

Interfacial Rheology of Ultra-Low Crosslinked and Regularly Crosslinked PNIPAM Microgels

Olli-Ville Laukkanen, Maximilian M. Schmidt, Colin Weyer and Walter Richtering

Institute of Physical Chemistry, RWTH Aachen University, Germany

ABSTRACT

Polymeric microgels adsorb spontaneously to fluid interfaces, and they can therefore be used to stabilize multiphase systems such as emulsions and foams. The stability of a microgel-laden interface depends strongly on its viscoelastic properties, among other factors. In this study, we investigate the viscoelastic behavior of poly-N-isopropylacrylamide (pNIPAM) microgel monolayers at the oil-water interface. In particular, the effect of crosslink density on the interfacial shear and dilatational rheology is assessed. The interfacial shear properties are correlated with the two-dimensional phase behavior of the microgel monolayers. Moreover, the effects of temperature and surface pressure on the dilatational rheology are analyzed.

INTRODUCTION

Microgels are crosslinked polymer networks of colloidal size that are swollen by a solvent.^{1,2} Their softness and the ability to respond to external stimuli such as temperature, pH, ionic strength and light make them interesting as soft model systems for fundamental colloid research as well as for a broad range of applications.^{3,4} The softness of microgels can be tuned by varying the crosslink density; densely crosslinked microgels resemble hard colloids in their behavior, while loosely crosslinked microgels bear a closer resemblance to flexible macromolecules.⁵ Moreover, when microgels are made out of thermoresponsive polymers, the microgel stiffness can be reversibly controlled by temperature. In the case of poly-N-isopropylacrylamide (pNIPAM) microgels, a transition from a swollen to a deswollen state around 32 °C is accompanied by a distinct increase in the elastic modulus.⁶⁻⁸

Despite not being amphiphilic, microgels adsorb spontaneously to fluid interfaces due to their ability to lower the surface energy of the interface.^{9,10} Their efficiency to stabilize fluid interfaces is further enhanced by their inherent softness, as interfacial tension-induced forces cause microgels to deform laterally along the interface.¹¹ It has been shown that the mechanical stability of a microgel-laden interface depends strongly on the deformability of microgels at the interface¹² as well as on the interfacial rheological properties¹³. Furthermore, due to their stimuli-responsiveness, microgels serve as building blocks for smart emulsions that can be broken and reformed on demand by mild changes in external conditions.¹⁴⁻¹⁷

In this paper, we study the interfacial shear and dilatational rheology of pNIPAM microgel monolayers at the oil-water interface. The effects of crosslink density and internal architecture

are investigated by comparing ultra-low crosslinked (ULC) and regularly crosslinked (5 mol% BIS) microgels, and the interfacial viscoelastic properties are correlated with the two-dimensional phase behavior of the microgel monolayers.

EXPERIMENTAL

Materials

Both microgels were synthesized by free radical precipitation polymerization using potassium peroxydisulfate (KPS) as an initiator. The ULC microgels were synthesized in the absence of a chemical crosslinker, while the regularly crosslinked microgels contained 5 mol% of N,N'-methylenebis(acrylamide) (BIS). In the synthesis of both microgels, sodium dodecyl sulfate (SDS) was used to control the microgel size. The hydrodynamic radii of the ULC and 5 mol% BIS crosslinked microgels at 20 °C were 138 nm and 166 nm, respectively, as measured by dynamic light scattering (DLS). Further details of the synthesis of ULC and 5 mol% BIS crosslinked microgels are described elsewhere^{18,19}.

Characterization methods

All interfacial experiments in this study were performed for microgel monolayers confined at the n-decane/water interface. Unless otherwise stated, these measurements were performed at 20 °C.

Interfacial shear rheology measurements were performed with a custom-built setup where a modified double wall ring (DWR) geometry^{20,21} is placed inside a Langmuir trough. This setup allows interfacial shear measurements of compressed microgel monolayers at defined surface pressures.^{22,23} Amplitude sweep measurements were performed to measure the linear and nonlinear viscoelastic response of the microgel monolayers at various surface pressures. In addition, linear viscoelastic properties were measured under the continuous compression of the monolayer to obtain more detailed information about the surface pressure dependence of the interfacial shear properties.

Dilatational rheological properties of the microgel monolayers were measured by oscillating barrier²⁴ and oscillating drop²⁵ techniques. The oscillating barrier technique was employed to perform amplitude sweep measurements, thus gaining information about the linear and nonlinear dilatational behavior of the microgel monolayers at various surface pressures. The oscillating drop technique was utilized to measure the temperature and surface pressure dependences of the dilatational properties in the linear viscoelastic region.

The two-dimensional phase behavior of the microgel monolayers was studied by depositing microgels from the n-decane/water interface to a silicon wafer in a Langmuir-Blodgett trough, and by using an atomic force microscope (AFM) to measure the height profiles of the deposited microgels.

SUMMARY OF RESULTS

Five distinct regimes were identified upon compression of the 5 mol% BIS crosslinked microgel monolayer: (I) diluted state, (II) corona-to-corona contact, (III) isostructural phase transition, (IV) core-to-core contact, and (V) the failure of the monolayer.²⁶ In contrast, the ULC microgel monolayer exhibited only three different phases upon compression. This can be explained by the radially homogeneous structure of the ULC microgels, resulting in only one type of hexagonal arrangement of microgels at the interface.²⁷

To study the effect of the two-dimensional phase behavior on the interfacial shear rheology of the microgel monolayers, amplitude sweep measurements were performed at various surface pressures. In the case of 5 mol% BIS crosslinked microgels, it is observed that the interfacial storage modulus measured in the linear viscoelastic region (LVR) is significantly higher in regimes (II) and (IV) than in regime (III). The higher interfacial shear stiffness and elasticity of the microgel monolayer in regimes (II) and (IV) is caused by the 2D crystalline structure of the monolayer; in regime (II) microgels are arranged in a loosely-packed hexagonal array, and in regime (IV) they are arranged in a close-packed hexagonal array. Regime (III), on the contrary, is characterized by the co-existence of these two crystalline phases. In this region, individual microgels or clusters of microgels can move more freely along the interface, thus causing reduction in the interfacial shear stiffness and elasticity. These correlations between the interfacial shear rheology and two-dimensional phase behavior were further confirmed by the measurement of interfacial shear response under the continuous compression of the microgel monolayer. In the case of the ULC microgel monolayer, the interfacial shear moduli are generally lower than for the 5 mol% BIS crosslinked microgel monolayer. Also, as the ULC microgel monolayer does not exhibit an isostructural phase transition between two different crystalline states, there is no drop in the interfacial storage modulus associated with it.

In terms of the nonlinear shear behavior, it is observed that the 5 mol% BIS crosslinked microgel monolayer exhibits a peak in the interfacial loss modulus around 10-20 % strain amplitude. This peak is prominent especially in regimes (II) and (IV), while it almost disappears in regime (III). This leads us to believe that the peak originates from the melting of the 2D microgel crystals at the interface. Furthermore, it is notable that the LVR of the ULC microgel monolayer becomes wider with increasing surface pressure.

Similarly to the interfacial shear rheology, dilatational viscoelastic properties are observed to correlate with the two-dimensional phase behavior of the 5 mol% BIS crosslinked microgels. The dilatational storage and loss moduli are observed to be systematically higher in regime (II) than in regime (III). The oscillating barrier measurements could not be performed at higher surface pressures in regime (IV) due to the possible formation of multilayers.²⁸ Interestingly, it is observed that the microgel crosslink density has only very minor effect on the dilatational viscoelasticity of microgel monolayers at low surface pressures (in regime (II)), as the data for the 5 mol% BIS crosslinked and ULC microgels overlap almost perfectly. At higher surface pressures (in regime (III)), the ULC microgel monolayer exhibits moderately higher dilatational stiffness than the 5 mol% BIS crosslinked microgel monolayer. This observation demonstrates that the dilatational stiffness of a microgel monolayer is not directly proportional to the stiffness of individual microgels. It is also worth noting that there is a transition from dilatational strain softening to dilatational strain hardening with increasing surface pressure. This change in the nonlinear dilatational response may have important practical implications as microgel monolayers experience large deformations and deformation rates in various real-life applications.

The oscillating drop measurements confirm the observation of higher dilatational stiffness of the ULC microgel monolayer at high surface pressures. Furthermore, these measurements demonstrate that the dilatational stiffness and elasticity decrease when microgels are heated significantly above their volume phase transition temperature (VPTT) of 32 °C. This effect is particularly pronounced for ULC microgels that experience a more distinct volume phase transition. It is further observed that in the case of the ULC microgel, the dilatational storage modulus exhibits a distinct peak (maximum) around the VPTT. However, the 5 mol% BIS crosslinked microgel does not exhibit such a peak. We are currently carrying out further studies to explain the origin of this phenomenon.

CONCLUDING REMARKS

This study demonstrates that the interfacial rheology of pNIPAM microgel monolayers is strongly correlated with their two-dimensional phase behavior. From this perspective, microgel monolayers bear resemblance to monolayers of hard colloids, showing similar type of structure-property relationship²⁹. However, microgel monolayers offer an additional capability to tune the interfacial viscoelasticity by means of varying the crosslink density and temperature. This further highlights the suitability of polymeric microgels as building blocks for smart materials such as stimuli-responsive emulsions.

ACKNOWLEDGEMENTS

The authors thank the Deutsche Forschungsgemeinschaft for funding within SFB 985 ‘Functional Microgels and Microgel Systems’. In addition, O.-V.L. acknowledges the Alexander von Humboldt Foundation for financial support.

REFERENCES

- (1) Pelton, R. Temperature-Sensitive Aqueous Microgels. *Advances in Colloid and Interface Science* **2000**, *85* (1), 1–33. [https://doi.org/10.1016/S0001-8686\(99\)00023-8](https://doi.org/10.1016/S0001-8686(99)00023-8).
- (2) Saunders, B. R.; Vincent, B. Microgel Particles as Model Colloids: Theory, Properties and Applications. *Advances in Colloid and Interface Science* **1999**, *80* (1), 1–25. [https://doi.org/10.1016/S0001-8686\(98\)00071-2](https://doi.org/10.1016/S0001-8686(98)00071-2).
- (3) Plamper, F. A.; Richtering, W. Functional Microgels and Microgel Systems. *Accounts of Chemical Research* **2017**, *50* (2), 131–140. <https://doi.org/10.1021/acs.accounts.6b00544>.
- (4) Karg, M.; Pich, A.; Hellweg, T.; Hoare, T.; Lyon, L. A.; Crassous, J. J.; Suzuki, D.; Gumerov, R. A.; Schneider, S.; Potemkin, I. I.; Richtering, W. Nanogels and Microgels: From Model Colloids to Applications, Recent Developments, and Future Trends. *Langmuir* **2019**, *35* (19), 6231–6255. <https://doi.org/10.1021/acs.langmuir.8b04304>.
- (5) Mourran, A.; Wu, Y.; Gumerov, R. A.; Rudov, A. A.; Potemkin, I. I.; Pich, A.; Möller, M. When Colloidal Particles Become Polymer Coils. *Langmuir* **2016**, *32* (3), 723–730. <https://doi.org/10.1021/acs.langmuir.5b03931>.
- (6) Li, G.; Varga, I.; Kardos, A.; Dobryden, I.; Claesson, P. M. Nanoscale Mechanical Properties of Core-Shell-like Poly-NIPAm Microgel Particles: Effect of Temperature and Cross-Linking Density. *Journal of Physical Chemistry B* **2021**, *125* (34), 9860–9869. <https://doi.org/10.1021/acs.jpccb.1c04173>.
- (7) Li, G.; Varga, I.; Kardos, A.; Dobryden, I.; Claesson, P. M. Temperature-Dependent Nanomechanical Properties of Adsorbed Poly-NIPAm Microgel Particles Immersed in Water. *Langmuir* **2021**, *37* (5), 1902–1912. <https://doi.org/10.1021/acs.langmuir.0c03386>.
- (8) Hashmi, S. M.; Dufresne, E. R. Mechanical Properties of Individual Microgel Particles through the Deswelling Transition. *Soft Matter* **2009**, *5* (19), 3682–3688. <https://doi.org/10.1039/b906051k>.
- (9) Style, R. W.; Isa, L.; Dufresne, E. R. Adsorption of Soft Particles at Fluid Interfaces. *Soft Matter* **2015**, *11* (37), 7412–7419. <https://doi.org/10.1039/c5sm01743b>.

- (10) Rey, M.; Fernandez-Rodriguez, M. A.; Karg, M.; Isa, L.; Vogel, N. Poly- N-Isopropylacrylamide Nanogels and Microgels at Fluid Interfaces. *Accounts of Chemical Research* **2020**, *53* (2), 414–424. <https://doi.org/10.1021/acs.accounts.9b00528>.
- (11) Guzmán, E.; Maestro, A. Soft Colloidal Particles at Fluid Interfaces. *Polymers*. 2022, p 1133. <https://doi.org/10.3390/polym14061133>.
- (12) Destribats, M.; Lapeyre, V.; Wolfs, M.; Sellier, E.; Leal-Calderon, F.; Ravaine, V.; Schmitt, V. Soft Microgels as Pickering Emulsion Stabilisers: Role of Particle Deformability. *Soft Matter* **2011**, *7* (17), 7689–7698. <https://doi.org/10.1039/c1sm05240c>.
- (13) Brugger, B.; Vermant, J.; Richtering, W. Interfacial Layers of Stimuli-Responsive Poly-(N-Isopropylacrylamide-Co- Methacrylicacid) (PNIPAM-Co-MAA) Microgels Characterized by Interfacial Rheology and Compression Isotherms. *Physical Chemistry Chemical Physics* **2010**, *12* (43), 14573–14578. <https://doi.org/10.1039/c0cp01022g>.
- (14) Wiese, S.; Tsvetkova, Y.; Daleiden, N. J. E.; Spieß, A. C.; Richtering, W. Microgel Stabilized Emulsions: Breaking on Demand. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2016**, *495*, 193–199. <https://doi.org/10.1016/j.colsurfa.2016.02.003>.
- (15) Ngai, T.; Behrens, S. H.; Auweter, H. Novel Emulsions Stabilized by PH and Temperature Sensitive Microgels. *Chemical Communications* **2005**, No. 3, 331–333. <https://doi.org/10.1039/b412330a>.
- (16) Richtering, W. Responsive Emulsions Stabilized by Stimuli-Sensitive Microgels: Emulsions with Special Non-Pickering Properties. *Langmuir* **2012**, *28* (50), 17218–17229. <https://doi.org/10.1021/la302331s>.
- (17) Brugger, B.; Rosen, B. A.; Richtering, W. Microgels as Stimuli-Responsive Stabilizers for Emulsions. *Langmuir* **2008**, *24* (21), 12202–12208. <https://doi.org/10.1021/la8015854>.
- (18) Scotti, A.; Denton, A. R.; Brugnoli, M.; Houston, J. E.; Schweins, R.; Potemkin, I. I.; Richtering, W. Deswelling of Microgels in Crowded Suspensions Depends on Cross-Link Density and Architecture. *Macromolecules* **2019**, *52* (11), 3995–4007. <https://doi.org/10.1021/acs.macromol.9b00729>.
- (19) Scotti, A.; Houston, J. E.; Brugnoli, M.; Schmidt, M. M.; Schulte, M. F.; Bochenek, S.; Schweins, R.; Feoktystov, A.; Radulescu, A.; Richtering, W. Phase Behavior of Ultrashort Spheres Show Stable Bcc Lattices. *Physical Review E* **2020**, *102* (5), 052602. <https://doi.org/10.1103/PhysRevE.102.052602>.
- (20) Franck, A.; Hodder, P. Measuring the Rheological Properties of Ultrathin Films at the Water-Air and Water-Oil Interface by Using a Novel Double Wall Ring (DWR) Geometry. *Annual Transactions of The Nordic Rheology Society* **2009**, *17*, 57–60.
- (21) Vandebril, S.; Franck, A.; Fuller, G. G.; Moldenaers, P.; Vermant, J. A Double Wall-Ring Geometry for Interfacial Shear Rheometry. *Rheologica Acta* **2010**, *49* (2), 131–144. <https://doi.org/10.1007/s00397-009-0407-3>.
- (22) Hermans, E.; Vermant, J. Interfacial Shear Rheology of DPPC under Physiologically Relevant Conditions. *Soft Matter* **2014**, *10* (1), 175–186. <https://doi.org/10.1039/c3sm52091a>.
- (23) Schmidt, M. M.; Laukkanen, O.-V.; Bochenek, S.; Scotti, A.; Richtering, W. Correlation between Mechanical Properties and Phase Behavior of Polyelectrolyte Microgels Confined to Oil-Water Interfaces. *In preparation*.

- (24) Lucassen, J.; van den Tempel, M. Dynamic Measurements of Dilational Properties of a Liquid Interface. *Chemical Engineering Science* **1972**, *27* (6), 1283–1291. [https://doi.org/10.1016/0009-2509\(72\)80104-0](https://doi.org/10.1016/0009-2509(72)80104-0).
- (25) Ravera, F.; Loglio, G.; Kovalchuk, V. I. Interfacial Dilational Rheology by Oscillating Bubble/Drop Methods. *Current Opinion in Colloid and Interface Science*. 2010, pp 217–228. <https://doi.org/10.1016/j.cocis.2010.04.001>.
- (26) Bochenek, S.; Scotti, A.; Ogieglo, W.; Fernández-Rodríguez, M. Á.; Schulte, M. F.; Gumerov, R. A.; Bushuev, N. v.; Potemkin, I. I.; Wessling, M.; Isa, L.; Richtering, W. Effect of the 3D Swelling of Microgels on Their 2D Phase Behavior at the Liquid-Liquid Interface. *Langmuir* **2019**, *35* (51), 16780–16792. <https://doi.org/10.1021/acs.langmuir.9b02498>.
- (27) Scotti, A.; Bochenek, S.; Brugnoli, M.; Fernandez-Rodriguez, M. A.; Schulte, M. F.; Houston, J. E.; Gelissen, A. P. H.; Potemkin, I. I.; Isa, L.; Richtering, W. Exploring the Colloid-to-Polymer Transition for Ultra-Low Crosslinked Microgels from Three to Two Dimensions. *Nature Communications* **2019**, *10* (1), 1418. <https://doi.org/10.1038/s41467-019-09227-5>.
- (28) Bykov, A. G.; Liggieri, L.; Noskov, B. A.; Pandolfini, P.; Ravera, F.; Loglio, G. Surface Dilational Rheological Properties in the Nonlinear Domain. *Advances in Colloid and Interface Science*. 2015, pp 110–118. <https://doi.org/10.1016/j.cis.2014.07.006>.
- (29) Barman, S.; Christopher, G. F. Role of Capillarity and Microstructure on Interfacial Viscoelasticity of Particle Laden Interfaces. *Journal of Rheology* **2015**, *60* (1), 35–45. <https://doi.org/10.1122/1.4935128>.