerization degree $N_{\mathrm{matrix}} = 1$ (wet brush), 10, 50, and 400 (dry brush)). The whole range of grafting densities (between 0.025 and 0.95) has been considered in simulations,[20] where concentration profiles in brushes swollen in a good solvent (wet) and in contact with a polymer melt (dry) have been determined.

In our previous studies, we have probed indirectly via diffusion and dynamical mechanical measurements the degree of brush swelling and the interaction potential between spherical brushes in a polymer melt, using frozen micelles with a glassy polystyrene (PS) core and a polyisoprene (PI) corona, embedded in a matrix of linear PI.[11−13] Interestingly, these micelles closely resemble the system treated by Martin and Wang concerning their grafting density and brush chain length, besides the important fact that we have studied brushes with spherical topology. The degrees of volume swelling deduced from the diffusion coefficients of our micelles with respect to an experimental hard-sphere reference system[14,15] are in plausible agreement with the calculated brush dimensions shown in Figure 5 of ref 8.

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In this article, we present studies of the effect of brush swelling on structure and dynamics for spherical brushes with polymeric brush chains and linear matrix chains both of much lower molecular weight, i.e., below the entanglement regime, in comparison to our previous system of copolymer micelles in an entangled homopolymer matrix. These new particles have been prepared by grafting-onto of polystyrene macromers on surface-functionalized polyorganosiloxane microgels. Here, it should be noted that the radius of the microgels before grafting is about 10 nm and therefore similar to the core radius of our previously studied frozen micelles with glassy polystyrene core and polyisoprene corona. Also, the grafting density, i.e., the number of corona chains per particle, is comparable for the new system and our previous micellar system. The synthesis of the new spherical brush particles and studies concerning their compatibility with linear polystyrene chains have been published elsewhere.[16,17] There are several advantages of polymer grafted microgels in comparison to copolymer micelles: (i) the microgels are not formed by self-organization as the copolymer chains. Therefore, their structure within a colloid−polymer mixture remains unchanged irrespective of particle concentration, whereas the micellar structure dissolves into isolated copolymer chains beyond the critical micelle concentration (cmc). Also, our previous studies showed that there is a minor change in micellar size even at copolymer concentrations above the cmc. (ii) While keeping the core size constant, the grafting density of the microgels easily can be adjusted by using the appropriate amount of macromers during the grafting-onto reaction.

Finally, we should mention also the disadvantages of the grafted microgels: (i) It is not possible to prepare high molecular weight brushes with high grafting density due to steric overcrowding during the grafting reaction. (ii) It is not easy to prepare dye-labeled tracer particles as in the case of the copolymer micelles used in our previous diffusion studies. Based on the particle synthesis, the dye molecules have to be incorporated after the grafting reaction. Therefore, to reach the reactive sites within the microgels the labels have to penetrate not only the porous microgel (which successfully has been demonstrated for microgels without polymer brush surface[14,15]) but also the polymer brush itself. So far, the degree of labeling achieved during preparation of dye-labeled spherical brushes based on polymer grafted microgels has been too low to obtain reliable diffusion data for the new system. Therefore, in contrast to our extensive work on copolymer micelles covering structural analysis as well as mechanical relaxation and self-diffusion measurements, this study will be limited to a more qualitative data treatment. We will discuss structure factors determined by X-ray scattering and dynamical mechanical relaxation for samples of various concentrations of spherical brushes in a polymer melt, investigating the effect of the ratio of brush length to chain length. One particular aspect will be the liquid−solid transition identified by the occurrence of an elastic plateau in the dynamical storage modulus of highly concentrated systems. As previously, swelling ratios will be deduced by comparing our results with the hard-sphere reference system.

Experimental Section

Materials. Spherical brushes with high grafting density (0.2−0.4 chains/nm^2) have been prepared by grafting-onto of polystyrene macromers on functionalized polyorganosiloxane microgels. The characteristics of the materials used in these studies are given in Table 1.

Table 1. Characteristics of Hairy Spheres Used in These Studies (from Ref 17)[a]

R_H (core), nm	M_w (PS hairs), g/mol	$\langle N_{hair} \rangle$
10.3	4200	310
8.0	9900	320
8.0	16800	150

[a] $\langle N_{hair} \rangle$ is the average number of polystyrene hairs per particle as determined by UV/vis absorption and from the refractive index increment dn/dc.

Details of the preparation of these particles and their characterization by various methods are described elsewhere.[16,17]

Homogeneous blends of the spherical brushes shown in Table 1 and of linear polystyrene chains of various molecular weight have been prepared by solution casting from THF solution. For this purpose, the appropriate amounts of PS chains and of colloidal particles are dissolved in THF, total solid content about 10 wt %. The solvent is slowly evaporated at room temperature and normal pressure. To remove all solvent and for equilibration, the as-cast films are vacuum-annealed for several days at a temperature 20 °C above the glass transition of the PS matrix chains (typically at 120 °C).

Mechanical Spectroscopy. The setup used for dynamic mechanical measurements as well as a typical result (the dynamic storage and loss modulus vs oscillation frequency) for a blend of spherical brushes in linear polymer chains is shown in Figure 1.

The rheological experiments have been performed at the MPI für Polymerforschung, Mainz, using a Rheometrics RMS 800, with plate−plate geometry and variable plate diameters (6 and 13 mm). The samples were subjected to small oscillatory shear strain, and the resulting stress was measured. Master curves for the real (G', storage modulus) and imaginary (G'', loss modulus) parts of the dynamic complex shear modulus have been obtained using the time−temperature superposition principle (i.e., shifting the data recorded at various temperatures only along the frequency coordinate).[18] All measurements have been performed above the glass transition temperature of the polystyrene matrix.

Small-Angle X-ray Scattering. SAXS measurements were conducted at the MPI für Polymerforschung, Mainz, using a rotating anode (Rigaku 18 kW) X-ray beam with a pinhole collimation and a two-dimensional detector (Simens) with 512 × 512 pixels. A double graphite monochromator for the Cu Kα radiation ($\lambda = 0.154$ nm) was used. The beam diameter was about 0.5 mm, and the sample-to-detector distance was 1.3 m. Measurements have been performed at room temperature for 1 mm thick samples quenched after equilibration at temperatures considerably higher than the calorimetric T_g. It is therefore assumed that the structures analyzed are characteristic for the molten states of the systems. The recorded scattered intensity distributions were integrated over the azimuthal angle and are presented here as functions of the scattering vector ($s = 2 \sin \theta/\lambda$, where θ is the scattering angle).

Results and Discussion

Dry Brushes. The typical result of the mechanical testing shown in Figure 1, obtained for a sample containing 45 wt % spherical brushes ($M_{w,hair} = 9900$ g/mol) in a matrix of $M_w = 4200$ g/mol (highly concentrated colloid polymer blend), clearly indicates three relaxation processes. It should be mentioned that the three relaxation processes have earlier been found both in melts of multiarm stars[21] and in our previous dynamic mechanical studies of copolymer micelles in a homopolymer melt.[12,13] The three relaxation modes are identified as follows: (1) the glass transition of the polystyrene, i.e., segmental relaxation, (2) chain relax-

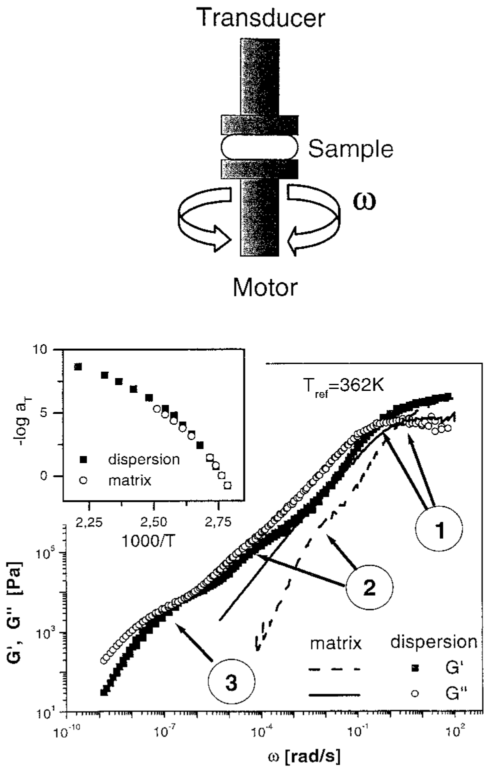

Figure 1. Sketch of the apparatus for dynamical mechanical measurements using oscillatory shear and typical results, i.e., the master dependencies of the real (G') and imaginary (G'') components of the complex shear modulus on the oscillation frequency ω at the reference temperature (T = 362 K). A comparison of the behavior of a concentrated dispersion of hairy spheres in a melt of linear polystyrene chains with the pure matrix polymer is shown. For the dispersion, three relaxation processes are detected: (1) segmental relaxation of the polystyrene (both hairs and matrix chains), (2) hair relaxation and chain relaxation of the polystyrene, and (3) a relaxation of the structure defined by the hairy spheres within the polymer matrix. The inset shows the temperature dependencies of the shift factors necessary for construction of the master dependencies.

ation both of the polystyrene hairs and the matrix chains, and finally (3) the structural relaxation of the spatial arrangement of the spherical brushes within the polymer matrix. For comparison with the behavior of the colloid polymer blend, properties of a corresponding melt of matrix chains are also shown in Figure 1. This result indicates a remarkable shift of the segmental relaxation rate (process 1) when the spheres with longer hairs are dispersed in the matrix of shorter linear chains. The effect becomes higher for higher ratio of hair length and the matrix chain length, as will be further seen in Figure 5a. Both the dispersions and the matrix polymers can be considered as thermorheologically simple. The shift factors determined by the construction of master curves (see the inset in Figure 1) have been well described by the WLF relation, and the corresponding fit parameters are given in Table 2 for most studied systems.

In this paper, we will further focus only on the terminal process (3), which exclusively controls the terminal flow of the studied dispersions and which provides a measure for the interbrush interactions and therefore for the brush swelling.

Figure 2 shows the dynamic storage modulus G' of a dry brush system with small chain lengths beyond the entanglement regime (hair molecular weight 4200 g/mol in a matrix of chains with the same molecular weight) at various brush concentrations, i.e., c = 15, 30, and 45 wt %.

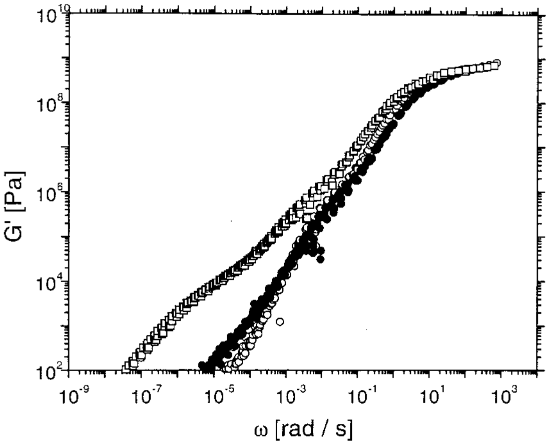

Figure 2. Frequency dependencies of the elastic shear modulus (G') at the reference temperature T = 362 K for samples containing 15 wt % (open circles), 30 wt % (filled circles), and 45 wt % (open squares) of hairy spheres (with hair molecular weight $M_{w,hair}$ = 4200 g/mol) in a matrix of linear polystyrene chains (M_w = 4200 g/mol).

Table 2. Parameters of the WLF Relation Determined by Means of Fitting the log(a_T) vs T Dependences

system				WLF parameters	
matrix	hairy spheres				
M_w/1000	M_w/1000	concn [%]	T_{ref} [K]	C_1	C_2
PS-0.6		0	293	12.2	77.9
	4.2	45		22.6	120.4
	9.9	45		16.4	80.3
PS-4.2		0	362	12.3	48.4
	4.2	15		12.2	52.9
	4.2	30		12.9	57.4
	4.2	45		11.5	55.2
PS-16.8		0	370	13.1	46.1
	9.9	15		12.4	44.2
	9.9	45		13.9	47.1

With increasing particle concentration, the terminal relaxation process attributed to structural relaxation of the arrangement of the spherical brushes is remarkably shifted to smaller frequencies. This corresponds to a slowing down of this relaxation process, which is also expected for colloidal particles dispersed in a molecular solvent. Compared to the slowing down of the structure relaxation, the two faster processes attributed to chain relaxations (see Figure 1) remain nearly unchanged with increasing particle concentration. Finally, it is important to note that even the sample with the largest concentration of 45 wt % still shows the structural relaxation, and therefore the liquidlike terminal flow at the lowest frequencies can be detected. Here, we have to consider that for example polydisperse colloidal hard spheres, which we chose as a reference system analogous to our previous studies of copolymer micelles, undergo a liquid−solid transition at a concentration of about 60 vol %.[10,15,19] Our spherical brushes are matched in density to the matrix polymer,[15] and therefore the particle weight concentration should be identical to the particle volume fraction. If our dry brush system shown in Figure 2 still exhibits liquidlike behavior at about 45 wt % = 45 vol %, the corresponding effective particle concentration also has to be smaller than 60 vol %. This leads us to the conclusion that for our dry brush system the particle hair corona could only slightly be swollen

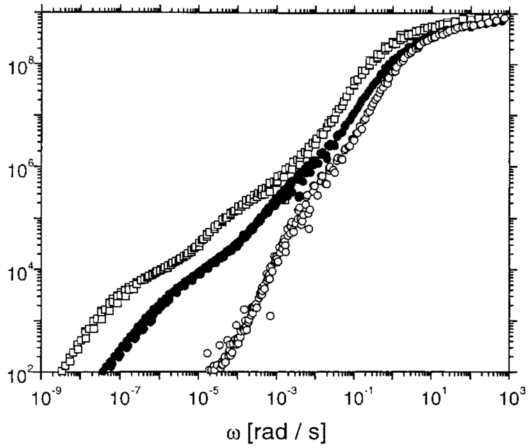

Figure 3. Frequency dependencies of the elastic shear modulus (G') at the reference temperature $T = 362$ K for linear polystyrene ($M_w = 4200$ g/mol) (open circles) and for samples containing 45 wt % hairy spheres ($M_{w,hair} = 4200$ g/mol) (filled circles) and 45 wt % of hairy spheres ($M_{w,hair} = 9900$ g/mol) (open squares) in a matrix of linear polystyrene chains ($M_w = 4200$ g/mol).

by the matrix polymer chains. Otherwise, strong swelling of the hair corona by matrix chains would increase the effective particle size and, correspondingly, the effective particle volume at a given weight concentration. In such a case, a more drastic slowing down of the structural relaxation would be observed which could be interpreted as a liquid–solid transition taking place already at weight concentrations much smaller than 60 wt %. This phenomenon indeed is found in the case of wet brush systems, as will be discussed further below.

Increasing the Length of the Brush Hairs. Figure 3 shows the relaxation moduli of the pure matrix and of the highly concentrated dry brush system already shown in Figure 2 in comparison with a highly concentrated intermediate brush system, i.e., 45 wt % hairy spheres with hair molecular weight $M_{w,hair} = 9900$ g/mol in a matrix of $M_w = 4200$ g/mol.

At given particle concentration (45 wt %) and given matrix chain length, the structural relaxation becomes slower with increasing length of the particle hairs. This corresponds to a more pronounced structure related to particle position correlation due to an increase of the effective particle volume fraction. This effect is caused by swelling of the brush, leading to an increase of the effective particle size. Figure 3 nicely demonstrates the difference between dry brushes and wet brushes. Note, however, that even the highly concentrated wet brush system shown in Figure 3 still exhibits the liquidlike behavior observed in the examined frequency window. This can be interpreted as the effective volume fraction being smaller than 60 vol %. Therefore, the swelling ratio in comparison to the dry brush system shown in Figure 2 is only slightly larger, and the difference in effective particle size correspondingly has to be less than 10% (estimated using the following assumptions: (i) the dry brush system ($M_{w,hair} = 4200$ g/mol) shows no volume swelling, i.e., its effective concentration wt % = vol % = 45%, and (ii) the wet brush system ($M_{w,hair} = 9900$ g/mol) still is in a liquid state, therefore its effective particle volume concentration could at most be as large as 60 vol %. The ratio of particle radii of swollen to nonswollen brushes therefore has to be smaller than $(60/45)^{1/3} = 1.10$). Increasing the molecular weight of the brush hairs by more than a factor of 2 seemingly only leads to a minor increase in brush size swelling by less than 10%.

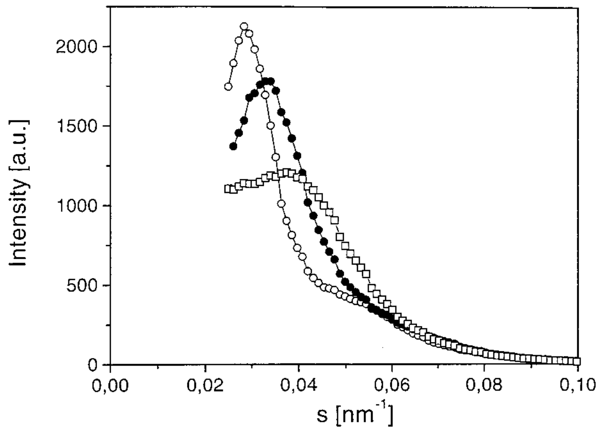

Figure 4. Scattered intensities measured by SAXS for samples containing 15 wt % hairy spheres ($M_{w,hair} = 4200$ g/mol (open squares), $M_{w,hair} = 9900$ g/mol (filled circles), and $M_{w,hair} = 16\,800$ g/mol (open circles)) in a matrix of linear polystyrene chains ($M_w = 600$ g/mol).

Wet Brushes in Low Molecular Weight Matrix Polymers. Next, let us consider how a much larger ratio of hair length vs chain length effects the volume swelling of the brushes and, correspondingly, the interparticle structure factor and the structural relaxation. For this purpose, we have investigated the spherical brush particles given in Table 1 in a low molecular weight PS matrix with $M_w = 600$ g/mol, corresponding to a ratio xr (hair molecular weight/chain molecular weight) = 7 ($M_{w,hair} = 4200$ g/mol), 16.5 ($M_{w,hair} = 9900$ g/mol), and 28 ($M_{w,hair} = 16\,800$ g/mol). Figure 4 shows the structure peaks of these wet brush systems at low concentrations of 15 wt % measured by SAXS.

Obviously, even at a particle concentration as low as 15 wt % the structure peak is well pronounced. Since colloidal hard-sphere systems at a particle concentration of 15 vol % only show very small and broad structure peaks,[10] this indicates that the effective particle volume fraction due to brush swelling in all cases shown in Figure 4 is much larger than 15 vol %. However, the peak height and sharpness increase with increasing hair length (increasing xr), corresponding to an increase in effective particle volume fraction and therefore in brush swelling, as expected.

Most interestingly, dynamic mechanical relaxation measurements of these wet brush systems exhibit a liquid–solid transition at particle weight concentrations where the dry and intermediate brush samples presented above (Figures 2 and 3) still are in a liquid state, i.e., show structural relaxation within the accessible frequency range. In contrast, the samples with the short matrix chains remain in the solid state in the whole frequency range examined and the structural relaxation process seems to be located just close to the low frequency edge of the studied range, as indicted in Figure 5a. Further examples are shown in Figure 5b in which only the real part of modulus is presented.

Comparing Figure 5 with Figures 2 and 3, it is obvious that the structural relaxation process usually occurring in a frequency regime of 10^{-5}–10^{-9} rad/s (see Figures 2 and 3) has disappeared for the concentrated wet brush systems. Instead, an elastic plateau is seen in this frequency regime in Figure 5, resembling the solid-state behavior of a “frozen structure”.

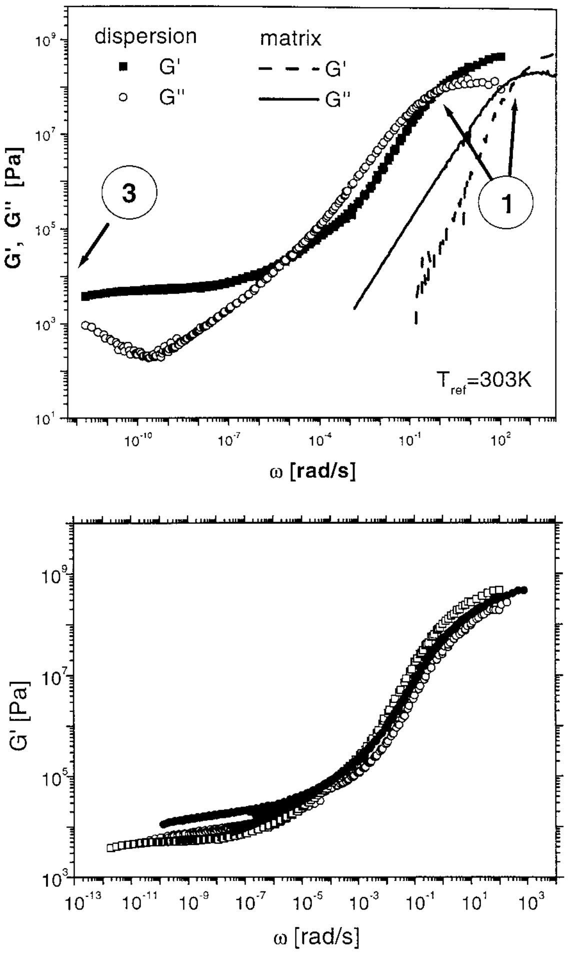

Figure 5. (a) Master curves (G' and G'' vs ω) for the dispersion of hairy spheres in a melt of short linear polystyrene chains and for the matrix with indication of the segmental relaxations (1) in both systems and of the structural relaxation (3) in the blend. (b) Frequency dependencies of the elastic shear modulus (G') at the reference temperature $T = 293$ K for samples containing 45 wt % of hairy spheres ($M_{w,hair} = 4200$ g/mol) (open circles), 45 wt % of hairy spheres ($M_{w,hair} = 9900$ g/mol) (solid circles), and 30 wt % of hairy spheres ($M_{w,hair} =$ 16 800 g/mol) (open squares), each in a matrix of linear polystyrene chains ($M_w = 600$ g/mol).

Here, we should mention that at smaller particle concentrations, i.e., 30 wt % for the two systems with $xr = 7$ and 16.5 ($M_{w,hair} = 4200$ and 9900 g/mol, matrix $M_w = 600$ g/mol) and 15 wt % for the system with $xr = 28$ ($M_{w,hair} = 16\,800$ g/mol, matrix $M_w = 600$ g/mol), these samples show a structural relaxation process in rheological measurements and therefore still are in the liquid state. Analogous to the procedure sketched above, we can estimate the swelling ratio of the particle radius if we assume that the liquid–solid transition occurs at an effective particle volume fraction of 60 vol %. For the sample with $xr = 28$, according to our rheological studies this transition occurs in a regime between 15 and 30 wt % and for the other two samples between 30 and 45 wt %. This leads to the following swelling ratios of the particle size: 1.26 ($(60/30)^{1/3}$) – 1.10 ($(60/45)^{1/3}$) for $xr = 7$ and $xr = 16.5$ and 1.59 ($(60/15)^{1/3}$) – 1.26 ($(60/30)^{1/3}$) for $xr = 28$. As expected, the swelling ratio of the system with the largest value xr also is larger than that of the other two systems; i.e., the wet brush character is most pronounced for the spherical brushes with the longest hairs. Finally, we should mention that a more accurate determination of the swelling ratios than given so far efforts much more detailed rheological measurements in the liquid–solid transition regime.

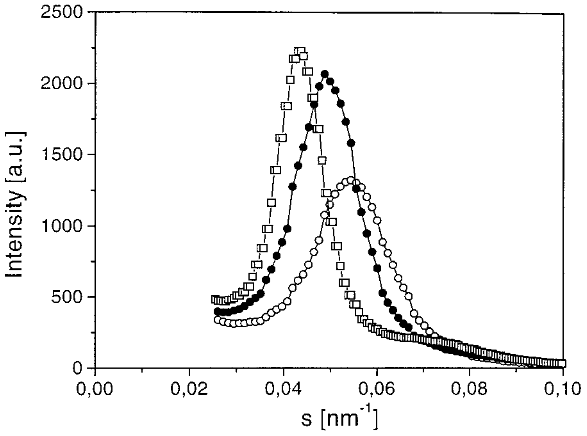

Figure 6. Scattered intensities measured by SAXS for the solid samples shown in Figure 5b, i.e., containing 45 wt % of hairy spheres ($M_{w,hair} = 4200$ g/mol) (open circles), 45 wt % of hairy spheres ($M_{w,hair} = 9900$ g/mol) (solid circles), and 30 wt % of hairy spheres ($M_{w,hair} = 16\,800$ g/mol) (open squares), each in a matrix of linear polystyrene chains ($M_w = 600$ g/mol).

The effective particle concentration can also be estimated from the static structure factor. The scattering curves obtained by SAXS from the solid-state wet brush samples (see Figure 5) are given in Figure 6.

For $xr = 7$, the structure peak is much lower and broader than in the case of the other two systems. The fact that the structure peaks shown in Figure 6 are not equal in height and sharpness signifies that the effective particle volume fractions of the three systems also are not identical. Since for the samples with $xr = 28$ ($c = 30$ wt %) and $xr = 16.5$ ($c = 45$ wt %) the structure peaks are nearly identical, we may assume that the corresponding effective particle volume fractions also are comparable. On the other hand, the effective volume fraction of the third sample ($xr = 7$, $c = 45$ wt %) definitely is much smaller than that of the two others. Therefore, the difference in swelling ratios especially for the systems $xr = 16.5$ and 7 is larger than has been deduced from the rheological measurements alone, where identical swelling ratios (1.26–1.10, see above) have been obtained. If we combine our analysis of the swelling ratios determined by mechanical spectroscopy and by SAXS, the most probable results are 1.1 (lower limit of the result estimated from rheological studies) for $xr = 7$, 1.25 (upper limit of the result estimated from rheological studies) for $xr = 16.5$, and 1.6 (upper limit of the result estimated from rheological studies) for $xr = 28$, with an accuracy of about ±0.05.

Here, it also should be noted that the spherical brushes studied in this article as well as the micellar systems investigated previously are deformable. Therefore, especially at very high particle concentrations where the interparticle interactions increase, nonneglectable particle deformability plays a role[22] and can in effect be regarded as a decrease of the particle volume swelling. This has been shown previously for the micellar systems by a detailed analysis of the concentration dependence of particle diffusion in comparison to a hard-sphere reference system.[13,15] In Table 3, we compare the swelling ratios determined here for highly concentrated spherical brushes with our previous results for copolymer micelles in an entangled polymer melt, the latter at an effective concentration of 45 vol

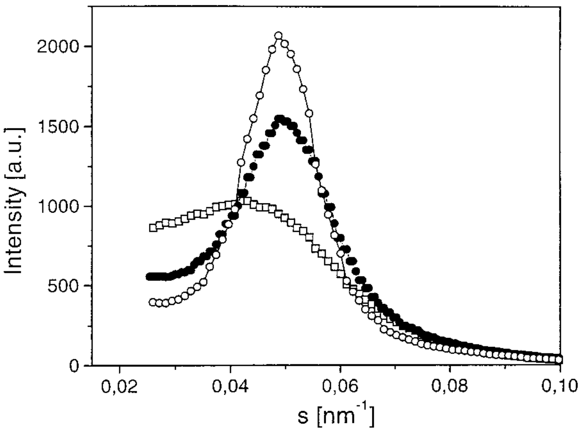

Figure 7. Scattered intensities measured by SAXS for samples containing 45 wt % of hairy spheres ($M_{\mathrm{w,hair}} = 9900$ g/mol) in different matrix polymers ($M_\mathrm{w} = 600$ g/mol (open circles), $M_\mathrm{w} = 4200$ g/mol (solid circles), and $M_\mathrm{w} = 16\,800$ g/mol (open squares)).

Table 3. Swelling Ratio of Particle Radius R/R_0 (with Respect to the Nonswollen State) in Dependence of the Ratio Hair Molecular Weight to Chain Molecular Weight *xr* for Copolymer Micelles in a Homopolymer Matrix (from Ref 13, at Effective Concentration 45 vol %) and for PS-Grafted Microgels in Low Molecular Weight PS Chains (M = 600 g/mol)

system	microgel	microgel	microgel	micelle	micelle	micelle
xr	7.0	16.5	28.0	10.0	2.2	1.0
R/R_0	1.10	1.25	1.60	1.37	1.26	1.09

%. We have chosen this high concentration limit since the swelling ratios determined for the new microgel system have been obtained only from a data analysis in the liquid–solid transition regime, i.e., at very high effective particle concentrations of about 60 vol %.

By comparison of the data given in Table 3, even at comparable values of *xr* the effective particle size swelling for the micellar system seems to be much more pronounced. One might argue that this difference is caused by the different concentration regimes, that is an effective volume fraction $\phi_{\mathrm{eff}} = 45$ vol % for the micellar system and $\phi_{\mathrm{eff}} > 60$ vol % for the grafted microgels. However, there definitely is a difference in volume swelling between the two systems also at comparable ϕ_{eff}, as proved by the fact that micelles ($M_{\mathrm{w,hair}} = 50\,000$ g/mol) with $xr = 2.2$ undergo a liquid–solid transition already at a particle concentration of 35 wt %, as has been shown in ref 13. On the other hand, a microgel system ($M_{\mathrm{w,hair}} = 9900$ g/mol) with $xr = 2.4$ still is in the liquid regime even at a particle concentration of 45 wt %, as is seen in Figure 3. Here, it remains an open question whether the different behavior of micelles and microgels is only caused by the fact that the polymeric molecular weight in the case of the micellar systems was much larger and well in the entangled regime. Alternatively, the different chemical composition of the polymers, i.e., polyisoprene for the micellar system and polystyrene for the microgels, also may play a role. Especially the temperature range of our studies with respect to the glass transition temperature of the respective polymers might also influence the swelling behavior. Here, however, it should be pointed out that Leibler and Pincus[9] have claimed that temperature should not effect the swelling behavior and the liquid–solid transition of spherical brushes in a matrix of linear polymer chains. A final answer to this problem concerning the universal character of wet brush and dry brush behavior, especially the volume swelling in dependence of the chain length ratio *xr* and of the absolute chain length, cannot be given at the present experimental stage.

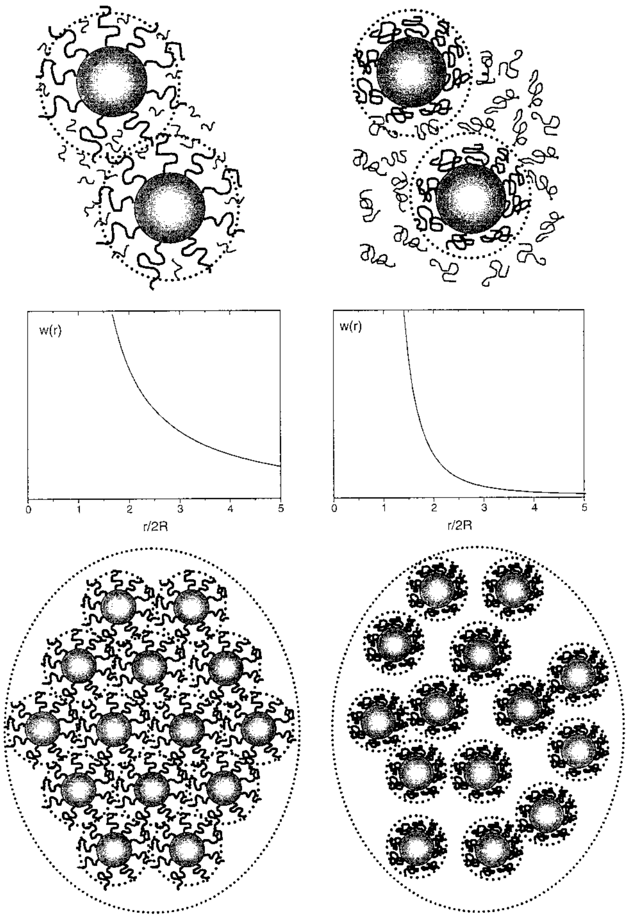

Figure 8. Comparison of hairy spheres embedded in a matrix of short linear chains (“wet brush”, left column) and in a matrix of long chains (“dry brush”, right column). The “wet brush” system shows strong swelling of the hairy particle corona by the matrix chains, leading to a long range soft repulsive interparticle interaction potential $w(r/2R)$ (R = particle core radius). In contrast, the “dry brush” system shows much less volume swelling and therefore an interaction potential which closely resembles that of hard spheres. At identical particle number densities, the “wet brush” system due to its strong volume swelling has a much larger effective particle volume fraction than the “dry brush” system. Therefore, the apparent fluid–solid transition for hairy spheres in a polymer matrix is shifted to lower particle concentration with decreasing molecular weight of the matrix chains (bottom, left: ordered solid phase of a “wet brush” system; right: disordered fluid phase of a “dry brush” system, at identical particle number density).

Polymer Brushes in Matrix Chains of Increasing Molecular Weight. Although the absolute size of the swelling effect according to the results discussed in the previous section may depend on the absolute molecular weight of the polymer chains, it is definitely a general phenomenon that the swelling ratio increases with increasing *xr*, i.e., relative molecular weight ratio of hairs and chains. This is nicely demonstrated by the structure peaks shown in Figure 7.

The samples shown in Figure 7 each consist of 45 wt % of identical spherical brushes ($M_{\mathrm{w,hair}} = 9900$ g/mol) in three different matrix polymers ($M_\mathrm{w} = 600$, 4200, and 16 800 g/mol). If the matrix molecular weight is smaller than that of the hairs ($xr > 1$), the peak position in both cases is identical, while the peak height and peak sharpness are increasing with xr. Here, it should be noted that of the three examples shown in Figure 7 according to rheological measurements only the sample with matrix molecular weight 600 g/mol ($xr = 16.5$) is in the solid state. There is a dramatic change if $xr < 1$. In this case, the structure peak not only is much less pronounced than in the other two cases, but its position is also shifted toward smaller s, corresponding to an increase in interparticle spacing detected by SAXS. According to what we learned previously about compatibility of our PS-grafted microgels with linear PS chains,[17] we believe that for $xr < 1$ the system shows microphase separation due to depletion. The particles tend to form clusters, and as a consequence the spacing between individual particles increases. Also, the structure peak in this case nearly disappears, meaning that the interparticle spacing in comparison to the samples with $xr > 1$ is defined only very roughly.

Summary

We have presented an experimental study about the swelling of spherical polymer brushes in a matrix of linear polymer chains. This swelling is caused by entropic effects only, i.e., a competition of the configurational entropy of the single chains (maximum configurational space or free volume) and of the stretching entropy of the brush hairs and the single chains. As a consequence, the swelling of the brush increases with increasing molecular weight of the brush hairs with respect to the molecular weight of the single chains. Strongly swollen systems are referred to as wet brushes. These wet brushes show an increase in effective particle size and correspondingly a long-range soft repulsive interaction pair potential. As a consequence, they exhibit a liquid−solid phase transition at particle weight concentrations comparatively lower with respect to that of their less swollen counterparts (dry brushes). This scenario is summarized in Figure 8.

Interestingly, not only the ratio of the molecular weight of the brush hairs with respect to the molecular weight of the single chains seems to influence the swelling behavior but also the absolute chain length. Comparison of previous results obtained for copolymer micelles with the new studies of brush systems with much shorter polymer chains presented in this article seems to imply that, at a given ratio of hair length to single chain length, the swelling increases with increasing absolute polymer length. However, the different chemical compositions of the two systems do not allow to ignore other potential effects on brush swelling, i.e., chemical nature of the polymer chains (chain flexibility, persistence length) or sample temperature with respect to the glass temperature of the polymers.

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