

Temperature-Controlled Transitions Between Glass, Liquid, and Gel States in Dense p-NIPA Suspensions

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Microgels are particles made by chemically cross-linking a polymer to form particles of a gel that are colloidal in size.^[1,2] Like their macroscopic counterparts, microgels can be swollen by a solvent, the degree of swelling depending on solvent quality and cross-link density.^[3,4] As the solvent quality is governed by external stimuli such as temperature, a remarkably versatile control over the degree of swelling can be achieved in these systems. This makes microgels very attractive, for instance, for drug delivery^[5,6] and sensing applications.^[7]

A particularly interesting polymer for microgels is poly-*N*-isopropylacrylamide (p-NIPA), since it has a lower critical solution temperature (LCST) of $T \approx 33$ °C, a temperature that is easily accessible in experiments and relevant for many applications.^[8,9] Below the LCST, p-NIPA microgels are swollen and interact repulsively. They can be packed well above the random close packing fraction for hard spheres, $\Phi_{\text{TCP}} \approx 0.64$, through compression and deformation of the particles. Such concentrated suspensions display viscoelastic properties that are reminiscent of those of pastes^[10,11] and colloidal glasses of hard spheres,^[12] with a frequency-independent elastic shear modulus which depends on the degree of compression.^[13,14] Raising the temperature above the LCST significantly affects the behavior of p-NIPA particles, which dramatically shrink in size, changing their volume by more than an order of magnitude. This effect can be directly observed in the viscoelastic response of microgel suspensions, which liquefy as a result of the size change and the associated change in particle volume fraction.^[10,13] However, in some cases this de-swelling is accompanied by a second effect, which surprisingly leads to an increasingly solidlike behavior as the temperature is increased.

Because the solvent quality decreases above the LCST, polymer chains tend to stick together, leading to an attractive interaction not just within a microgel, but also between microgel particles. As a result, aggregation or even gelation can occur.^[4,15] Interestingly, because the interparticle potential changes from repulsive to attractive around the LCST, we expect it to vanish at some temperature, and a liquidlike state should be achieved for packings even above Φ_{TCP} , with transitions to solidlike states occurring both upon increasing and decreasing the temperature. While both glassy and gel states have been studied separately, the occurrence of colloidal liquid, glass, and gel phases have not been observed within the same sample, and hence it has been difficult to directly study the connection between the glass and gel phases.

In this article we demonstrate that concentrated p-NIPA suspensions in a low-temperature glassy state can liquefy and then solidify again as the temperature is raised across the LCST. Our system exhibits all the typical responses of disordered colloidal suspensions, but the behavior is controlled by temperature. Below the LCST it shows the behavior typical of a colloidal glass, near the LCST it behaves like a liquid, while above the LCST it exhibits the properties typical of a colloidal gel. Moreover, we show that the elasticity of these suspensions exhibits critical-like behavior as a function of temperature both above and below the LCST, with a critical temperature that corresponds to the LCST. Our results thereby suggest interesting analogies between the glass and gel phases of these thermosensitive microgel particles.

We use temperature- and pH-responsive particles made of p-NIPA copolymerized with about 5% acrylic acid and cross-linked with 0.5% *N,N'*-methylenebisacrylamide. To measure the LCST of the particles, we perform differential scanning calorimetry (DSC) and find an endothermic peak ranging from 29 to 31 °C while heating a suspension at pH \approx 3. The LCST of the particles thus lies within this range, which is slightly shifted downwards with respect to the LCST of pure p-NIPA.

Below this temperature, the particles are highly swollen and can therefore be packed up to very high concentrations, conveniently described by a generalized volume fraction, $\zeta = n \cdot V$.^[16] Here, n is the particle number concentration and V the volume of the particle measured under dilute suspensions conditions ($n \rightarrow 0$). For ζ close to or above 1, a particle does not reach its swelling equilibrium because of the steric compression due to the other particles; in this case, ζ is a measure of the compression of the particles relative to their equilibrium size.

To determine the temperature dependence of the particle volume, $V(T)$, we use dynamic light scattering (DLS); meanwhile to determine the temperature dependence of the particle

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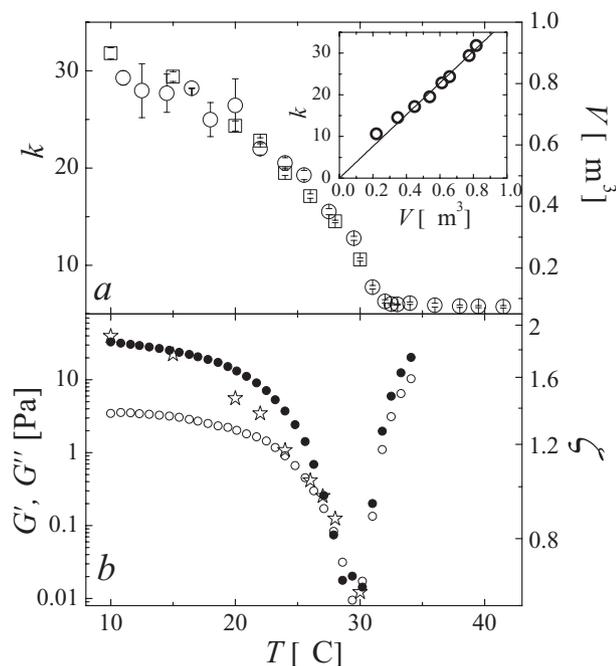


Figure 1. a) Temperature dependence of the intrinsic volume fraction $k = \zeta/\omega_t$ (squares) and particle volume V (circles). The inset shows the linear relationship between k and V . The slope of the linear fit represents the inverse of the average mass of polymer per particle, m_p . b) Temperature dependence of the linear viscoelastic moduli G' (solid circles) and G'' (open circles), and particle volume fraction ζ as obtained by viscosity measurements (stars).

volume fraction, $\zeta(T)$, we measure the viscosity using an Ubbelohde tube. Since the solution density is essentially equal to that of water, $1 \text{ g}\cdot\text{cm}^{-3}$, the intrinsic volume fraction, $k = \zeta/\omega_t$, becomes $k = V/m_p$, where ω_t is the polymer weight fraction, and m_p is the average polymer mass per particle. As a result, $k(T)$ and $V(T)$ must have the same temperature dependence enabling us to cross-check the size and viscosity measurements. Indeed, we find that $k(T)$ and $V(T)$ display the same temperature dependence, as shown in **Figure 1a**, and are linearly interrelated, as shown in the inset of **Figure 1a**, also consistent with our expectations. The inverse of the slope of the linear fit equals $m_p \approx 2.5 \times 10^{-14} \text{ g}$, which allows us to determine the radius of a completely collapsed particle, $R \approx (3m_p/4\pi)^{1/3} = 180 \text{ nm}$. Since the smallest radius we measure by DLS is $R = 260 \text{ nm}$ at $41.5 \text{ }^\circ\text{C}$, our result suggests that even in the de-swollen state, p-NIPA particles contain a high amount of water, consistent with previous observations.^[2]

To follow the temperature dependence of the linear viscoelastic moduli of a dense microgel suspension, we fix both frequency and strain applied to the sample, and slowly vary T . A typical response is shown in **Figure 1b** for a sample at a polymer weight fraction $\omega_t = 0.062 \pm 0.005$ and a frequency $\omega = 1 \text{ rad}\cdot\text{s}^{-1}$. The variation of ζ is reported in the same figure, as it also changes with T . For $T < 26 \text{ }^\circ\text{C}$, the elastic modulus dominates over the viscous modulus. As the temperature increases from 10 to $26 \text{ }^\circ\text{C}$, both moduli decrease and their difference gets progressively smaller. This solidlike behavior and the absence of any visible Bragg peaks in these samples suggest that the suspen-

sion behaves like a glass. As temperature increases above $26 \text{ }^\circ\text{C}$, G' and G'' become comparable, and finally, G'' becomes larger than G' at $T \approx 28 \text{ }^\circ\text{C}$, which indicates a liquidlike behavior. Interestingly, here the particle volume fraction still corresponds to a ζ above random close packing. However, as the temperature is increased further, a sudden increase of the moduli is observed. It is well known that the interaction between p-NIPA microgels changes from repulsive to attractive at temperatures around the LCST. We thus identify the LCST of our microgel particles as the temperature at which both G' and G'' reach a minimum, $T \approx 29 \text{ }^\circ\text{C}$. For $T > 29 \text{ }^\circ\text{C}$, we attribute the steep increase of the viscoelastic moduli to the increase of attractive interactions and the resultant formation of a volume-spanning colloidal gel. This is consistent with previous observations reporting the formation of clusters at low particle concentrations.^[15]

To characterize the relaxation dynamics in the glassy, liquid, and gel phases, we analyze the frequency dependence of the viscoelastic moduli. At low temperatures, G' shows a frequency-independent plateau and G'' shows a marked minimum at a frequency ω_m , as shown in **Figure 2a** for three different temperatures. These features are a hallmark of glasslike systems. For $\omega > \omega_m$, $G''(\omega)$ increases with frequency as $G'' \sim \omega^{0.5}$, consistent with results for spherical particles stabilized by grafted polymer layers,^[12,17] and with theoretical analysis of the high frequency response of concentrated suspensions of Brownian spheres interacting through a continuous repulsive potential.^[18] The increase of G'' with decreasing ω for $\omega < \omega_m$ is indicative of the presence of a structural relaxation at even lower frequencies, a feature that typifies glassy materials.^[19,20] Physically, this behavior is due to the additional energy dissipation produced by a particle when escaping from the cage formed by the neighboring particles. Qualitatively the measured frequency dependencies of $G'(T, \omega)$ and $G''(T, \omega)$ for concentrated, swollen microgels, resemble those of glassy hard sphere suspensions and concentrated emulsions.^[21,22] However the origin of the elastic response is different. In hard sphere systems, the elasticity is entropic in nature; it results from changes in the equilibrium pair-correlation function due to the applied deformation. In emulsion and microgel suspensions such an entropic contribution is expected up to $\zeta_g \approx 0.58$. Above this point, emulsion droplets start deforming and the elasticity increases with particle concentration as $G' \sim \zeta - \zeta_c$, with $\zeta_c \approx 0.64$; this results from the energy associated to the additional surface area per drop, which is opposed by the Laplace pressure, and from the random microstructure of the system.^[22]

In contrast to emulsions, swollen microgels do not have surface tension. However, since far from the LCST of the microgel the bulk modulus of a particle is higher than its shear modulus,^[3] we expect the particles to deform without significantly changing their volume for $0.64 \leq \zeta \leq 1$. At $\zeta \approx 1$, however, the particles start de-swelling as a consequence of their finite osmotic compressibility which allows packing at $\zeta \gg 1$, as shown in **Figure 1b**. In this region the suspension elasticity increases as a consequence of the increased bulk modulus of the individual particles, as they are forced to shrink in volume with increasing concentration;^[23] this emphasizes the importance of the particle's elastic modulus which plays no relevant role for suspensions of incompressible particles, such as rigid spheres or drops.^[16]

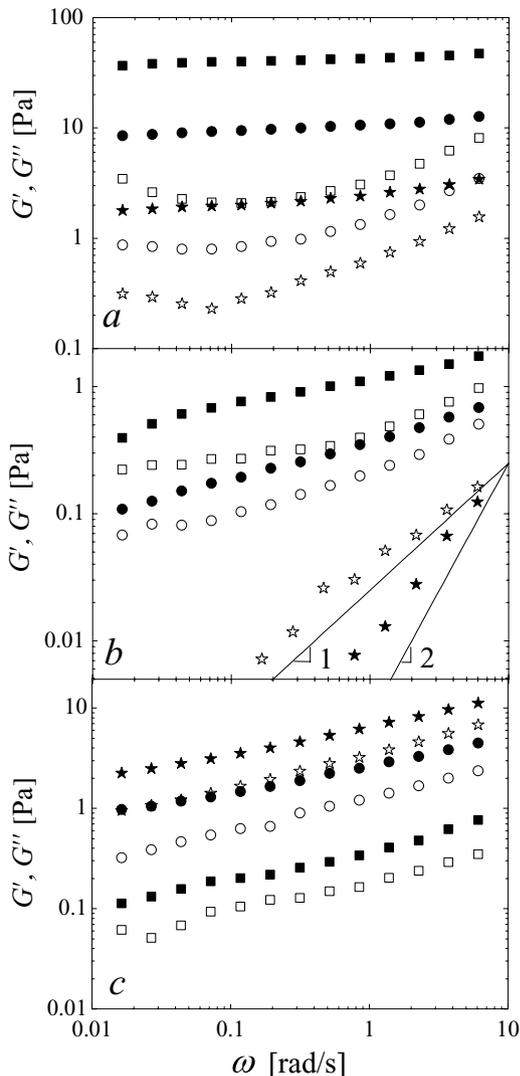


Figure 2. Frequency dependence of the elastic G' (solid symbols) and viscous G'' (open symbols) moduli as a function of temperature: a) glassy regime at 10 (squares), 20 (circles), and 24 (stars) °C; b) liquidlike regime at 26 (squares), 27 (circles), and 28 (stars) °C; c) the solid lines show the expected low-frequency behavior of a viscoelastic liquid; d) gel-like regime at 31 (squares), 33 (circles), and 35 (stars) °C. Measurements are taken after an aging time of 150 min.

For temperatures above 25 °C, the suspension dynamics changes. Both G' and G'' exhibit a clear frequency dependence, as shown in Figure 2b for 26 and 27 °C. Remarkably, at 28 °C the frequency dependencies of both moduli approach the terminal behavior of a viscoelastic liquid, $G' \sim \omega^2$ and $G'' \sim \omega^1$, reflecting the liquidlike nature of the sample.

Above the LCST, however, the frequency dependence of the viscoelastic moduli again exhibits a qualitative change. We find that both G' and G'' are characterized by a power law of the type $G \sim \omega^{0.3}$ in the whole frequency range investigated, as shown in Figure 2c for three different temperatures. At these high temperatures, the interparticle attraction is related to the Flory parameter, which increases with temperature.^[3] The observed increment of the moduli is a direct consequence of

this increase in the attraction strength with temperature.^[24] A power law relaxation spectrum is characteristic of transient particle networks.^[25] In particular, while gels characterized by short-range attractive potentials exhibit a G' with a well-defined plateau,^[26] gels characterized by high filler volume fractions and long-range attraction display marked relaxation dynamics.^[27] In this last case, it has been suggested that gelation results from crowding of clusters of weakly sticking particles. Since above the LCST dilute solutions of p-NIPA particles form stable aggregates with a size that depends on temperature,^[15] we speculate that the elasticity of the gel arises from crowding of stable clusters.^[28,29] In analogy with hard sphere glasses, the slow rearrangements in a glass of clusters would result in the weak frequency dependence of the viscoelastic moduli, just as we observe experimentally for our p-NIPA particle gels.

The previous analysis highlights an unexpected behavior around the LCST. In fact we have shown that a liquid phase can be reached even at concentrations ζ clearly above random close packing, suggesting that, in contrast to hard spheres, ζ is not the only variable that changes with temperature. We suggest that the repulsive interaction between particles also changes as the LCST is approached and that this repulsion softening plays a relevant role in the mechanical response of our system. To better understand this, we analyze the variation of the elastic plateau modulus, G'_p , as a function of temperature around the LCST, as shown in Figure 3a for two different polymer concentrations, $w_t = 0.062$ and $w_t = 0.112$. Close to the liquidlike state, G' does not show a plateau; in this case, we choose G'_p as the inflection point of the elastic modulus, which is the last point before the slope of the modulus starts to increase with decreasing frequency. This corresponds to G' at $\omega \approx 0.04 \text{ rad} \cdot \text{s}^{-1}$ for both $T = 26 \text{ °C}$ and $T = 27 \text{ °C}$ in Figure 2b. In the gel state, we choose G'_p as the value of G' at a frequency of $0.1 \text{ rad} \cdot \text{s}^{-1}$. Remarkably, the data can be well described by critical-like behavior, $G'_p \sim (T - T_c)^\gamma$. In general, the interparticle repulsion depends on the osmotic pressure within a microgel, which in turn depends on the Flory solvency parameter χ , which depends upon temperature, and has been shown empirically to

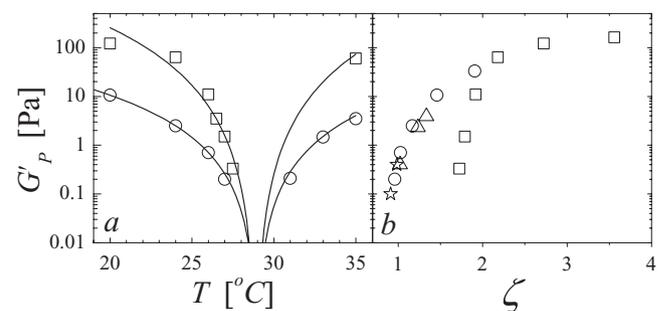


Figure 3. a) Temperature dependence of G'_p for two different polymer concentrations: $w_t = 0.062$ (circles) and $w_t = 0.112$ (squares). The lines are fits to the equation $G'_p \sim (T - T_c)^\gamma$. We find that $\gamma = 2.4$ for $w_t = 0.062$ and $\gamma = 3.3$ for $w_t = 0.112$. However, for both concentrations, $T_c \approx 29 \text{ °C}$. b) Dependence of G'_p on ζ for different polymer concentrations and temperatures. For each polymer concentration, the temperatures are reported from top to bottom: 0.112 (squares: 10, 20, 24, 26, 27, 27.5 °C); 0.062 (circles: 10, 20, 24, 26, 27 °C); 0.042 (triangles: 10, 15, 20 °C); 0.031 (stars: 15, 20 °C).

also depend upon polymer volume fraction within a particle ϕ : $\chi(T, \phi) = \chi_1(T) + \chi_2 \cdot \phi + O(\phi^2) + \dots$.^[3] Above random close packing, $\zeta > 0.63$, ϕ is fixed by ζ and does not depend on temperature which only determines the degree of compression. As a consequence, the critical temperature can slightly shift for samples at different ζ . The result shown in Figure 3a, however, suggests that this effect is negligible in our experiments where the internal volume fraction is at most $\phi_i \approx 0.15$. In fact, while the exponent γ increases with polymer content, the critical temperature, T_c , remains nearly unchanged at $T_c \approx 29$ °C for both polymer concentrations. This temperature is very close to the LCST of our p-NIPA microgels.

The possibility of describing both gel and glassy states of our microgels within a general framework provides support of the continuity of these two transitions. Glass and gel are kinetically arrested metastable states, where the fluid-to-solid transition depends on ζ and interparticle potential. Continuity between the critical-like behaviors describing the glass and gel phases, as observed here, necessarily requires passing through a liquid state which is approached as the interparticle potential vanishes. This decrease in repulsion should be caused by a change in the elastic properties of the particles as the LCST is approached. However, we recognize that in the experiments in Figure 3a the viscoelastic moduli are subjected to both the effect of decreasing the interparticle repulsion and of decreasing ζ . To explore the relative importance of these two effects we measure G'_p for different temperatures and polymer concentrations, and express the results as a function of ζ . If the behavior were dominated solely by the effect of particle concentration, then all the data should collapse onto a single curve. This would mean that at any given degree of particle compression, temperature does not affect the repulsion between particles. Our results indicate that this is not the case. We find deviations for the sample at the highest polymer concentration and for temperatures close to T_c , as shown in Figure 3b. Thus, the elastic properties of the particles and the resulting repulsive forces at $\zeta > 0.64$ must change as the temperature is increased towards the LCST. In particular, the bulk modulus of a single particle is expected to change as the LCST is approached because around the LCST the change in osmotic pressure required to change the volume of a particle is very small. Indeed, the bulk modulus of p-NIPA hydrogels and microgels drops considerably as the LCST is approached, while the shear modulus increases continuously through the LCST.^[3,30] This behavior is also consistent with the theory of Flory.^[31] This effect can be so strong that it leads to a negative Poisson ratio in these materials near the LCST, where the shear modulus is found to exceed the bulk modulus. This in fact means that it is easier for the particle to change its volume than it is to change its shape. This phenomenology could indeed indicate that the morphology and the elastic properties of packed microgel particles could qualitatively change as the LCST is approached, consistent with the lack of scaling we see in Figure 3b. A deeper understanding of the physical mechanisms that govern the behavior of these systems will require further investigation of how temperature affects the mechanical properties of a single particle; information at the single-particle level would enable a better understanding of the relative influences of packing density and repulsive interactions.

In conclusion we have shown that concentrated suspensions of temperature-sensitive microgel particles may experience

transitions between glassy, liquidlike, and gel-like behavior as the temperature is varied through the LCST. Moreover, the macroscopic mechanical response of the system does not only depend on the effective particle volume fraction. As expected, in the gel-like state the effective interparticle potential is the key parameter determining the viscoelastic response. Surprisingly, also in the transition between the glassy and liquid-like states, even by adjusting the generalized volume fraction, ζ , the elastic modulus can be orders of magnitude smaller than that expected for hard spheres. We pointed out that temperature might not just be changing the suspension volume fraction, but may effectively change the interparticle potential, which could result from a reduction in the bulk modulus of the single microgel particles.

We hope that our findings will promote more experimental and theoretical works aimed at elucidating the surprising elastic behavior at the transition as well as the microscopic origins of the fascinating elastic properties of these materials.

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Supporting Information

Supporting Information is available online at Wiley InterScience or from the authors.

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- [1] G. Chen, A. S. Hoffman, *Nature* **1995**, 373, 49.
- [2] M. J. Snowden, B. Z. Chowdhry, B. Vincent, G. E. Morris, *J. Chem. Soc. Faraday Trans.* **1996**, 92, 5013.
- [3] S. Hirotsu, *Phase Transitions* **1994**, 47, 183.
- [4] Y. Hirose, T. Amiya, Y. Hirokawa, T. Tanaka, *Macromolecules* **1987**, 20, 1342.
- [5] N. A. Peppas, R. Langer, *Science* **1994**, 263, 1715.
- [6] C. M. Nolan, C. D. Reyes, J. D. Debord, A. J. Garcia, L. A. Lyon, *Biomacromolecules* **2005**, 6, 2032.
- [7] Z. Guo, H. Sauterau, D. E. Kranbuehl, *Macromolecules* **2005**, 38, 7992.
- [8] S. Xu, J. Zhang, C. Paquet, Y. Lin, E. Kumacheva, *Adv. Mater.* **2003**, 13, 468.
- [9] J. D. Debord, S. Eustis, S. B. Debord, M. T. Lofye, A. Lyon, *Adv. Mater.* **2002**, 14, 856.
- [10] H. Senff, W. Richtering, *J. Chem. Phys.* **1999**, 111, 1705.
- [11] M. Cloitre, R. Borrega, F. Monti, L. Leibler, *Phys. Rev. Lett.* **2003**, 90, 068303.
- [12] T. G. Mason, D. A. Weitz, *Phys. Rev. Lett.* **1995**, 75, 2770.
- [13] H. Senff, W. Richtering, *Colloid. Polym. Sci.* **2000**, 278, 830.
- [14] D. A. Sessoms, I. Bishofberger, L. Cipelletti, V. Trappe, *Phys. Trans. R. Soc. A* **2009**, 367, 5013.
- [15] K. Kratz, T. Hellweg, W. Eimer, *Colloids Surf. A* **2000**, 170, 137.
- [16] J. Mattsson, H. M. Wyss, A. Fernandez-Nieves, K. Miyazaki, Z. Hu, D. R. Reichman, D. A. Weitz, *Nature* **2009**, 462, 83.
- [17] J. Van Der Werff, C. de Kruif, C. Blom, J. Mellema, *Phys. Rev. A* **1989**, 39, 795.
- [18] R. A. Lionberger, W. B. Russel, *J. Rheol.* **1994**, 38, 1885.
- [19] P. Sollich, F. Lequeux, P. Hebraud, M. E. Cates, *Phys. Rev. Lett.* **1997**, 78, 2020.

- [20] H. M. Wyss, K. Miyazaki, J. Mattsson, Z. B. Hu, D. R. Reichman, D. A. Weitz, *Phys. Rev. Lett.* **2007**, *98*, 238303.
- [21] T. G. Mason, D. A. Weitz, *Phys. Rev. Lett.* **1995**, *75*, 2051.
- [22] M.-D. Lacasse, G. S. Grest, D. Levine, T. G. Mason, D. A. Weitz, *Phys. Rev. Lett.* **1996**, *76*, 3448.
- [23] J. R. Seth, M. Cloitre, R. T. Bonnecaze, *J. Rheol.* **2006**, *50*, 353.
- [24] V. Trappe, V. Prasad, L. Cipelletti, P. N. Segrè, D. A. Weitz, *Nature* **2001**, *411*, 772.
- [25] W. Walters, D. Van Den Ende, V. Breedveld, M. H. G. Duits, A. Potanin, R. H. H. Wientjes, J. Mellema, *Phys. Rev. E* **1997**, *56*, 5726.
- [26] V. Trappe, D. A. Weitz, *Phys. Rev. Lett.* **2000**, *85*, 449.
- [27] V. Prasad, V. Trappe, A. D. Dinsmore, P. N. Segrè, L. Cipelletti, D. A. Weitz, *Faraday Discuss.* **2003**, *123*, 1.
- [28] P. N. Segrè, V. Prasad, A. B. Schofield, D. A. Weitz, *Phys. Rev. Lett.* **2001**, *86*, 6042.
- [29] S. Manley, H. M. Wyss, K. Miyazaki, J. C. Conrad, V. Trappe, L. J. Kaufman, D. R. Reichman, D. A. Weitz, *Phys. Rev. Lett.* **2005**, *95*, 238302.
- [30] S. M. Hashmi, E. R. Dufresne, *Soft Matter* **2009**, *5*, 3682.
- [31] P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY **1953**.