

Self-assembly of block copolymer micelles directed by metal-ligand interactions

Our goal is to study the formation of hierarchical structures from block copolymers bearing a terpyridine ligand at the chain end (A-*b*-B- []). The first level of organization is generated by self-assembling those copolymers in a selective solvent of the B block to form micelles decorated with the ligands. The second level of organization is obtained by addition of transition metal salts to form metal-ligand complexes. According to the experimental conditions (copolymer concentration, amount of metal ions,...) different structures can be obtained (Figure 1). If the complexes are formed within a micelle, flower like micelles will be obtained.¹ If the complexes are formed between micelles, a gel will be obtained.² DLS and rheology experiments have evidenced the validity of this approach.

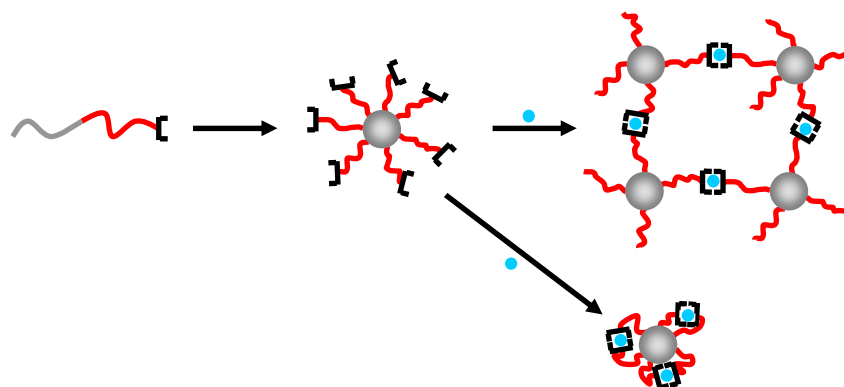


Figure 1: Hierarchical assembly of a block copolymer. Formation of flower like micelles or gels depending on the copolymer concentration.

The copolymers used in this study are based on polystyrene (PS) as the insoluble block, and on poly(terbutylacrylate) (PtBA) as the soluble block. The latter block bears a terpyridine ligand ([]) at the chain end. Two PS-*b*-PtBA- [] were synthesized by NMP polymerization using a terpyridine-functionalized initiator: PS₄₇-*b*-PtBA₅₅- [] and PS₈₀-*b*-PtBA₂₀₀- [] .

The purpose of the stay at the ESRF was to characterize by SAXS these systems. The X-ray wavelength was $\lambda = 1.55 \text{ \AA}$. SAXS patterns were collected with a two-dimensional multiwire gas-filled detector. The wavenumber scale ($q = 4\pi \sin \theta/\lambda$, where 2θ is the scattering angle) was calibrated using a sample of wet collagen (rat tail tendon).

For the dilute system, the PS₄₇-*b*-PtBA₅₅- [] copolymer was used. Micelles were prepared in ethanol (a selective solvent for the PtBA block) at 0.3% and the effect of the addition of metal ions on the characteristic features of the micelles has been studied. Three metal ions have been considered, i.e., Ni²⁺, Fe²⁺, and Zn²⁺. For a metal ion/terpyridine molar ratio was 1/2, a collapse of the coronal chains has been observed, in agreement with the intramicellar formation of *bis*-terpyridine-metal ion complexes. Indeed, the R_g decreases to a value of 10 nm as evidenced by SAXS with a gaussian curve fitting (Figure 2). This result are in good agreement with those obtained by DLS. To the CONTIN histogram, an hydrodynamic radius R_h of 8 nm was evidenced.

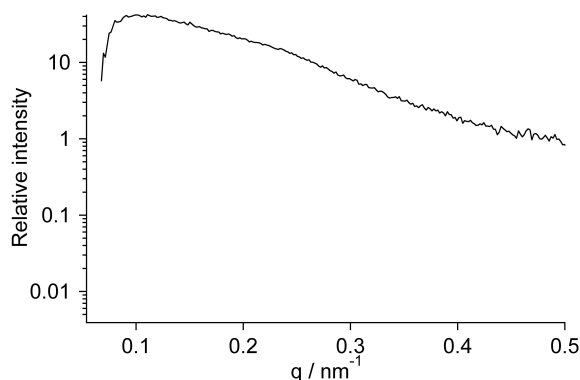


Figure 2. Small angle X-ray scattering of PS₄₇-*b*-PtBA₅₅-[copolymer with 0.5 eq. of Zn²⁺ in ethanol. Here the raw spectra were corrected from the background of the solvent by conventional method.

For the concentrated system, the PS₈₀-*b*-PtBA₂₀₀-[copolymer was used. Micelles were prepared in ethanol at 12% and the effect of the addition of metal ions (Ni²⁺, Fe²⁺, and Zn²⁺) has been studied. A gel has been obtained for the two metal ions forming strong complexes with the terpyridine (nickel and iron), and an increase of viscosity has been observed for the zinc sample, which form rather weak complexes.

The SAXS curves show for all samples a scattering peak associated to the intermicellar distance. This distance was estimated to 35 nm which is in good agreement with the 40 nm of the micellar diameter determined by DLS. For the iron and nickel samples this peak is slightly shifted toward large q values compare to the blank sample without metal ion (Figure 3). This indicates that the formation of the gel upon addition of the metal ions does not modify strongly the intermicellar distance, but induces only a slight contraction of the network. The scattering peak for the zinc sample is less visible but the behavior seems to be similar to the other meal ions.

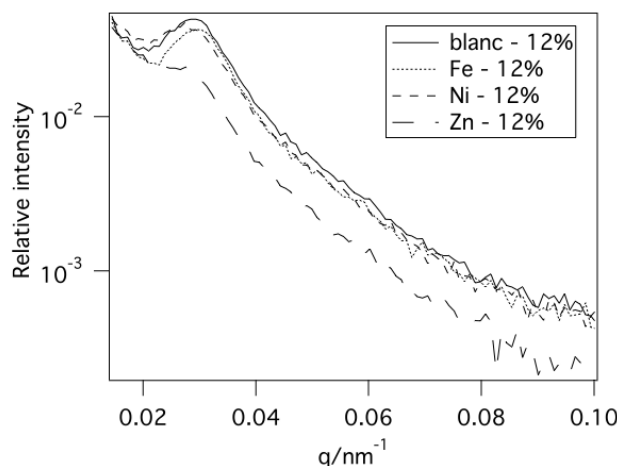


Figure 3. Small angle X-ray scattering of PS₈₀-*b*-PtBA₂₀₀-[copolymer with different metal ions in ethanol.

References

- (1) P. Guillet, C.A. Fustin, C. Mugemana, C. Ott, U.S. Schubert, J.F. Gohy, *Soft Matter* **2008**, 4, 2278-2282.
- (2) P. Guillet, C. Mugemana, F.J. Stadler, U.S. Schubert, C.A. Fustin, C. Bailly, J.F. Gohy, *Soft Matter* **2009**, 5, 3409-3411.