From microscopic flower-like micelles to macroscopic hydrogels: exchange dynamics of associated amphiphilic triblock copolymers with different compositions.

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Résumé

The hydrophobic blocks of amphiphilic triblock copolymers (BAB: hydrophobic B block and hydrophilic A block) spontaneously associate in aqueous solution to form flower-like micelles. Bridging between the micelles leads to aggregation and, at sufficiently high concentrations, to a network. The bonds of the hydrogel are transient if the B-blocks can exchange between micellar cores. The dynamic mechanical properties of the gel depend on the concentration and lifetime of bridges between micelles in the network. Therefore, being able to tune the exchange dynamic, or the bond lifetime, is key to control the systems properties and applications. Multiple ways of tuning the exchange dynamic are available such as the type of polymers (chemistry, composition, etc.) and the environment (T, solvent, etc.). The addition of pH-sensitive hydrophilic units inside the B-block is one useful tool to tune the dynamic, not only by tuning the hydrophobicity of the block but also by adding ionizable units. This was first illustrated by D. Bendejacq(1) who demonstrated that frozen (no dynamic) diblock copolymers with pure B-blocks became dynamic when copolymerized with acrylic acid (AA). Also, A. Shedge(2) et al tuned the AA proportion in order to control triblocks dynamic. However, none of the studies investigated the intrinsic effect of a small amount of charges, its distribution and its ionization. Here, we focus on BAB triblock copolymers consisting of two moderately hydrophobic poly (2-methoxy ethyl acrylate) (PMEA) B-blocks and a central hydrophilic poly(dimethylacrylamide) (PDMA) A-block. We studied P(MEAy-co-AAx)100-b-PDMAC400-b-P(MEAy-co-AAx)100 triblock copolymers with (x,y)=(0,100) and (5,95), with a statistical and random distribution of the AA units in the B-blocks. Close to 20◦C, triblocks formed a percolated transient network(3) above their percolation concentration. In spite of the addition of hydrophilic units, no major impact on the exchange

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[*] Intervenant

dynamic was observed with no charge on the AA units. Surprisingly, only 10% of ionization of the AA units led to an exchange rate 10 times faster. We also observed a subtle impact of the charges distribution onto the polymer chain on the network behavior. Overall, these results may help to understand the intrinsic effect of charge addition and distribution on the exchange dynamic. In addition, they point to effective methods to tune the properties of multi-sensitive transient networks.

(1) Bendejacq, D.D.; Ponsinet,V.; Joanicot, M.; Vacher, A.; Airiau, M. *Macromolecules* **2003**, 36, (19), 7289-7295 Bendejacq, D. D.; Ponsinet, V.; Joanicot, M. *Langmuir* **2005**, 21, (5), 1712-1718

(2) Shedge, A. Macromolecules **2014** *47* (7), 2439-2444

(3) Coudert, N.; Debrie, C.; Rieger, J.; Nicolai, T.; Colombani, O. Macromolecules **2022** *55* (23), 10502-10512