Contribution ID: **102** Type: **Poster**

Ouzo phase occurrence with sequence control copolymers: influence of the lateral amphipathic units on the size and structure of nanoparticles

Sequence regulation can be assured by the selection of monomer couples with reactivity ratios close to zero, which allows spontaneous cross-propagation copolymerization. The specific control of the polymer backbone strongly impacts the physicochemical properties of polymer materials. For instance, monomer design and customization of the solvent–monomer interactions open the way to functional copolymers showing molecular self-assembly relevant to their regular amphipathic structure. In this work, we show that the design of comonomers with adequate reactivities and interactions can be used to direct copolymer self- assembly on a mesoscopic scale. We investigate spontaneous formation of nanoparticles through solvent/non-solvent interactions using the so-called ''Ouzo effect''. In this way, an ouzo diagram was built to determine the operation window for the self-assembly, in aqueous suspensions, of alternating copolymers consisting of vinyl phenol and maleimide units carrying long alkyl-pendant groups ($C_{12}H_{25}$ or $C_{18}H_{37}$). Also, investigations were pursued to account for the influence of the lateral lipophilic pendant units on the size and structure of the nanoaggregates formed during one-shot water addition. Structure characterization by light scattering techniques (DLS and SLS), small-angle neutron scattering (SANS) and transmission electron microscopy (cryo-TEM and TEM) confirmed the self-assembly of copolymer chains into nanoparticles (size range: 60-300 nm), the size of which is affected by the lipophilicity of the alternating copolymers, solvent–water affinity and the solvent diffusion in water. Altogether, we present here the spontaneous ouzo effect as a simple method to produce stable alternating copolymer nanoparticles in water without the addition of stabilizing agents.

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Session Classification: Poster Session and Wine&cheese