

Interfacial shear and dilatational rheology of polyelectrolyte microgel monolayers at the oil-water interface

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ABSTRACT

Due to their interfacial activity, microgels can be used to stabilize multiphase systems such as emulsions and foams. The stabilization efficiency strongly depends on the viscoelastic properties of the microgel monolayer at the interface. In this study, we investigate polyelectrolyte microgels that exhibit pH-responsive behavior. The interfacial rheological properties are measured both in shear and dilatation, and these properties are correlated with the two-dimensional phase behavior of the microgels.

INTRODUCTION

Numerous industrial applications require precise control over the stability of multiphase systems such as emulsions and foams. Such systems are traditionally stabilized by surfactants or solid colloidal particles. However, for the past 15 years or so, microgels have been successfully employed for this purpose as well.¹⁻³ Microgels are three-dimensional, crosslinked polymer networks that are of colloidal size and swollen by the solvent in which they are dissolved.^{4,5} The properties of microgels can be conveniently tuned by tailoring their chemistry and architecture⁶, as well as by means of external stimuli (e.g. temperature, pH, light, or ionic strength). For example, the softness of microgels can be readily adjusted by varying their crosslink density or by switching between the swollen and collapsed state of the microgel.

Microgels adsorb spontaneously to fluid interfaces, forming a well-defined monolayer.⁷ The mechanical stability of microgel-laden interfaces and, thus, emulsion stability is determined by the softness (deformability) of the microgels, as well as by the viscoelastic properties of the microgel monolayer at the interface.^{8,9} Due to the stimuli-responsiveness of microgels, microgel-stabilized emulsions (a.k.a. Mlickering emulsions) can be broken and reformed reversibly by mild changes in external conditions.¹⁰⁻¹² This makes stimuli-responsive microgels ideal building blocks for smart emulsions.

In this study, we investigate the interfacial rheology of poly-N-isopropylacrylamide (pNIPAM)-based polyelectrolyte microgels both in shear (at constant area) and dilatation (at changing area). Furthermore, these observations are discussed in relation to the two-dimensional phase behavior of the microgels.

EXPERIMENTAL

Materials

The investigated polyelectrolyte microgels were synthesized by Geisel et al.¹³ by standard precipitation polymerization with surfactant. These microgels consisted of N-isopropylacrylamide (NIPAM), N,N'-methylenebis(acrylamide) (BIS) and methacrylic acid (MAA). BIS acts as a cross-linker, while MAA provides pH-responsiveness. The carboxyl groups within

the MAA moieties are protonated at pH 3, while they are deprotonated at pH 9. The more pronounced swelling of the microgels at pH 9 ($R_{h,pH9} = 222 \pm 2 \text{ nm} > R_{h,pH3} = 146 \pm 1 \text{ nm}$) is caused by electrostatic interactions and the osmotic pressure of the counterions. The pH-dependent behavior of these microgels at the oil-water interface has been previously investigated by Geisel et al.¹⁴ and Schmidt et al.¹⁵

Methods

All interfacial shear and dilatational rheology measurements were performed on monolayers of the polyelectrolyte microgels at the n-decane/water interface at a constant temperature of 20 °C.

For interfacial shear rheology measurements, a stress-controlled rotational rheometer (DHR-3, TA Instruments) was equipped with a modified double wall ring (DWR) geometry^{16,17}. The DWR geometry is positioned in a custom-made Langmuir trough, allowing active control of the compression state of the spread microgel monolayer during the measurement of interfacial shear properties.¹⁸ Amplitude sweep measurements ($\gamma_0^s = 0.1\text{-}100 \%$) were performed at various surface pressures that correspond to the different regimes of the surface pressure-area isotherm¹⁹. Moreover, isochronal measurements at $\omega = 1 \text{ rad/s}$ were performed during the continuous compression of the microgel monolayer to obtain a more detailed picture of the surface pressure dependence of the interfacial shear properties.

A Langmuir-Blodgett trough (KN 1004, Biolin Scientific) was used to investigate the dilatational rheological properties of spread polyelectrolyte microgel monolayers by means of oscillating barrier and step compression experiments. Oscillating barrier experiments²⁰ were performed at various surface pressures, again corresponding to the different regimes of the surface pressure-area isotherm. The area oscillation amplitude was varied in the range of 0.6 to 31.6 % to

investigate both the linear and nonlinear dilatational behavior, and the frequency dependence of the dilatational response was evaluated by performing the experiments at the oscillation frequencies of 0.02, 0.05 and 0.1 Hz. The relaxation behavior of spread microgel monolayers was further investigated by means of step compression experiments where the interfacial area was suddenly decreased by 2.5, 5, 10 or 20 % and the resulting time-dependent change in the surface pressure was monitored.

In addition, the dilatational properties of adsorbed microgel monolayers were investigated by the oscillating drop method. These experiments were performed using a drop shape analyzer (DSA100, Krüss) that was equipped with a computer-controlled oscillating drop module (DS3270, Krüss). A drop of 0.01 or 0.03 wt% aqueous microgel dispersion was immersed in n-decane and oscillated at a frequency of 0.2 Hz while microgels were spontaneously adsorbing to the n-decane/water interface. This type of experiment allows the measurement of dilatational rheological properties of an adsorbed monolayer continuously over a wide range of surface pressures.¹⁹

RESULTS

Interfacial shear rheology experiments revealed the highly elastic behavior of the polyelectrolyte microgel monolayers ($G^s \gg G^s''$) over the whole range of surface pressures both in the uncharged (pH 3) and charged (pH 9) state. Interfacial shear moduli are observed to increase systematically with increasing surface pressure – i.e. with increasing lateral compression of the microgel monolayer – until about $\pi = 20 \text{ mN/m}$. Around this surface pressure, the monolayer enters a regime that is characterized by an isostructural phase transition between a non-close-packed and close-packed arrangement of the microgels at the interface²¹. This leads to the decrease of the interfacial shear moduli until around $\pi = 30 \text{ mN/m}$ where the isostructural phase

transition is completed. After this, the interfacial shear moduli increase again as the microgels are arranged in close-packed hexagonal lattice. The observed trends are in good agreement with the results of Rey et al.²¹ obtained by interfacial microrheology.

Interfacial shear amplitude sweep measurements also revealed the widening of the linear viscoelastic region (LVR, measured as a function of the interfacial shear stress) up to $\pi \approx 20$ mN/m, followed by the narrowing of the LVR between $\pi \approx 20$ mN/m and $\pi \approx 30$ mN/m, and a second widening of the LVR above $\pi \approx 30$ mN/m. Moreover, a pronounced local maximum is observed in interfacial loss modulus curves just outside the LVR, and the maximum value of G'' is discovered to follow a similar type of surface pressure dependence as the interfacial shear moduli in the LVR.

When interfacial shear properties are measured under continuous compression of the microgel monolayer, a clear difference is observed between the uncharged and charged state of the microgel. The drop in the interfacial shear moduli in the isostructural phase transition regime is observed to be much more significant in the uncharged state (pH 3) than in the charged state (pH 9). This can be attributed to the shorter and less pronounced phase transition region of the charged microgels as compared to that of the uncharged microgels.¹⁵

Similarly to the interfacial shear experiments, the dilatational rheology experiments demonstrate the highly elastic nature of the polyelectrolyte microgel monolayers ($E^s \gg E^{s'}$) both in the uncharged (pH 3) and charged (pH 9) state. The oscillating barrier and oscillating drop experiments demonstrated increasing dilatational moduli with increasing surface pressure below $\pi \approx 15$ mN/m, a maximum around $\pi \approx 15$ mN/m, and decreasing dilatational moduli with increasing surface pressure above $\pi \approx 15$ mN/m. Somewhat surprisingly, dilatational strain hardening is

observed in the oscillating barrier experiments at small dilatational strain amplitudes (typically below $\alpha_0^s \approx 10\%$). The nonlinearity of the viscoelastic response is also evidenced by the appearance of higher harmonics in the Fourier spectrum of the surface pressure signal²².

The surface pressure relaxation data from the step compression experiments could be fitted with a double-exponential function. This indicates that the relaxation of microgel monolayers is governed by two mechanisms, one of them occurring in the time scale of tens of seconds and the other one in the time scale of hundreds of seconds. However, further studies with complementary characterization techniques are necessary to properly identify these relaxation mechanisms.

CONCLUDING REMARKS

We have shown that polyelectrolyte microgels form a highly elastic monolayer at the oil-water interface, facilitating their use in emulsion stabilization. The interfacial rheological properties of polyelectrolyte microgel monolayers can be modulated with pH as the charge state of these microgels affect their swelling and conformation at the interface. The surface pressure dependence of the interfacial rheological properties is correlated with the two-dimensional phase behavior of the microgels which is associated with the isostructural phase transition between a non-close-packed and close-packed hexagonal arrangement. With further studies, a more comprehensive understanding of the role of interfacial rheology in stimuli-responsive emulsions will be developed.

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