

Study of colloidal suspensions of multi-responsive microgels

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Research on colloidal systems has attracted great interest in the last years, due to the variety of their technological applications and for the investigation of physical fundamental problems. Among these, suspensions of soft colloids have an even more complex and interesting behaviour with respect to hard ones. In particular, multi-responsive soft microgels, particles of typical size in the range $1 \text{ nm} \div 1 \mu\text{m}$, are characterized by the swelling behaviour, the ability to absorb and release a large amount of solvent in response to temperature variations (figure 1). The system undergoes a volume phase transition (VPT) from a swollen, hydrated phase to a shrunken, dehydrated one. This property strongly characterizes the microgel and leads to its application in many fields, such as pharmaceutical (drug delivery [1]), biomedical and bio-engineering (bioactive paper [2]). Microgel suspensions are also very important for the study of the glass transition, their softness gives rise to a variety of behaviours with respect to hard colloids [3]. In this study we focus on Interpenetrated Polymer Network (IPN) microgels of PNIPAM (thermo-responsive polymer) and PAAc (pH-responsive polymer) [4,5] two homopolymeric networks that respond independently to temperature and pH. Dynamical properties have been investigated through Dynamic Light Scattering (DLS) and the relaxation time, related to the hydrodynamic radius of the particle, has been measured. The relaxation time of PNIPAM microgels as a function of temperature shows a sharp discontinuity at the volume phase transition temperature (VPTT) since the particles expel the solvent and decrease drastically in size. IPN microgels at increasing PAAc content show a progressive reduction of the volume phase transition amplitude (figure 1). Moreover the relaxation time increases after the VPTT for increasing microgel concentration, diverging more significantly for high PAAc content (figure 2). Structural properties have been investigated through Small Angle X-Ray Scattering (SAXS) performed at the European synchrotron radiation facility ESRF. At low PAAc content and high concentrations, IPN microgels exhibit a crystal-to-liquid transition in correspondence of the VPTT (as found in pure PNIPAM microgels). At high PAAc content they show a crystal-to-liquid transition at low concentrations and a liquid-to-glass transition at high concentrations. With this study a first experimental phase diagram for IPN microgels has been drawn (figure 3).

- [1] S. V. Vinogradov, *Curr. Pharm. Des.*, 12:4703-4712, 2006.
- [2] S. Su, Md Monsur Ali, C.D.M. Filipe, Y. Li, R. Pelton, *Biomacromolecules* 9:935-9419, 2008.
- [3] J. Mattsson, H. M. Wyss, A. Fernandez-Nieves, et al., *Nature* 462:83-86, 2009.
- [4] V. Nigro, R. Angelini, M. Bertoldo, et al., *Journal of Non-Crystalline Solids* 407:361-366, 2015.
- [5] X. Xia and Z. Hu., *Langmuir*, 20:2094-2098, 2004.

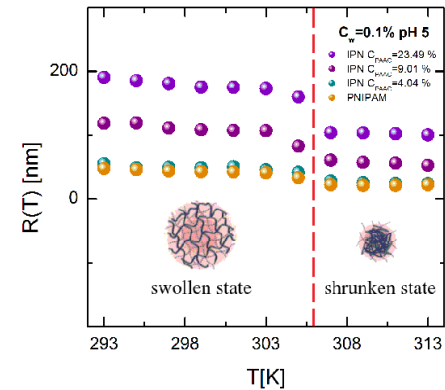


Figure 1. Hydrodynamic radius, as a function of the temperature, of PNIPAM and IPN PNIPAM/PAAc microgels.

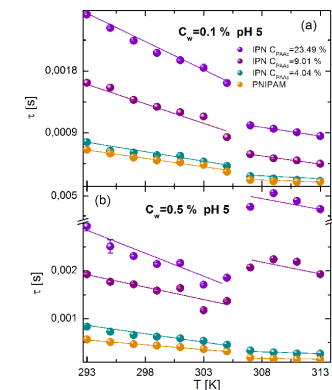


Figure 2. Relaxation time as a function of the temperature under varying PAAc content at low (a) and high (b) microgel concentration.

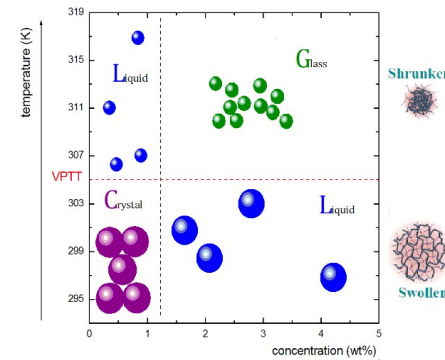


Figure 3. Phase diagram of IPN microgels at high PAAc content.