

## Thermally responsive poly(acrylic acid)-*b*-poly(N,N-diethylacrylamide) particles via nitroxide-mediated living free-radical aqueous dispersion polymerization.

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Submicronic polymer particles with a thermally responsive core of poly(N,N-diethyl acrylamide) (PDEAAm) and pH responsive hair of poly(sodium acrylate) (PNaA) are prepared in situ using nitroxide-mediated controlled free-radical dispersion polymerization.

In a first step, a short poly(acrylic acid) block with an alkoxyamine reactive end-group is synthesized by direct polymerization of acrylic acid in 1,4-dioxane using the nitroxide SG1 as a mediator. In a second step, it is used as a macroinitiator for the polymerization of N,N-diethyl acrylamide in water at alkaline pH (20 wt.% monomer, 112 or 120 °C, 3 bar). N,N-Diethyl acrylamide is a water-soluble monomer and the polymer exhibits a LCST of approximately 32 °C. Consequently, at the reaction temperature the system has the characteristics of a dispersion polymerization and polymer particles form, the stability of which is ensured by the PNaA corona. Such particles are composed of assembled amphiphilic PNaA-*b*-PDEAAm diblock copolymers at  $T > LCST$ , with short PNaA block and long PDEAAm one. Typically, the initiation occurs in the aqueous solution, then the self-association process takes place in the early polymerization stage when the PDEAAm block is short and it is followed by propagation leading to chain extension in the hydrophobic core of the so-formed particles. After polymerization, at room temperature and alkaline pH, the particles dissociate to form a solution of hydrophilic diblock copolymers; when the temperature is increased above the LCST, the copolymer chains self-assemble again, but the particles exhibit a larger size than the original ones; at low  $T$  and low pH, they form "inverse" particles, whereas precipitation occurs at low pH and high  $T$ .

When N,N'-methylene bisacrylamide (MBAAm) is used as a crosslinker from the onset of the dispersion polymerization reaction, crosslinked particles form when the concentration of the difunctional monomer is low (typically 3 mol% based on the DEAAm monomer), whereas macrogelation is observed at larger concentration. To overcome this insufficient control over particle size, the introduction of the crosslinker is performed after the nucleation step. In such conditions (from 3 to 10 mol% MBAAm), macrogels are not observed anymore, but thermo-responsive hydrogel particles exhibiting a diameter close to 100 nm or below, with a crosslinked, thermally responsive core stabilized by covalently attached PNaA chains.

As a conclusion, the method presented here combines many advantages over classical self-assembly of preformed diblock copolymers. In particular, particles can be synthesized with a limited number of steps, directly in the water phase, without the need of added organic co-solvent. A crosslinking reaction can be performed simultaneously to the growth step and, thanks to the living character of the polymerization, the crosslinker addition can be triggered at any time, while preserving the possibility of covalently binding all growing chains.

### References

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