

Supporting Information

Connecting Micelles by Metallo-Supramolecular Interactions: Toward Stimuli Responsive Hierarchical Materials

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Materials and instrumentation

The chemicals used for this work were either purchased from Aldrich, Fluka, or Acros. All monomers were freshly purified on an AlO_x -filtration column prior to use in order to remove the inhibitor. $^1\text{H-NMR}$ were recorded on a Bruker spectrometer using frequency of 500 MHz at 25°C. Chemical shifts are given in ppm downfield from TMS. Gel permeation chromatography (GPC) was carried out a system composed of two PSS Gram columns, 100 Å and 1000 Å, connected to a Waters 410 differential refractometer and a Waters UV detector with DMF as the eluent. Different poly(styrene) were used as standards. The initiator has been synthesized according to well-known procedures.^[1]

Synthesis of the terpyridine-functionalized poly(*t*-butylacrylate) (PtBA)

A solution of the initiator, 2,2,5-trimethyl-3-(1-(4'-(4''-terpyridinyloxy)methyl)phenoxy)-4-phenyl-3-azahexane, in 3.6 g of purified *tert*-butylacrylate (2.34×10^{-2} mol) was prepared. For a degree of polymerization (DP) of 400 (at 100 % conversion), the corresponding amount of initiator was 38 mg (6.47×10^{-5} mol) and 7.0×10^{-4} g (6.47×10^{-6} mmol) for the free nitroxide (5 % with respect to the initial initiator amount). Ten freeze-pump-thaw-cycles were applied to remove oxygen before immersing the reaction vessels in an oil bath at 125 °C. The polymerization was carried out during 22 hours to reach a conversion of 50 %. Polydispersity indices were determined by size exclusion chromatography, whereas $^1\text{H-NMR}$ was used for the determination of the degree of polymerization by careful integration of the polymer backbone to the terpyridine end group signals.

After analysis, poly(*tert*-butylacrylate) was precipitated twice from THF into methanol/water (50/50). Analytical data are for PtBA₂₀₀: ¹H-NMR (CDCl₃): δ= 8.66 (m, 2H; H_{6,6''}), 8.58 (m, 2H; H_{3,3''}), 8.08 (m, 2H; H_{3',5'}), 7.83 (m, 2H; H_{4,4''}), 7.57-7.18 (m, 22H; *H*_{aromatics}, H_{5,5''}), 5.35 (m, 2H; tpyOCH₂), 2.45-0.53 (m, 2400H; *H*_{PtBA backbone aliphatics}).

GPC : M_n (PDI): 26,300 g.mol⁻¹ (1.12).

Terpyridine-functionalized PtBA-*b*-PS

A terpyridine functionalized poly(*tert*-butylacrylate) macro-initiator (350 mg, DP=200, 1.37×10⁻⁵ mol), anisole (1.2 mL) and styrene (180 mg, 1.73 mmol) were transferred into a Schlenk tube. After ten freeze-pump-thaw-cycles the vessel was transferred in an oil bath at 125 °C. The polymerization was carried out during 19 hours. Polydispersity indices were determined by size exclusion chromatography, whereas ¹H-NMR was used for the determination of the degree of polymerization by careful integration of the polymer backbone to the terpyridine end group signals. After analysis, poly(*tert*-butylacrylate)-*b*-polystyrene was precipitated twice from THF into methanol/water (50/50).

Analytical data are for PtBA₂₀₀-*b*-PS₈₀ : ¹H-NMR (CDCl₃): δ= 8.69 (m, 2H; H_{6,6''}), 8.62 (m, 2H; H_{3,3''}), 8.20 (m, 2H; H_{3',5'}), 7.93 (m, 2H; H_{4,4''}), 7.57-6.32 (m, 400H; *H*_{PS backbone aromatics}, *H*_{aromatics}, H_{5,5''}), 5.35 (m, 2H; tpyOCH₂), 2.45-0.53 (m, 2640H; *H*_{PS backbone aliphatics}, *H*_{PtBA backbone aliphatics}).

GPC : M_n (PDI): 28,500 g.mol⁻¹ (1.11).

Micelle preparation

The copolymers were dissolved directly in ethanol at a concentration slightly above 120 g/L. The solution was left to stir during several days before any measurements. Half an equimolar (relative to the amount of terpyridine groups) of the appropriate metal chloride salt (NiCl₂.6H₂O, FeCl₂.4H₂O, ZnCl₂) dissolved in ethanol was then added to the copolymer solution under vigorous stirring, to yield a final copolymer concentration of 120 g/L. Prior to use, the metal chloride salts (except the iron salt) were dried in a vacuum oven at 110°C for 48 hours. Ascorbic acid (5% wt) was added to the solution of FeCl₂.4H₂O to prevent the oxidation of Fe²⁺ ions.

Dynamic and static light scattering measurements. (DLS and SLS)

DLS and SLS experiments were performed on a Malvern CGS-3 apparatus equipped with a He-Ne laser with a wavelength of 633 nm. The measurements were done at 25 °C at several angles and at different concentration. The method of the cumulants was used to analyze DLS results, while size distribution histograms were obtained by the CONTIN method (*cf.* Figure S1 as a typical example). The polydispersity index (PDI) of the micelles was estimated from the Γ_2/Γ_1^2 ratio in which Γ_1 and Γ_2 represent the first and second cumulant, respectively. A hydrodynamic radius R_h of 20 nm was found by extrapolating the data at scattering vector $q = 0$ and concentration $C = 0$. In addition to DLS, static light scattering experiments (SLS) were performed in ethanol with concentration ranging from 1 to 10 g/L. The analysis of the scattering intensities using a Zimm plot (Figure S2) yields the weight averaged molar mass, $M_{w,app}$, and the z -averaged radius of gyration, R_g (Table S1). SLS yields a $R_g = 15$ nm. Comparing this value to the R_h previously determined ($R_h = 20$ nm), a ratio $R_g/R_h = 0.75$ (the so-called ρ -parameter) is found, which is close to the values expected for a uniform sphere (0.774). An estimation of the aggregation number of the micelle, N_{agg} , is obtained by dividing the apparent molecular weight of the micelle by the molecular weight of the corresponding diblock copolymer.

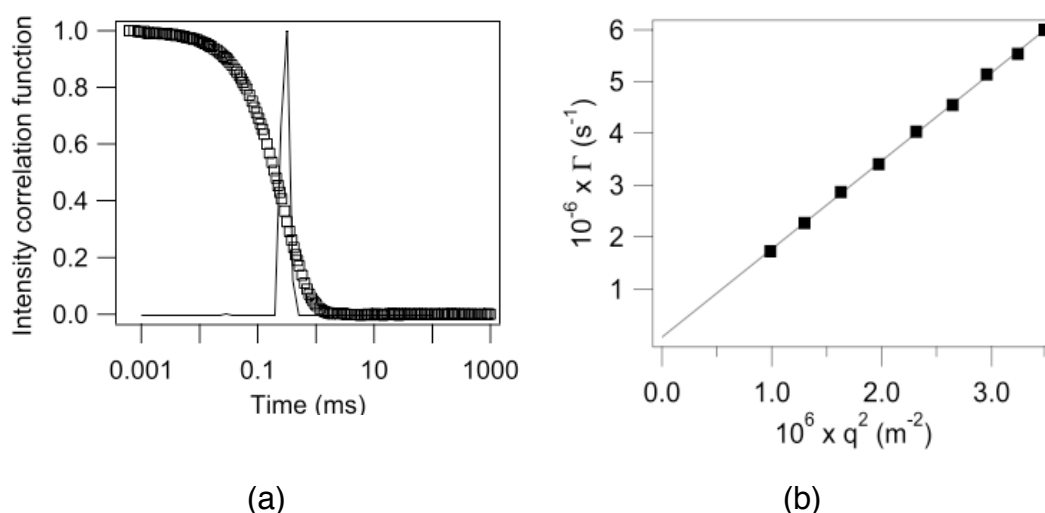


Figure S1: Intensity autocorrelation function and CONTIN analysis of PS-*b*-PtBA- micelles in ethanol at 90°(a), and dependence of the first cumulant frequency (Γ) with the square magnitude of the scattering vector (q^2) at 4 g/L (b).

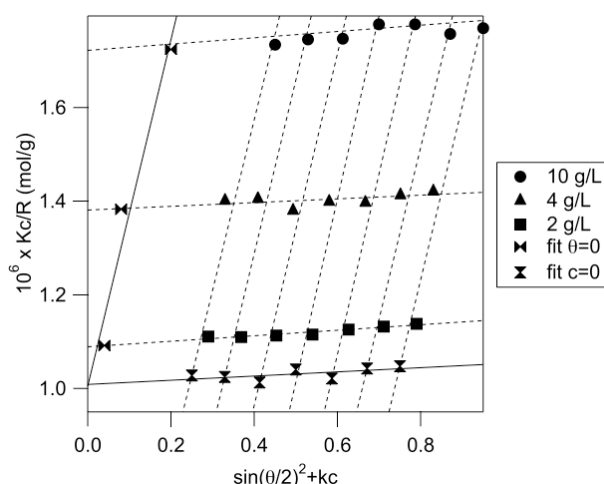


Figure S2: Zimm plot of PS₈₀-*b*-PtBA₂₀₀-[micelles in ethanol at 25 °C.

Table S1. Characteristic parameters of the micelles formed from the PS₈₀-*b*-PtBA₂₀₀-[copolymer in ethanol as deduced from dynamic and static light scattering experiments.

R_h (nm)	R_g (nm)	R_g/R_h	$M_{w,app}$ (g/mol)	N_{agg}
20	15	0.75	950,000	28

Rheological experiments

The rheological characterization was performed 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 (\approx 20 °C) in an ethanol saturated atmosphere to minimize evaporation of the solvent.

Figure S3 shows the evolution of the two moduli G' and G'' over a wide range of frequencies. In sharp contrast with the sample loaded with Zn^{2+} ions (Newtonian behavior), the two other samples (Ni^{2+} and Fe^{2+} ions) exhibit constant values of the two moduli over the range of investigated frequencies. This behavior 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.

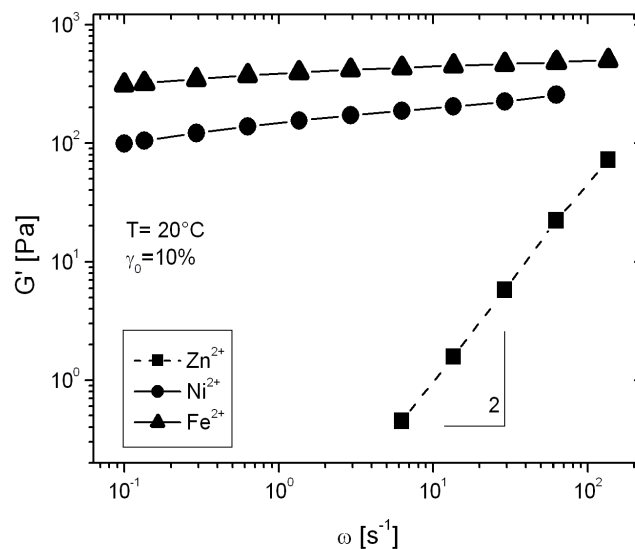


Figure S3. Storage modulus G' as a function of angular frequency ω at a deformation of 10% for a micellar solution at a concentration of 12% w/v containing 0.5 equivalent of different metal salts compared to the terpyridine ligands.

Chemical induced breaking of the gels

20 μ L of an ethanol solution of KCN salt (6 eq., 1.42×10^{-6} mol) were added to a Fe-based and Ni-based gels (12 % wt., 150 μ L). Stirring was allowed during several minutes before observing the breaking of the gel and the return to a viscous solution.

References

- [1] B. G. G. Lohmeijer, U. S. Schubert, *J. Polym. Sci. A: Polym. Chem.* **2004**, *42*, 4016-4027.