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# When Colloidal Particles Become Polymer Coils

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**ABSTRACT:** This work concerns interfacial adsorption and attachment of swollen microgel with low- to medium-level cross-linking density. Compared to colloids that form a second, dispersed phase, the suspended swollen microgel particles are ultrahigh molecular weight molecules, which are dissolved like a linear polymer, so that solvent and solute constitute only one phase. In contrast to recent literature in which microgels are treated as particles with a distinct surface, we consider solvent—solute interaction as well as interfacial adsorption based on the chain segments that can form trains of adsorbed segments and loops protruding from the surface into the solvent. We point out experimental results that support this discrimination between particles and microgels. The time needed for swollen microgels to adsorb at the air/water interface can be 3 orders of magnitude shorter than that for dispersed particles and decreases with decreasing cross-linking density. Detailed analysis of the microgels deformation, in the dry state, at a solid surface enabled discrimination particle like microgel in which case spreading was controlled predominantly by the elasticity and



molecule like adsorption characterized by a significant overstreching, ultimately leading to chain scission of microgel strands. Dissipative particle dynamics simulations confirms the experimental findings on the interfacial activity and spreading of microgel at liquid/air interface.

# 1. INTRODUCTION

Microgels are ultrahigh molecular mass molecules of an intramolecularly cross-linked network of polymer chains swollen with a solvent.<sup>1,2</sup> Aspects of microgel suspensions have been exploited in numerous applications and have received attention at the fundamental level.<sup>3</sup> Unlike a dispersion of elastomer particles, also referred to as microgels, highly swollen microgels comprise an open structure with a diffuse outer boundary, where also the inner segments are wellsolvated, so that the solute and solvent form a single phase.<sup>1,4–7</sup> Thus, the suspended solvent-swollen microgel particles are dissolved like a linear polymer in a good solvent. In opposition with a polymer solution, however, the network expands until the elasticity of the chains counteracts the expansive excluded volume repulsion. The high fraction of solvent inside the microgel together with steric stabilization ensures dissolution. The open structure enables swelling/deswelling as well as mechanical deformation of the elastic network structure. Such peculiarities form a basis for switchability as single objects. Because of these distinctions from the hard particles, it may be expected that the interfacial adsorption of microgels demonstrates specific characteristics that are atypical for dispersed hard particles.<sup>8</sup>

At liquid—liquid interfaces dispersed colloids exhibit a strong interfacial activity often referred to as the "Pickering effect" attributed to the wetting properties of the particles.<sup>9</sup> Similarly, microgels are expected to exhibit interfacial activity but less effective than the hard colloids due to compatibility of a highly swollen microgel with one or even both solvents. However, experimentally a pronounced interfacial activity can be observed which is accompanied by significant deformation of the microgel.<sup>10-12</sup>

Also at liquid—solid interfaces, adsorption of dispersed nanoand microparticles has been studied intensively.<sup>13</sup> Rigid particles are well-known to form highly regular, mostly hexagonally packed monolayer structures. Here the driving forces are colloidal interaction and most importantly capillary forces exerted by the meniscus that evolves upon evaporation of the solvent at the solvent/air/particles interface.<sup>14</sup> For soft particles, elastic compliance can be considered by contact mechanics theory<sup>15</sup> that accounts for the variation of the adhesive contact by balancing adhesion energy, which favors large contact area, against elastic energy, which opposes deformation.<sup>16,17</sup>

In both cases, hard or soft particles, the contact is described by considering a surface area and the particle geometry. Concerning the open structure of microgels, one may consider them as a homologue in the row of linear molecules brush (comblike) molecules hyperbranched and arborescent molecules and finally microgels, characterized by radial distribution of the cross-link density. Considering the brush molecules, the adsorption is controlled on the length scale of the polymer

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Figure 1. Normalized hydrodynamic radius of the PVCL/NIPAm microgels with different cross-linker fraction versus temperature (a). The cross-linker fraction in the legends are in mole percent. The absolute hydrodynamic radius depending on the cross-linker fraction at 20 and 50 °C (b).

segments in contrast to the length scale of the molecular particle as a whole. Furthermore, the brush molecules can undergo a strong conformational transition from a 3D coiled state to stretched rod-like conformation.<sup>18</sup> As consequence of the enormous stress exerted on the polymer backbone, adsorption caused chain scission has been observed.<sup>19,20</sup> Similar molecular spreading has been observed for block copolymer micelles with a solvent swollen corona<sup>21</sup> and actually also for microgels, where adsorption of the constituent polymer segments and conformational changes in the particles structure can play a dominant role.<sup>22</sup> Hence, for dissolved microgels in which shape alteration is controlled by water molecules that move freely in the viscoelastic network, interfacial contact should result from the competition between microgel elasticity, osmotic stress, and molecular spreading.

In this work we address the issue of the interfacial attachment of microgels depending on the cross-linking density. For this purpose, we prepared monodisperse and colloidally stable microgels, composed of micrometer sized poly(N-vinylcaprolactam-co-N-isopropylacrylamide). The cross-link density and therefore the shear modulus of microgel were systematically varied to cover 3 orders of magnitude, whereas molecular mass and composition were kept constant. We assessed the interfacial tension of the microgel at the water/air interface. Particular emphasis is to measure to what extent microgel softness enhances adsorption and spreading dynamics. Furthermore, adsorption on a solid surface deforms microgels; we measure the height profile and contact radius with scanning force microscopy (SFM). The results highlight the interplay of the surface forces, the shape, and the microgel internal structure, i.e., a radial density distribution of an ultrahigh molecular mass. The experimental data complemented with dissipative particle dynamics (DPD) simulations to provide consistent insight into the microgel at fluid/fluid interfaces.

## 2. EXPERIMENTAL SECTION

**Materials.** *N*-Vinylcaprolactam (VCL) (Sigma-Aldrich) and *N*-isopropylacrylamide (NIPAm) (Sigma-Aldrich) were purified by high-vacuum distillation at 80 °C. The initiator, 2.2'-azobis(2-methylpropioamidine) dihydrochloride (AMPA), and the cross-linker, *N*,*N*'-methylenebis(acrylamide) (BIS), were obtained from Sigma-Aldrich and used as received.

**Synthesis of Microgels.** Microgels are synthesized according to previously reported procedures as a precipitation polymerization at a temperature above the phase volume transition.<sup>23</sup> Briefly, 1.220 g of VCL, 0.993 g of NIPAm (VCL:NIPAM molar ratio 1:1), and appropriate amounts of cross-linker (0.05–3 mol % of total monomer amount) were added to 145 mL of deionized water. After the synthesis, all microgel suspensions were dialyzed by Millipore Labscale

TFF system with Pellicon XL Filter (PXC030C50) for 4 days. During the dialysis process the microgel solution was pumped continuously through the membrane with a pore size much smaller than the size of microgels to remove small organic molecules and oligomers. Chemical compositions of the copolymers were assessed by NMR and have been published elsewhere.<sup>24</sup>

Swelling Behavior of Microgels. Volume phase transitions were monitored by the apparent hydrodynamic radius measured with an ALV/LSE-5004 light scattering multiple tau digital correlator and electronics with the scattering angle set at 90°. The samples were measured at different temperatures (from 20 to 60 °C), and the temperature fluctuations were below 0.1 °C. Prior to the measurement, microgel samples were diluted with water for chromatography from Merck Millipore, which is filtered through a 100 nm filter before use.

Inferred from the DLS measurement, the hydrodynamic radii ( $R_h$ ) of PVCL/NIPAm microgels of variable cross-linker concentrations are normalized by the value in the collapsed state ( $R_{h,collapsed}$ ) and plotted as a function of the temperature. The volume phase transition (~35 °C) was hardly affected by the intramolecular cross-linking degree. Higher cross-linking limits the equilibrium swelling of microgels. The average swelling ratio varied from 1.5 for densely cross-linked to 2.5 for loosely cross-linked ones. In the collapsed state, the microgel particles still contain a considerable amount of water and therefore possess a larger size compared to completely dehydrated particles.<sup>11,21</sup>

Dynamic surface tension measurements were carried out with a DSA 100 tensiometer (Kruss, Germany) through the pendant drop method at room temperature ( $\sim$ 23 °C). Aqueous dispersions of microgels were prepared with deionized water (Milli-Q Academic A-10 system, Millipore). The concentration of the microgel solution was 0.2 g/L, the same as used for spin-coating. To avoid water evaporation from the drop, the measurement was taken in a sealed cuvette saturated with water vapor.

**Deposition of Microgels on a Solid Substrate.** The deposition of microgels was carried out on a spin-coater (Convac 1001S, Germany). Silicon wafer was cleaned with ultrasonication in isopropanol for 10 min, dried in air stream, and treated with  $UV/O_2$  for 12 min. For the spin-coating, a drop of 75  $\mu$ L was deposited on the silicon wafer surface, and the wafer was rotated at a speed of 3000 rpm for 1 min. The macroscopic homogeneity of the surface was evaluated with an optical microscope (Zeiss Axioplan 2). A microgel solution with a concentration of 0.2 g/L yields separate particles on the silicon surface.

Scanning force microscopy (AFM) images were recorded on an Agilent 5500 atomic force microscope in tapping mode. Cantilevers with resonance frequencies of 250-300 kHz and spring constants around 42 N/m were used. Picoimage software provided by Agilent was used to analyze the recorded AFM results.

#### 3. COMPUTER SIMULATION

The dissipative particle dynamics  $(DPD)^{25,26}$  was employed for the simulation of the microgel structure according to the

approach we used earlier for block copolymer.<sup>27,28</sup> As a starting configuration, we considered microgel particles of equal molecular weight but different cross-linking density (Figure 2) in a diamond lattice like network structure. To provide a



**Figure 2.** Initial (before annealing) diamond lattice structures of weakly (a) and highly (b) cross-linked microgels. The total number of beads in the microgel, the number of the beads per subchain, and the number of the subchains are 1787, 19, 64 (a) and 1785, 8, 212 (b), respectively.

"spherical" shape of the particle, the network is placed into a sphere with further deleting the outer beads. Loosely crosslinked microgel consists of 64 subchains, each of 19 beads; 571 beads form dangling chains, so that the total number of the beads in the particle is equal to 1787. The densely cross-linked particle consists of 1785 beads including 212 subchains, each of 8 beads, and 89 beads in the dangling chains, as seen in Figure 2.

In order to study mobility of the microgel particles in solution, each particle was placed in a cubic box of a constant volume  $V = L_x \cdot L_y \cdot L_z = 50 \cdot 50 \cdot 50$  with periodic boundary conditions in the x, y, and z directions. We set the total number density in the system as  $\rho = N/V = 3$ , so that the total number of the microgel and solvent beads (denoted as M and S, respectively) in the box was  $N = 3.50^3$ . Repulsion between the beads of the system is quantified by interaction parameters  $a_{ii}$ ,  $i_i$ j = M, S, which can be related to the Flory-Huggins parameters according to the formula  $\chi_{ij} = (0.286 \pm 0.002)(a_{ij} - a_{ii})$  at  $\rho = 3.^{27,29}$  Annealing of the microgels was performed in a good solvent ( $a_{MS} = 28$ ,  $a_{MM} = a_{SS} = 25$ ). After attaining the equilibrium swelling degree, an average velocity of the center of mass of the microgel was examined. The velocity  $\mathbf{v}(t)$ is defined as a derivative of the coordinate of the center of mass  $\mathbf{R}(t)$  with respect to time t,  $\mathbf{v}(t) = d\mathbf{R}/dt \approx \Delta \mathbf{R}/\Delta t$ , which can be approximated as a displacement of the center of mass  $\Delta \mathbf{R}$ during short time interval  $\Delta t$ : the shorter the interval, the better the approximation. We measured the absolute value of  $\Delta \mathbf{R}$ every  $\Delta t = 5000$  simulation steps and plotted the total path length  $D = |\Delta \mathbf{R}_1| + |\Delta \mathbf{R}_2| + \dots$  as a function of time  $t = \Delta t + \Delta t +$ .... The slope of D(t) quantifies the average velocity.

In order to simulate a water/nonsolvent interface (nonsolvent stands for a nonpolar organic solvent or even air regarding the surface activity), we considered two immiscible liquids (denoted by W and A) in the simulation box which were strongly segregated ( $a_{WA} = 60$ ,  $a_{WW} = a_{AA} = 25$ ). One of the liquids (A) was considered to be poor for the microgel (M),  $a_{MA} = 40$ , whereas both dense and loose microgels were in the swollen state in the second liquid,  $a_{MW} = 28$ . Such a choice of the parameters provided localization of the microgels at the interface. Computer simulations were performed in a box of a constant volume  $V = L_x L_y L_z = 50.50.40$  with periodic boundary conditions in the *x* and *y* directions. The upper part of the box was filled by a poor solvent (A) which occupied 30% of the box. The bottom part of the box was filled by the good solvent (W). The dense and the loose microgels were first preannealed in one-component good solvent ( $a_{MW} = 28$ ,  $a_{WW} = a_{MM} = 25$ ). Then the corresponding swollen microgel was placed into the bottom subphase in such a way to make a contact with the interface through one or two polymer beads. Such contact was enough to keep the particles at the interface and initiate spreading.

# 4. RESULTS AND DISCUSSION

**Interfacial Activity at the Air/Water Interface.** To study the effect of the cross-linking concentration on the microgel deformation (spreading) at the air/solid interface, we first investigated the adsorption of microgels at the water/air interface by measuring the surface tension as a function of time. Figure 3 shows that regardless of the cross-linking degree of the



**Figure 3.** (a) Dynamic surface tension for microgels with different cross-linker fractions. (b) Half-time  $t^*$  corresponds to the inflection point of the dynamic surface tension curves (a) (see text for details). The microgel concentration was kept constant and corresponds to 0.2 g/L.

microgel, the surface tension decreases and eventually reaches a steady state with an equilibrium value equal to about 46 mN/m. Since the microgel contains 50 mol % VCL, we expected the surface tension to be different from previously reported equilibrium surface tension for PNIPAm microgels (~42 mN/m).<sup>30</sup>

Remarkably the time required to achieve a steady state of the surface tension increases with the particle cross-linking density. To make a more explicit comparison, we plotted in Figure 3b the half-time  $t^*$ , defined by the inflection point corresponding to the time it takes for the surface tension  $\gamma(t) = (\gamma_0 + \gamma_{eq})/2$ .<sup>31</sup>  $\gamma(t)$  is the surface tension at time t,  $\gamma_0$  is the surface tension at the instant that the drop is formed and is assumed equal to the surface tension of water (72 mN/m at 23 °C),<sup>32</sup> and  $\gamma_{eq}$  is the surface tension at the steady state. The data demonstrate that weakly cross-linked microgels exhibit significantly higher adsorption and spreading rates compared to highly cross-linked ones.

In general, adsorption depends on (i) the concentration, (ii) the diffusion rates and in the case of the soft microgels, and (iii) the conformational flexibility that allows eventually for some cooperativity in the molecular spreading at the air/water interface. The surface tension data do not differentiate between these effects but clearly show that more flexible microgels adsorb and saturate the air/water interface in a short time. The effect that the interfacial activity of the microgel depends on their conformational flexibility is in agreement with the observation that microgels strongly deform upon adsorption

Scheme 1. (a) Height Image of Dry Microgel on Solid Surface and (b) a Scheme of the Height Profile and (c) Its Density Profile of a Swollen and Collapsed Microgel According to Ref 5 To Highlight the Relation between the Dense Core and Height as Well as Hydrodynamic Radius and Contact Area



at an interfaces.<sup>8,10,24,30,33,34</sup> Indeed, the looser the microgel, the larger their lateral size. Therefore, we need a less number of loose microgels to saturate the interface (in comparison with the highly cross-linked microgels). The diffusion rate of swollen (loose microgels) in water is lower because they are larger than the dense microgels of the same molecular mass. On the other hand, the larger the microgels, the higher the probability to reach the water—air interface. Therefore, the factor that favors reduction in the surface tension are (i) faster spreading rate, (ii) faster surface saturation, and (iii) higher probability to reach the surface of weakly cross-linked microgels those are. The only limiting effect is the slower mobility of the weakly cross-linked microgels in water.

Morphology of Dry Microgels on Solid Substrates. In order to investigate the extent of the molecular deformation, i.e., the spreading of the microgels upon interfacial adsorption, we studied the deposited microgels by scanning force microscopy. Single isolated microgels were adsorbed/deposited from dilute solution on a silicon wafer and imaged in the dry state, i.e., after solvent evaporation as they were adsorbed. The experiment is based on the assumption that the monitored molecular structure will indicate whether the segments adsorb from solution or whether the molecules are just deposited as the solvent evaporates. Indeed, the flat and spread shape of the microgel indicates adsorption from solution. Notably, the weakly cross-linked molecules extend on the surface with a contact radius exceeding its hydrodynamic radius in solution, as it will be shown below. Because the microgel exhibits a radial gradient in the cross-liker concentration, it is expected that they adopt a conformation, where the softer outer parts are strongly flattened than the densely cross-linked core.<sup>5,35,36</sup>

Scheme 1 summarizes the structural parameters of the following discussion. When a compliant colloidal particle with radius R is adsorbed on a flat surface, the ratio of the reduced height in the vertical direction  $\Delta h/(2R)$  describes the extent of its deformation (Scheme 1).<sup>37</sup> A hard spheres does not deform  $(\Delta h \sim 0)$ , whereas a highly flexible particles may flatten. In contrast, to an elastic particle that adsorbs via surface contacts, a highly flexible molecule can unfold so that an increasing number of chain segments get in contact to the surface and the vertical deformation may approach its diameter ( $\Delta h \sim 2R$ ). Because of the radial gradient in the cross-linker concentration, the shell and core of a microgel respond differently. Actually, for microgel adsorbed from solution on a solid surface, we observe a hemispherical core surrounded by a flattened corona of adsorbed polymer chains. The radius of the whole structure is denoted the contact radius,  $R_{\text{cont}}$ . At the periphery, the height of the corona is molecular and corresponds to the diameter of the constituent polymer chains. The height h of the core is due to the limited deformability of the more strongly cross-linked inner segments of the microgel. As a reference for the lateral deformation we refer to the hydrodynamic radius of the wellsolubilized microgel below the VPT  $R_{h,20}$  and for the vertical deformation (flattening) to the hydrodynamic radius of the collapsed particle above the VPT represented by  $R_{h,50}$ . The parallel between conformations of microgel adsorbed on a solid surface with respect to the freely swollen allows to highlights the conformational flexibility in opposition to shape elasticity of colloidal particles. Maximum size in the swollen state compared to the lateral extension on surface, while material compressibility limits the vertical deformation on the surface in comparison with the collapsed size as the smallest achievable dimension in solution.



**Figure 4.** Morphology of adsorbed microgels with different cross-linker contents: (a) 3, (b) 1, (c) 0.5, and (d) 0.05 mol %. For each image, the scan size is  $5 \times 5 \mu m^2$ , and the upper is a phase image and the graph below it is a cross-section profile of topographic image at the same position along the horizontal line as indicated. The inset in the height profile highlights the outer-shell-like part.

In the limit of a compact particle like behavior where the adsorption is controlled by the surface to surface adhesive contact, we expect mostly the hemispherical shape as depicted for the core. In the case of a loosely cross-linked highly flexible microgel for which adsorption is controlled also by the inner segments, we expect flat structure as depicted for the corona.

This is indeed observed for microgels when the cross-linking is varied. In Figures 4a and 4b, the height profiles for particles with 3 and 1 mol % cross-linker, respectively, show a hemispherical shape. The diameter of the hemisphere is roughly in agreement with the hydrodynamics radius of the well-solubilized microgel. A different observation has been encountered when the cross-linking density has been reduced to 0.5 and 0.05 mol % cross-linker. In the first case the adsorbed molecules exhibit a well-pronounced "fried egg" shape with an extended molecularly flat (1 nm) corona around a hemispherical core (Figure 4c). In the second case, the molecules are further spread and the hemispherical core is significantly reduced in height. The widespread corona exhibits a height corresponding to tightly adsorbed trains of the polymer segments (1 nm). Quantitatively, Figure 5 depicts the heights (h) of the hemispheres and the radii of the spread



**Figure 5.** Microgel dimensions in contact with the solid surface and in solution depending on the cross-linker fraction. The shape of the microgel on SiO<sub>2</sub> is described by its height and contact radius denoted by  $R_{\text{cont}}$ . For comparison, the hydrodynamic radius in swollen  $(R_{\text{h},20})$  and collapsed state  $(R_{\text{h},50})$ .

molecules including the corona, i.e., the contact radius  $(R_{\text{cont}})$  depending on the cross-linking density. For comparison, we

also depicted the hydrodynamic radii of the microgel in solution, under good solvent (at 20  $^{\circ}$ C) as well as under bad solvent conditions (collapsed microgel at 50  $^{\circ}$ C). The graph demonstrates that the profile of microgels on surface and the dimensions in solution correspond for highly cross-linked spheres. However, a gradual decrease in the cross-linking density results in extended contact radius and concurrently flattens the profile to almost monomer thickness.

The diagram in Figure 6 presents the dimensions of an adsorbed microgel depending on the cross-linking state where



**Figure 6.** Contact radius, normalized to the hydrodynamic radius in the swollen state, as a function of the cross-linker concentration (full symbol). Reduced height of the microgel, normalized to the hydrodynamic radius in the collapsed state as a function of the cross-linker fraction (empty symbol). The contact radius and height results from a balance between adsorption which tends to maximize the contact area and the restoring network elasticity which tends to minimize deformation of the microgel on the solid surface. In contrast, the hydrodynamic radius of the microgel in solution results from a balance of osmotic pressure and network elasticity of the microgel.

(i) the contact radius has been normalized to the hydrodynamic radius in the highly swollen state respectively and (ii) the vertical deformation is relative to microgel diameter in the collapsed state,  $(2R_{\rm h,50} - h)/2R_{\rm h,50}$ . The latter parameter would be zero for a hard sphere and approach one for a tightly adsorbed molecule. Considering that the contact diameter is related to the radius of the highly swollen microgel  $R_{\rm h,20}$  particle as it gets adsorbed at ambient temperature below the volume phase transition, the height measured in the dried state should be correlated to the particle in the collapsed state,  $R_{\rm h,50}$ .

For the least cross-linked molecules we indeed observe, that the vertical shrinkage is approaching a value of 0.95 while the contact radius is exceeding the hydrodynamic radius of the welldissolved microgel by a factor of almost 6, demonstrating significant overstretching at low cross-linking. In contrast, the highly cross-linked microgels exhibit a behavior more typical for an elastic particle that adsorbs by its surface contact. This transition from a particle-like to a flexible-molecule-like adsorption is discontinuous, although the transitions points in height and diameter do not coincide with respect to the degree of cross-linking. This is explained by the open threedimensional structure and the diffuse boundary delimiting core and corona. It must be noted that we cannot distinguish between "spreading" by adsorption from solution and spreading after the solvent was evaporated. As adsorption is controlled by the solvent quality, we assume both processes are equivalent with regard to the final structure, with air presenting the worst solvent. Indeed, the microgels readily adsorb and spread on the substrate. Figure 6 clearly indicates the physical behavior of microgel on surface may be separated in three regimes of dissimilar cross-link density. (1) Spreading of a highly crosslinked microgels is defined by the elastic stresses that develop upon deformation. The influence of the surface tension is reduced to the microgel edge. The physical behavior of the microgel is completely dominated by the elastic properties of the network. (2) Intermediate cross-link state where spreading forces and elastic stresses conjointly defines the shape of the microgel on surface. (3) Loosely cross-link microgel flattens to form a very thin pancake. The thickness is defined by the longranged van der Waals interactions<sup>38</sup> described by the Hamaker constant A,  $h \sim (A/S)^{1/2}$ . Connectivity and a radial gradient of cross-linker density limit the lateral extension whereby the central part of the adsorbed microgel is slightly thicker. In this regime, the microgel is highly stretched; the physical behavior is dominated by the elastic properties of the individual chains.

In particular, a loosely cross-linked microgel sustains large deformation due to swelling, and adsorption further amplifies the strain and eventually may induce uncontrolled CC-bonds scission leading to partial fragmentation of the microgel. Indeed, Figure 7 shows that adsorption induces scission of polymer strand essentially observed at the periphery of the microgel. Evidently, is not as severe as in the bottle brushes in which the spreading of the side chain focuses the bond tension on the backbone leading to degradation.<sup>20</sup> Because of the radial distribution of the cross-link density, the outer shell undergoes large strain compared to the more cross-linked core. Therefore, most of the bond/strand tension, which breaks the polymer



Figure 7. SFM Height images of microgel with fragmented polymer strand at their periphery.

strands, is on the loose ends in the periphery which can adsorb tightly while they are tethered to the elastic core.<sup>39</sup>

**Computer Simulations of the Interfacial Activity of Microgels.** In order to explain the difference in the rates of variation of the surface tension coefficient (Figure 3), we have to examine two issues of the process: (i) mobility of the microgels and their volume in the solution (water) and (ii) spreading dynamics and equilibrium shape of the particles at the interface.

*i. Mobility and Volume of the Microgels in Solution.* Figure 8 shows that mobility of the microgels depends on its cross-



Figure 8. Pathway length D of the dense (red) and loose (black) microgels in a good solvent as a function of time steps t.

linking density. The slope of the pathway length D(t)corresponds to the average velocity v of the microgel in the good solvent. The denser microgel is more mobile,  $v_{\text{dense}}/v_{\text{loose}}$  $\approx$  1.2, which can be explained by a model of impenetrable spheres: the friction coefficient obeys to the Stokes' law and proportional to the radius of the microgel. The characteristic sizes of the swollen microgels measured in units of the box cell are  $R_{\text{dense}} = 6.68$  and  $R_{\text{loose}} = 8.87$ . Hence, regarding the volume fraction of microgels of equal weights but differing in the crosslinking density, the probability to reach the surface for the loose particles is higher because they have more than 2-fold excess in volume,  $(R_{\text{loose}}/R_{\text{dense}})^3 \approx 2.34$ . This effect can counterbalance the 20% reduction in the mobility. Faster saturation of the interface by the loosely cross-linked particles may partially explain the faster decay of the surface tension coefficient in the case of the loosely cross-linked particles.

*ii.* Spreading Dynamics and Equilibrium Shape of the Microgels at the Interface. The spreading dynamics of dense and loose microgels is presented in Figure 9. The lateral extension of the microgel  $R_{xy}$  is calculated versus time steps, i.e., the tangent to each point, represents the instantaneous spreading rates. The loose microgel spreads faster in each stage of the process because of the lower elastic moduli. The spreading rate slows when approaching the equilibrium state (plateau value of  $R_{xy}$ ). Therefore, the spreading dynamics of the



Figure 9. Average lateral diameter  $R_{xy}$  of the adsorbed dense and loose microgel particle as a function of time steps and snapshots of the equilibrium structures.

loose microgel is an extra contribution to the faster decay of the surface tension coefficient.

Finally, we have to compare the equilibrium shapes of the loose and dense microgels at the interfaces (Figure 9). One can see that the loose microgel has more flat shape with characteristic diameter  $R_{xy}^{\text{loose}} \approx 15.7$  and height  $R_z^{\text{loose}} \approx 2.3$  in comparison with the denser microgel  $R_{xy}^{\text{dense}} \approx 11.1$  and  $R_z^{\text{dense}} \approx 2.9$ . Therefore, one needs a smaller number of the loose microgels in order to cover the water/air interface, and its saturation occurs earlier with the loose particles. This fact is also in favor of the faster decrease of the surface tension coefficient in the case of loosely cross-linked microgels.

#### 5. CONCLUDING REMARKS

This work addresses the question to which extent soft particles with an open structure depict a molecular-like behavior characterized by structural concepts such as conformational transitions related to the flexibility of the constituent chain segments, their solubilization, and their little restricted ability to orient themselves to the outside. In this aspect the poly(Nvinylcaprolactam-co-N-isopropylactylamide) microgels studied here are a relatively simple example, where the segment flexibility and chain mobility are coupled to the elastic deformation of the network. As the degree of cross-linking can be varied at constant molecular weight, particles of different flexibility can be compared directly. Detailed analysis of the microgels deformation at a solid surface enabled discrimination of particle like microgels in which case spreading was controlled by the elasticity and molecule-like adsorption characterized by a significant overstretching. In a coarse approximation one may consider the observed conformational changes of slightly crosslinked microgels as a folding process, which involves all segments of the microgel and which might thus be considered a molecular transition. More complex examples that undergo strong molecular transitions are proteins whose segment flexibility is coupled to specific interactions of the segments.

We could show that a high molecular flexibility of microgels has remarkable consequences at the example of an unexpectedly improved surface activity for microgels with lower cross-linking as well as by the transformation from a spherical shape to a flat adlayer upon adsorption and the concomitant occurrence of high stresses that can even break the bonds. The time needed for swollen microgels to adsorb at the air/water interface can be 3 orders of magnitude shorter than that for dispersed particles and decreases with decreasing crosslinking density. Dissipative particle dynamics simulations at liquid/air interfaces of the microgel as an ideal network confirms the experimental data.

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#### Notes

The authors declare no competing financial interest.

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