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SMART MICELLAR GELS FROM METALLO-SUPRAMOLECULAR COPOLYMERS

Jean-François Gohy,* Clément Mugemana, Manuela Chipper, Bhavesh Bharatiya, Pierre Guillet, Charles-André Fustin, Dietmar Auhl, Florian Stadler, Christian Bailly

Bio and Soft Matter (BSMA), Institute of Condensed Matter and Nanosciences (IMCN) Université catholique de Louvain (UCL), Place Pasteur 1, 1348 Louvain-la-Neuve, Belgium. E-mail: jean-francois.gohy@uclouvain.be

Introduction

The advent of supramolecular chemistry in the last decades of the 20th century has provided chemists with a wealth of new possibilities to synthesize molecular structures and materials that are held together by relatively weak, non-covalent interactions, such as hydrogen bonding, coordinative interactions, electrostatic and van der Waals interactions.¹ The creation of even more complex supramolecular architectures has recently become possible by applying the concept of hierarchical self-assembly, i.e., the non-covalent organization of molecules and macromolecules which takes places over distinct multiple levels, in which the assembly processes gradually decrease in strength. The hierarchical structure of supramolecular assemblies leads to a parallel hierarchy of dynamic processes. Following these principles, the goal of this work is to gain unprecedented control over the structure, self-organization and molecular dynamics of soft-matter systems by exploiting a combination of classical macromolecular architectures and specific supramolecular interactions. This will enable the building of macromolecular assemblies with adaptive structure and stimuli-responsive properties. Our original strategy is to tune the self-assembly of block copolymers via metal-ligand interactions. Firstly, block copolymers bearing a ligand at the chain end will be synthesized. Secondly, systems presenting a hierarchy in both dynamics and structure will be obtained by relying on the interplay between the self-assembling ability of copolymers into micelles and the formation of metal-ligand complexes. Thirdly, the dynamic properties of these structures will be analyzed in solution by rheology.

Experimental

Materials. Terpyridine functionalized]-PtBA-*b*-PS diblocks were synthesized by nitroxide mediated radical polymerization (NMP) according to a procedure already described.² Terpyridine functionalized Pluronics were obtained by grafting 4'-chloro-terpyridine to the hydroxyl end-groups of Pluronics according to a procedure already described.³

Micelle preparation. The]-PtBA-*b*-PS copolymers were dissolved directly in ethanol at a concentration 12 g/L. The terpyridine functionalized Pluronics were dissolved in water or water/ethanol mixtures at various concentrations ranging from 2 to 12 g/L. Those solutions were allowed to stand during several days before any measurements. Half an equimolar of the appropriate metal chloride salt (Zn^{II}, Ni^{II}, Fe^{II}) was then added, and the solution was stirred for 24 hours.

Instrumentation. Rheological characterizations were performed on]-PtBA-*b*-PS micellar gels with a TA Instruments AR-G2 using a 20 mm/1° cone and plate geometry, or an ARES with a 25 mm/0.02 rad cone and plate. The measurements were carried out at RT (≈ 20 °C) in an ethanol-saturated atmosphere to minimize evaporation of the solvent.

Results and Discussion

Systems based on terpyridine-functionalized polystyrene-*block*-poly(*tert*-butylacrylate) copolymers. We have synthesized diblock copolymer micelles bearing terpyridine ligands at the periphery of the corona. The addition of metal ions to a solution of these micelles induces the formation of intermicellar *bis*-terpyridine-metal complexes, leading to the assembly of the micelles into a network. This strategy can be viewed as the hierarchical self-assembly of the block copolymer, the first level being the formation of micelles based on solvophobic forces, and the second level the formation of the network via metal-ligand interactions.

The first step is thus the synthesis of the building blocks that will be the basis of the hierarchical assemblies. The selected compounds are block copolymers based on polystyrene, PS, and poly(*tert*-butylacrylate), PtBA,

end-capped by a terpyridine ligand (]-) on the PtBA side. Several of those copolymers were synthesized by nitroxide mediated radical polymerization (NMP) using a functional initiator bearing the terpyridine ligand.⁴ The copolymers will be noted as PS_x-*b*-PtBA_y-] where the subscripts refer to the average degree of polymerization of each block.

The first level of self-assembly is the preparation of micelles by direct dissolution of this copolymer in ethanol, a selective solvent for the PtBA block. Those micelles are thus composed of a PS core and a PtBA corona decorated with terpyridines at the periphery. Well defined, monodisperse, spherical micelles were obtained as revealed by dynamic and static light scattering experiments.⁵ Three metal ions were selected to trigger the second level of assembly: Zn²⁺, Fe²⁺, and Ni²⁺ (as their chloride salts). Micellar solutions of the PS₈₀-*b*-PtBA₂₀₀-] copolymer at a concentration of 12% w/v were prepared, and half an equivalent of the different metal ions, with respect to the terpyridine, were then added under stirring. For the Fe²⁺ and Ni²⁺ samples, a hard gel withstanding the tube inversion test is rapidly formed in about one minute. For the Zn²⁺ sample, a significant increase of the viscosity is observed but no gelling. This first interesting observation is to be related to the strength of the formed complexes. Zinc forms relatively weak complexes with terpyridines, while iron and nickel form much stronger complexes. The next step was to test different copolymer concentrations to determine the limits of the system. Iron and nickel are able to induce the formation of a gel at copolymer concentrations as low as 9% w/v, while zinc is still unable to form gels at 20% w/v. An important point that should be stressed, is that the micellar solution formed by the PS₈₀-*b*-PtBA₂₀₀-] copolymer with no added metal salt does not form a gel even at a concentration of 25% w/v.

To gain more insight into the properties of the networks obtained with the different metal ions, rheological characterizations have been performed. **Figure 1** shows the storage, G', and loss, G'', moduli measured for the investigated samples. Depending on the metal ion used, the values change distinctly. For the metal-free sample (blank) a simple Newtonian behavior is found. The sample containing Zn²⁺ ions has a higher viscosity (factor 30) than the blank, and shows a very weak but measurable elasticity, evidencing thus an essentially Newtonian behavior. In sharp contrast, the samples containing Ni²⁺ and Fe²⁺ ions are characterized by much higher moduli and are dominated by elasticity since their storage moduli G' are significantly larger than the loss moduli G''. Furthermore, G'(ω) and G''(ω) are approximately constant over a wide range of frequencies, which is typical of a rubbery network, in agreement with the presence of cross-links between the micelles due to the formation of the metal complexes. As the elastic moduli are very low, these materials are best described as ultrasoft elastic gels. These first results show that the mechanical properties of the obtained hierarchical supramolecular material can be easily tuned simply by changing the metal ions used for the formation of the intermicellar complexes.

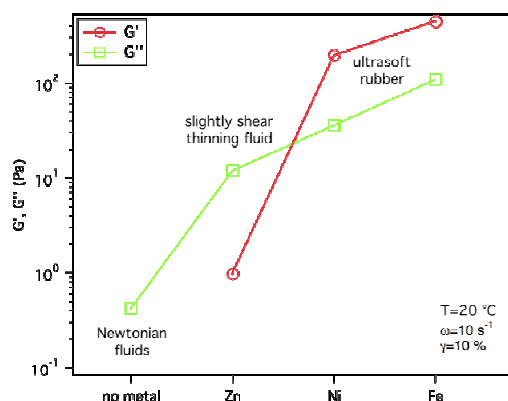


Figure 1. Storage modulus G' and loss modulus G'' at ω=10 s⁻¹ and at a deformation of 10% for micellar solutions at a concentration of 12% w/v containing 0.5 equivalent of different metal salts compared to the terpyridine ligands together with the reference sample containing no metal salt.

The observed behavior shows some characteristics of entangled and cross-linked materials, but also striking differences. The sample remains in

linear viscoelastic regime up to $\gamma_0 \approx 40\%$, meaning that the structure is unaffected. At deformations just below $\gamma_0 = 100\%$, a small peak appears for G' that can be attributed to a stretching of the chains connecting the micelles. This behavior has been rarely described. Further linear-viscoelastic characterization using creep tests indicate very long relaxation times that can just be accessed by creep tests. In **Figure 2**, an example of such data are shown for a $\text{PS}_{140}\text{-}b\text{-PtBA}_{200}\text{-[}$ converted into dynamic moduli and fitted by multi-mode Maxwell model in order to determine the longest relaxation time from the cross-over of the moduli. Apart from the difference in the modulus the sample with Ni^{2+} and Zn^{2+} ions also differ significantly in the longest relaxation time.

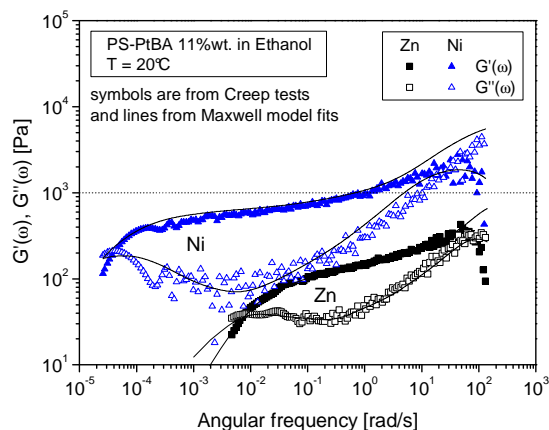


Figure 2. Storage and loss modulus G' , G'' as a function of angular frequency ω from creep tests for a micellar solution of $\text{PS}_{140}\text{-}b\text{-PtBA}_{200}\text{-[}$ at a concentration of 11% w/v containing 0.5 equivalent of different metal salts compared to the terpyridine ligands.

The next step was to evidence the stimuli responsive character of the obtained materials. The iron and nickel based gels were exposed to an excess of KCN and hydroxyethyl ethylenediaminetriacetic acid trisodic salt, HEDTA (strong competing ligands). KCN was able to break the micellar network from both nickel and iron, while HEDTA was only able to break the iron network. In addition to chemical stimuli, we have tested the possibility to reversibly break the micellar network by mechanical forces. To this aim, a pulse program has been applied (**Figure 3**).⁶

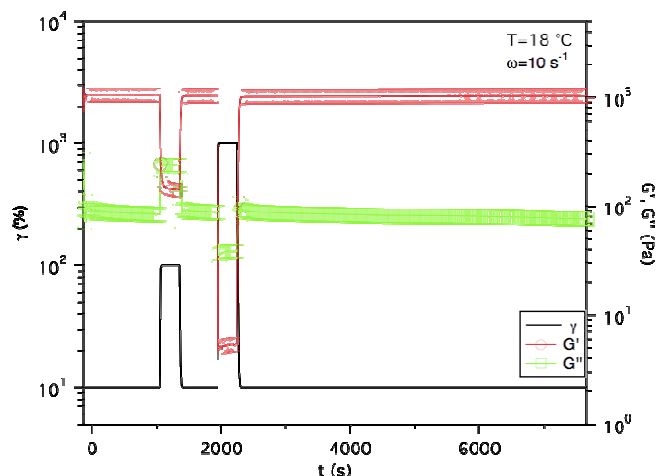


Figure 3. Evolution of G' and G'' with time following two successive pulses of high deformation (full lines), recorded on a gel based on the Fe^{2+} ions at a copolymer concentration of 14%.

At a deformation γ_0 of 100%, G' is reduced by about a factor 10, while G'' increases by factor 2.5, leading to a critical gel-like response (G' and G'' are similar). After switching back to a small deformation, the moduli go back to their original values after about 10 s, which is very close to an instantaneous recovery. At a deformation of 1000%, G'' is significantly larger than G' , indicating that the material shows liquid-like characteristics. However, the metal-ligand complexes are not totally destroyed since under these drastic conditions the viscosity is still decades higher than the blank sample. Once again, the moduli go back almost instantaneously to their original values after switching back to small deformation (10%). This highly interesting behavior demonstrates the fully recoverable nature of the network thanks to the supramolecular nature of the bonds responsible for the cohesion of the network.

Systems based on terpyridine-functionalized poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) copolymers. The commercial availability and the interesting temperature-responsive properties of Pluronics[®] prompted us to combine the concept of metallo-supramolecular block copolymer micelles based on *bis*-terpyridine metal complexes to the telechelic Pluronics[®] chemistry. As Pluronics[®] block copolymers are terminated by hydroxyl groups, they can directly be linked to supramolecular chelating ligands, such as terpyridines.

Bis-terpyridine Pluronic[®] and metallo-*bis*-terpyridine Pluronics[®] have been thus synthesized starting from commercially available P105 and P123 hydroxy telechelic Pluronics[®]. The grafting of terpyridine ligands at the extremity the Pluronic[®] chains results in the further association of the Pluronic[®] micelles in water due to hydrophobic interactions among terpyridine groups.³ Increasing temperature on those aqueous micellar solutions has two opposite effects. On one hand it decreases the solubility of the Pluronics[®] and on the other hand it increases the solubility of the terpyridine groups. Addition of ethanol increases the solubility of both Pluronic chains and terpyridine groups. Finally the addition of one half equivalent of Ni^{2+} ions compared to terpyridine groups induces formation of *bis*-terpyridine Ni^{2+} complexes and disrupts the initial hydrophobic terpyridine aggregates. In that case, formation of flower-like micelles in which the terpyridine Ni^{2+} complexes are looping the coronal chains is observed in the dilute regime. In more concentrated micellar solutions, the addition of Ni^{2+} ions results in the formation of a gel, similarly to the $\text{PS-}b\text{-PtBA-[}$ system.

Conclusions

We have demonstrated that the addition of metal ions to micelles formed by $\text{[PtBA-}b\text{-PS}$ copolymers in ethanol, and consisting of a PS core and PtBA coronal chains with terpyridine ligands at their extremity, allows the formation of stimuli-responsive gels by promoting inter-micellar connections through metal-ligand complexation. The same approach has been also used for terpyridine-modified Pluronics. We believe that this new approach significantly broaden the scope of utilization of metal-ligands complexes in self-assembled micellar systems.

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