Rheology and phase behaviour of multi-responsive soft microgels

S. Franco [ab], B Ruzicka [bc], V. Nigro [d], E. Buratti [bc], M. Bertoldo [e], E. Zaccarelli[bc] and R. Angelini[bc],

[a] Dipartimento di Scienze di Base e Applicate per l'Ingegneria (SBAI), Sapienza Università di Roma, 00185 Roma, Italy
[b] Istituto dei Sistemi Complessi del Consiglio Nazionale delle Ricerche (ISC-CNR), UOS Sapienza, 00185 Roma, Italy
[c] Dipartimento di Fisica, Sapienza Università di Roma, 00185 Roma, Italy
[d] ENEA Centro Ricerche Frascati, Via Enrico Fermi, 45, 00044 Frascati, Italy
[e] Istituto per la Sintesi Organica e la Fotoreattività del Consiglio Nazionale delle Ricerche (ISOF-CNR), via P. Gobetti 101, 40129 Bologna, Italy

e-mail: silvia.franco@uniroma1.it

Keywords: microgel, molecules, soft matter, colloids

Soft colloids have attracted great interest in the last few years for both technological applications and theoretical implications. Indeed, they are very good model systems for understanding the general problem of dynamic arrest, since their larger tunability with respect to atomic and molecular systems leads to complex phase behaviours. Among them multi-responsive microgels, colloidal suspensions of micro- or nanometre-sized hydrogel particles, are very intriguing systems due to their high responsiveness to external stimuli such as pH, temperature, electric field, ionic strength, solvent, external stress or light pulses.

These systems play an important role in several biophysics applications and they are widely used in pharmaceutics industries, cosmetic products, artificial organs, drug delivery, sensors, biomedical application, medical diagnostic and tissue engineering [1].

One of the most studied microgel is the thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) whose thermo-responsiveness is strongly related to the temperature induced coil-to-globule transition of the NIPAM polymer. At room temperature indeed, PNIPAM microgels are in a swollen state, due to the polymer hydrophilicity that leads to dominant polymer-solvent interactions and to the retention of a great amount of water. By increasing temperature, across the volume phase transition (VPT) (T~ 305K), the polymer becomes hydrophobic, polymer-polymer interactions become stronger, water is completely expelled and particles reach a shrunken state.

In this work we study an Interpenetrating Polymer Network (IPN) microgel composed of PNIPAM and a pH-responsive polymer as poly(acrylic acid) (PAAc) [2,3]. The IPN preserves the same VPT temperature of pure PNIPAM microgel and permits to control polymer/polymer and polymer/solvent interactions through pH [4]. Here we report rheological and differential scanning calorimetry measurements on aqueous suspensions of PNIPAM-PAAc microgels as a function of temperature, weight concentration and PAAc content. The frequency dependent linear viscoelastic properties across the typical swollen-shrunken volume phase transition (Fig.1) are deeply investigated [5] and a preliminary phase diagram is reported.

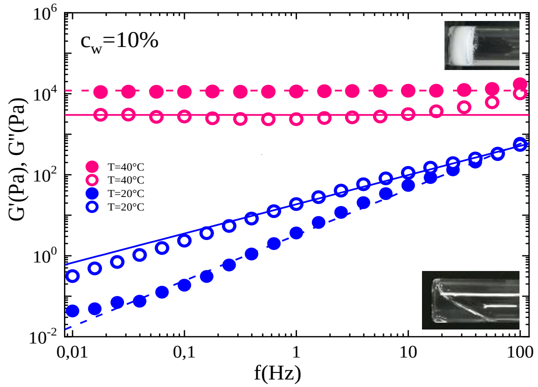

Figure 1. Storage (G') (●) and Loss (G'') (o) moduli for a PNIPAM microgel at c_w=10%, T=20°C (blue symbols) below the VPT and T=40°C (red symbols) above the VPT.

[1] R. Pelton, *Advances in Colloid and Interface Science*, **85**, 1-33 (2000).
[2] X. Xia and Z. Hu, *Langmuir*, **20**, 2094-2098 (2004).
[3] V. Nigro, R. Angelini, M. Bertoldo, F. Bruni, M.A. Ricci, and B. Ruzicka, *Soft Matter*, **13**, 5185-5193 (2017).
[4] V. Nigro, R. Angelini, B. Rosi, M. Bertoldo, E. Buratti, S. Casciardi, S. Sennato, B. Ruzicka, *Journal of Colloid and Interface Science* **545**, 210-219 (2019).
[5] S. Franco et al. *Manuscript in preparation* (2019).