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Metallo-supramolecular hydrogels based on copolymers bearing terpyridine side-chain ligands

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A well-defined amphiphilic poly(triethyleneglycol methylether methacrylate)-*block*-polystyrene (PTEGMA-*b*-PS) block copolymer with terpyridine groups randomly distributed within the water-soluble block has been sequentially synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. Its self-assembly into micellar structures was analyzed in dilute aqueous solution by dynamic light scattering measurements (DLS). Metallo-supramolecular hydrogels were obtained after the addition of Ni(II) ions to either the precursor PTEGMA homopolymer solution or the PTEGMA-*b*-PS micellar solution. The PTEGMA-*b*-PS micelles formed gels at a much lower concentration than the corresponding PTEGMA homopolymer, thus evidencing the influence of the hydrophobic PS block on the critical gelation concentration. The mechanical properties of both hydrogels were finally investigated by rotational rheometry.

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Introduction

Supramolecular chemistry has attracted great interest within the scientific community over the last few decades.[1] The ability to form complex architectures through several self-assembly or self-recognition processes of (macro)molecules represents a versatile approach for the synthesis of materials with *e.g.* self-healing properties.[2] Supramolecular interactions have been recognized as an alternative molecular connection to "classical" covalent bonds. Various supramolecular connections like hydrogen bonds,[3] van-der-Waals forces,[4] hydrophobic interactions,[5] π–π-stackings,[6] electrostatic bondings[7] or metal–ligand coordinations[8] have been investigated thoroughly. The architectures made from supramolecular interactions are usually weaker than those originating from covalent ones. Consequently, supramolecular materials often show stimuli-responsive and self-healing properties.

Supramolecular interactions within polymeric amphiphiles have been extensively investigated recently.[9–12] In this context, the metal–ligand coordination of terpyridine with various metal ions has been used to tune the properties of self-assembled materials. Especially, micellar gels could be obtained through a self-assembly process when transition metal salts are added to a micellar solution of amphiphilic block copolymers featuring terpyridine extremities.[9,10] The self-assembly process leading to micellar gels was first demonstrated by Guillet *et al.*[10] In a first level of self-assembly, the block copolymer was dissolved in a block selective solvent (ethanol) which solubilized only one block. The obtained polymeric micelles were constituted of an insoluble core and a soluble corona containing terpyridine functionalities at the chain ends and differed in shape and size depending on the micelle preparation method, the corresponding block lengths and the solvophilic–solvophobic balance. In a second level of self-assembly, the added transition metal salts induced supramolecular interactions by forming metal–ligand bis-complexes with the terpyridine moieties. Depending on the concentration of the micellar solution, either flower-like micelles or micellar gels could be obtained.[10,12] So far, terpyridine groups within amphiphilic block copolymers have only been used as supramolecular linkers located at the coronal chain end.[9,12]

In the present study, we report on micellar hydrogels made from an amphiphilic block copolymer synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. The copolymer consists of a soluble poly(triethyleneglycol methylether methacrylate) (PTEGMA) block having terpyridine repeating units randomly incorporated as side chain ligands and a polystyrene (PS) block that forms the core of the polymeric micelles. Above a given concentration, hydrogels are formed from both PTEGMA homopolymer and block copolymer solutions in water when Ni(II) ions are added. The rheological properties of the obtained metallo-supramolecular hydrogels are then investigated by rotational rheometry.

Experimental section

Materials

All chemicals were purchased from Aldrich or Acros. Solvents of analytical grade were used unless otherwise stated.

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Triethyleneglycol methylether methacrylate (TEGMA) and styrene were both passed through a short column filled with activated basic aluminum oxide (Brockmann I) before use. Dichloromethane (DCM) and 1,4-dioxane were distilled over calcium hydride. Dimethylsulfoxide (DMSO) was stirred for 24 h at room temperature with calcium hydride and then distilled under vacuum. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from diethyl ether. $NiCl_2 \cdot 6H_2O$ was kept in a glove box and weighed out under an argon atmosphere. Thin layer chromatography (TLC) measurements were made on TLC aluminum oxide 60 F_{254} neutral plates from Merck. Column chromatography was performed using neutral aluminum oxide (Brockmann I, 50–200 μm).

Instrumentation

All ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 500 MHz Avance spectrometer in deuterated solvents containing trimethylsilane (TMS) as an internal standard. Chemical shifts (δ) are given in ppm relative to TMS. Gel permeation chromatography (GPC) was performed in dimethylformamide (DMF) containing 2.5 mM NH_4PF_6 to determine the molecular weights and the molecular weight distributions M_w/M_n of polymer samples with respect to polystyrene standards (PSS). The measurements were carried out on a system composed of two PSS Gram columns (100 Å and 1000 Å) connected to a Waters 410 differential refractometer (35 °C, 0.5 mL min^{-1}). UV/Vis spectra were recorded on a UV/Vis Varian Cary 50 equipped with a thermostat. The measurements were performed in a 1 cm sample quartz cell. Dynamic light scattering (DLS) experiments were performed on a Malvern CGS-3 apparatus equipped with a He–Ne laser with a wavelength of 632.8 nm and a thermostat. The measurements were performed at 20 °C at different angles (45°, 90°, and 135°) and at 1 g L^{-1}. The method of the cumulants was used to analyse DLS results, while the size distribution histograms were obtained by the CONTIN method. The rheological characterizations were performed on a Kinexus Ultra (Malvern Instruments) equipped with a heat exchanger and modified with a solvent trap. The measurements were carried out using a 20 mm plate–plate geometry, in a water saturated atmosphere to minimize evaporation of the solvent. The gap was adjusted between 50 and 150 μm to ensure that the geometry is completely filled.

Synthesis of 4′-(3-hydroxypropoxy)-2,2′:6′,2″-terpyridine

804 mg (0.0106 mol, 5 equiv.) of 1,3-propanediol and 4.7 mL of dry DMSO (distilled *in vacuo* over calcium hydride) were placed in a flask equipped with a magnetic stirrer under an argon atmosphere. 593 mg (0.0106 mol, 5 equiv.) of dry potassium hydroxide (pellets 85%) were added and the mixture was stirred for 10 min at 60 °C. Then, 566 mg (0.00211 mol, 1 equiv.) of 4′-chloro-2,2′:6′,2″-terpyridine were added. The reaction was continued for 2 days at 60 °C under an argon atmosphere. The mixture was cooled down to ambient temperature and poured onto an ice-water mixture, where the product started to precipitate. The pH was then adjusted to 6 using dilute hydrochloric acid. The precipitated product was filtered through a glass frit and washed with cold water. After drying in a vacuum oven at 35 °C overnight, 536 mg (0.00174 mol – 83% yield) of 4′-(3-hydroxypropoxy)-2,2′:6′,2″-terpyridine were obtained as a white powder.

^{1}H-NMR (500 MHz, CDCl3): δ/ppm: 8.61 (d, 2H, $^3J_{H,H} = 5.7$ Hz), 8.54 (d, 2H, $^3J_{H,H} = 8.1$ Hz), 7.95 (s, 2H), 7.78 (t, 2H, $^3J_{H,H} = 8.1$ Hz), 7.26 (t, 2H, $^3J_{H,H} = 6$ Hz), 4.33 (t, 2H, $^3J_{H,H} = 6$ Hz), 3.88 (t, 2H, $^3J_{H,H} = 6$ Hz), 2.05 (quin, 2H, $^3J_{H,H} = 6$ Hz).

Synthesis of 2-methylacrylic acid-3-(2,2′:6′,2″-terpyridine-4′-yloxy)propyl ester

518 mg (0.00169 mol, 1 equiv.) of 4′-(3-hydroxypropoxy)-2,2′:6′,2″-terpyridine were dissolved with 0.41 mL (0.00295 mol, 1.7 equiv.) of triethylamine in 15 mL of dry DCM. 0.28 mL (0.00289 mol, 1.7 equiv.) of methacryloyl chloride was added dropwise under stirring at 0 °C (ice bath). After 2 h, the cooling bath was removed and stirring of the reaction mixture was continued overnight. The solution was diluted with 15 mL of DCM, transferred to a separation funnel and then washed twice with a sodium carbonate (5% w/v) solution and once with pure water. The organic layer was isolated and dried over sodium sulfate. The solvent was removed *in vacuo* at 30 °C. The residue was purified through column chromatography using neutral aluminum oxide and hexane : ethyl acetate (3 : 1 v/v) as eluent ($R_f = 0.51$). After evaporation of the solvent, 400 mg (0.00107 mol – 63% yield) of pure 2-methylacrylic acid-3-(2,2′:6′,2″-terpyridine-4′-yloxy)propyl ester were obtained as white fluffy needles.

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm: 8.61 (d, 2H, $^3J_{H,H} = 4.5$ Hz), 8.54 (d, 2H, $^3J_{H,H} = 8.1$ Hz), 7.95 (s, 2H), 7.77 (t, 2H, $^3J_{H,H} = 8.1$ Hz), 7.25 (t, 2H, $^3J_{H,H} = 6$ Hz), 6.05 (s, 1H), 5.49 (s, 1H), 4.31 (t, 2H, $^3J_{H,H} = 6$ Hz), 4.27 (t, 2H, $^3J_{H,H} = 6$ Hz), 2.17 (quin, 2H, $^3J_{H,H} = 6$ Hz), 1.88 (s, 3H).

^{13}C-NMR (500 MHz, $CDCl_3$): δ/ppm: 167.3, 167.0, 156.9, 155.9, 148.9, 137.0, 136.2, 125.7, 123.9, 121.5, 107.5, 64.7, 61.3, 28.5, 18.4.

Synthesis of PTEGMA

0.4 mg (2.44×10^{-6} mol, 0.128 equiv.) of AIBN, 5.3 mg (1.90×10^{-5} mol, 1 equiv.) of 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid, 78.4 mg (2.09×10^{-4} mol, 11 equiv.) of 2-methylacrylic acid-3-(2,2′:6′,2″-terpyridine-4′-yloxy)propyl ester and 1724.6 mg (7.43×10^{-3} mol, 391 equiv.) of TEGMA were placed in a Schlenk-tube equipped with a magnetic stirrer. 5 mL of dry 1,4-dioxane were added as a solvent. Four freeze–pump–thaw cycles were then applied to degas the solution. The reaction tube was filled with argon, sealed and placed in a preheated oil bath at 80 °C. The polymerization was stopped (by placing the Schlenk tube in liquid nitrogen) after 18 h at a monomer conversion of approx. 59% as calculated from NMR integration. The copolymer was isolated by precipitation (4 times) into hexane. The highly viscous copolymer was carefully decanted (or centrifuged) after each precipitation step and finally dried in a vacuum oven at 35 °C overnight. 940 mg of PTEGMA copolymer was obtained.

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm: 8.61 (br d, 4H), 7.99 (br s, 2H), 7.83 (br s, 2H), 7.31 (br s, 2H), 4.30 (br s, 2H), 4.02 (br s, 73H), 3.58 (br s, 294H), 3.49 (br s, 77H), 3.32 (br s, 110H), 2.14 (br s, 2H), 1.80 (br d, 78H), 1.25 (br d, 17H), 0.89 (br d, 110H).

M_n (GPC) = 63 000 g mol^{-1}, M_w/M_n (GPC) = 1.24; M_n (UV/Vis) = 54 000 g mol^{-1}; M_n (NMR) = 56 000 g mol^{-1}.

Synthesis of PTEGMA-*b*-PS

0.07 mg (4.27×10^{-7} mol, 0.118 equiv.) of AIBN, 202 mg (M_n = 56 000 g mol^{-1}, 3.607×10^{-6} mol, 1 equiv.) of PTEGMA and 105 mg (1.008×10^{-3}, 280 equiv.) of styrene were placed in a Schlenk-tube equipped with a magnetic stirrer. 1.5 mL of dry 1,4-dioxane was added as a solvent. Four freeze–pump–thaw cycles were then applied to remove all of the oxygen within the solution. The reaction tube was filled with argon, sealed and placed in a preheated oil bath at 80 °C. The polymerization was stopped (by placing the Schlenk tube in liquid nitrogen) after 24 h. The block copolymer was isolated by precipitation into hexane. The waxy block copolymer was carefully decanted (or centrifuged) and finally dried in a vacuum oven at 35 °C overnight. 130 mg of PTEGMA-*b*-PS block copolymer were obtained.

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm: 8.69 (br d, 4H), 8.06 (br s, 2H), 7.90 (br s, 2H), 7.40 (br s, 2H), 7.20–6.20 (br m, 25H), 4.37 (br s, 2H), 4.07 (br s, 95H), 3.64 (br s, 382H), 3.54 (br s, 99H), 3.38 (br s, 143H), 1.84 (br d, 96H), 1.40 (br s, 22H), 0.95 (br d, 142H).

M_n (GPC) = 74 000 g mol^{-1}, M_w/M_n (GPC) = 1.30; M_n (UV/Vis) = 61 000 g mol^{-1}; M_n (NMR) = 59 000 g mol^{-1}.

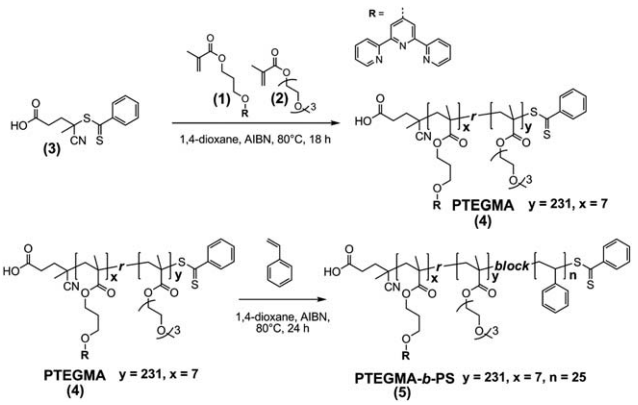
General preparation of the gels

Different concentrated solutions of PTEGMA-*b*-PS or PTEGMA were prepared according to the following method. A given amount of PTEGMA-*b*-PS or PTEGMA was weighed out into different small reaction vessels and a defined amount of MilliQ water was added. The sealed reaction vessels were placed in a fridge overnight and shaken slightly from time to time to form homogeneous concentrated solutions. The gels were then readily obtained upon addition of half an equivalent of $NiCl_2 \cdot 6H_2O$ (with respect to the terpyridine content) dissolved in a defined amount of MilliQ water to each of the concentrated solutions. The reaction vessels were then placed in an ultrasonic bath and sonicated for 1 min to ensure a homogeneous gelation process. Afterwards, the vessels were placed again overnight in the fridge for the stabilization of the gels.

Results and discussion

Synthesis of PTEGMA

PTEGMA polymers are known to be biocompatible and to feature thermo-responsive properties.[13] For the preparation of PTEGMA, RAFT (co)polymerization of the terpyridine monomer 2-methylacrylic acid-3-(2,2′:6′,2″-terpyridine-4′-yloxy)propyl ester (**1**) with commercially available triethyleneglycol methylether methacrylate (TEGMA) (**2**) was carried out under an argon atmosphere at 80 °C using azobisisobutyronitrile (AIBN) as an initiator (Scheme 1). Since the chemical nature of both monomers is comparable, a random incorporation of the terpyridine ligand is reasonably assumed.



Scheme 1 Synthesis of the PTEGMA-*b*-PS block copolymer with terpyridine pendant groups randomly distributed within the PTEGMA block.

As a chain transfer agent (CTA), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (**3**) was used. For the polymerization, a molar ratio between the AIBN initiator and the chain transfer agent of 1 : 8 was used. The polymerization of the PTEGMA random copolymer (**4**) was quenched after 18 h at a monomer conversion of 59% as calculated from NMR. The characterization of the first block was performed by NMR, UV/Vis and GPC measurements. In the ^{1}H-NMR spectrum of PTEGMA in deuterated chloroform, all signals originating from the ethylene oxide side chains at 4.02 ppm, 3.58 ppm and 3.49 ppm, as well as from the terpyridine groups between 8.61 ppm and 7.31 ppm, could be assigned (see Fig. 1).

Comparison of the integrations of the two aromatic protons of the terpyridine at 7.31 ppm with the two characteristic protons (at 4.02 ppm) of TEGMA proved an average amount of 3% of terpyridine randomly incorporated. Given the starting ratio between the terpyridine monomer and triethyleneglycol methylether methacrylate, this average amount was in good agreement with a random copolymerization process. An average

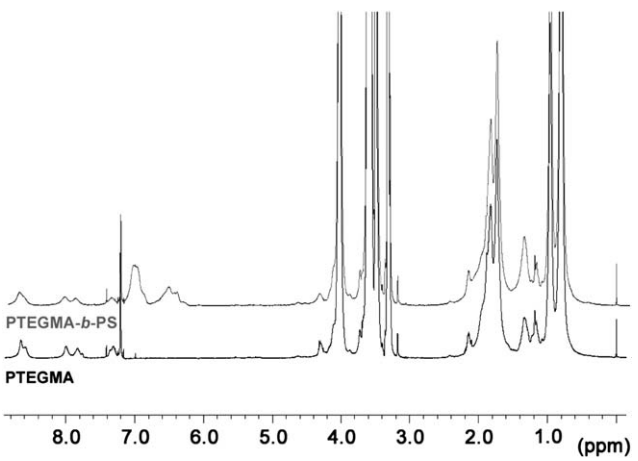


Fig. 1 ^{1}H-NMR spectra of PTEGMA (black line) and PTEGMA-*b*-PS (gray line) measured in deuterated chloroform.

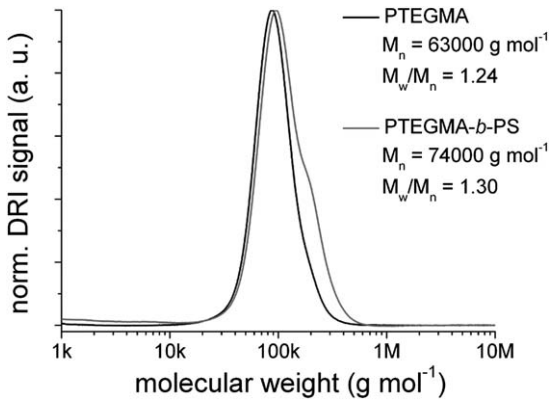


Fig. 2 GPC curves of PTEGMA (black line) and PTEGMA-*b*-PS (gray line).

degree of polymerization (DP_n) of 238 was calculated from the initial monomer-to-CTA ratio as well as from the monomer conversion determined by NMR. This corresponds to a molecular weight of M_n (NMR) = 56 000 g mol^{-1} for the PTEGMA considering an average amount of 3% of incorporated terpyridine-containing monomer. The molecular weight by GPC was measured to be M_n (GPC) = 63 000 g mol^{-1}, which was much higher than the calculated molecular weight from conversion (M_n (NMR) = 56 000 g mol^{-1}). In fact, this divergence can be explained by the use of polystyrene standards, which could have a very different hydrodynamic volume than PTEGMA chains. A rather narrow molar mass distribution was however obtained (M_w/M_n of 1.24). The GPC curve of the PTEGMA block is presented in Fig. 2.

The molecular weight of the PTEGMA block was alternatively determined using UV/Vis spectroscopy. For that, a series of CTA solutions in chloroform at different concentrations was measured. The absorption coefficients at 507 nm (visible band of the dithioester) were then plotted *versus* concentration. The absorption coefficient of the synthesized PTEGMA copolymer having (in the ideal case) one dithioester at the end of the chain was then compared with the values from the concentration row. Consequently, a number-averaged molecular weight could be calculated. A M_n (UV/Vis) of 54 000 g mol^{-1} was found, a value which is in good agreement with the molecular weight as measured from monomer conversion (M_n (NMR) = 56 000 g mol^{-1}). It is worth pointing out here that this value has then been used for all further calculations in this study.

Synthesis of PTEGMA-*b*-PS diblock copolymer

In a next step, styrene was polymerized starting from the PTEGMA (**4**) block as a macroinitiator (Scheme 1). The polymerization was carried out at 80 °C under an argon atmosphere. A huge excess of styrene monomer (280 equiv.) was necessary. The reaction was quenched after 24 h at a styrene conversion of approximately 9%. The obtained PTEGMA-*b*-PS (**5**) block copolymer was then analyzed by NMR and GPC. In the NMR spectrum, the signals of the PS block between 7.20 and 6.20 ppm are clearly visualized (see Fig. 1). The DP_n of the PS block was determined by NMR integration. An average number of 25 repeating units of styrene was calculated. Consequently, a total M_n (NMR) of 59 000 g mol^{-1} could be obtained. In addition, GPC measurements were performed to determine the molecular weight and the molecular weight distribution of the PTEGMA-*b*-PS block copolymer. The GPC trace of this block copolymer as shown in Fig. 2 is shifted to a higher molecular weight indicating the successful formation of the second block. The mass distribution shows a shoulder at about twice the molecular weight of PTEGMA-*b*-PS, suggesting the presence of a small amount of the PTEGMA-*b*-PS-*b*-PTEGMA triblock. The molecular weight was further calculated by UV/Vis measurements. A M_n (UV/Vis) of 61 000 g mol^{-1} which was in the same range as the calculated molecular weight by NMR was obtained. Again, the calculated molecular weight of PTEGMA-*b*-PS by NMR (M_n (NMR) = 59 000 g mol^{-1}) has then been used for other calculations in this study.

Self-assembly of PTEGMA-*b*-PS in the diluted regime

Due to its amphiphilic character, the PTEGMA-*b*-PS block copolymer is capable of self-assembly in aqueous solution to form micelles. This process was first investigated in diluted solution. It is well-known that amphiphilic block copolymers self-assemble in block-selective solvents, which solubilize only one but not the other block, forming micelles of various morphologies depending on the composition of the starting block copolymer. The shape and the size of these nano-objects are further dependent on the method of preparation.[14]

In the case of amphiphilic block copolymers with a short insoluble core-forming block, the direct dissolution can be used to prepare micellar solutions. In this study, this method was applied by dissolving the PTEGMA-*b*-PS block copolymer in MilliQ water to reach a concentration of 1 g L^{-1}. The solution was then placed in a fridge for several days until an equilibrated homogeneous solution was obtained. Block copolymer micelles formed of a hydrophobic PS core and hydrophilic PTEGMA coronal chains bearing randomly distributed terpyridine groups were investigated by DLS measurements. The particle size distributions calculated by CONTIN analysis were obtained at 20 °C at an angle of 90° (see Fig. 3).

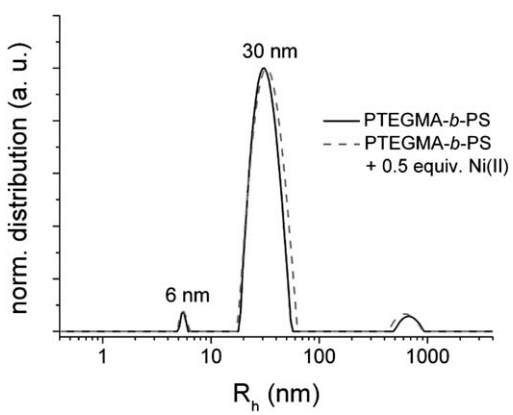


Fig. 3 Particle size distribution by CONTIN analysis of PTEGMA-*b*-PS in MilliQ water (1 g L^{-1}) at an angle of 90° and a temperature of 20 °C before (black line) and after (gray dashed line) the addition of 0.5 equiv. of Ni(II).

The first distribution at 6 nm represents the unimers, *i.e.* non-associated PTEGMA-*b*-PS chains, in solution. These loose block copolymer chains are in equilibrium with the corresponding micelles. The apparent hydrodynamic radius R_h of the micelles ranges from approximately 20 to 60 nm. The DLS signals do not show any angular dependency, indicating the formation of spherical structures.

The impact of Ni(II) addition on the diluted micellar system was then investigated. 0.5 Equiv. of $NiCl_2 \cdot 6H_2O$ was added to a solution of PTEGMA-*b*-PS at 1 g L^{-1} (with respect to the average amount of terpyridine groups). The DLS measurement shows essentially the same result as the starting micellar solution with no metal ions added. Moreover, no gelation originating from intermicellar supramolecular interactions occurred.

Self-assembly of the PTEGMA-*b*-PS in the concentrated regime

The self-assembly process of the PTEGMA-*b*-PS block copolymer was further investigated in concentrated aqueous solutions (above 4 wt% (w/v)). Different concentrated solutions were prepared and investigated under similar conditions as those already applied in the diluted regime. The concentrated micellar solutions were obtained by weighing out a given amount of PTEGMA-*b*-PS in a reaction vessel followed by the addition of MilliQ water. The reaction vessels were sealed and placed in a fridge overnight for dissolution, yielding different homogeneous and concentrated micellar solutions. Half an equivalent of Ni(II) ions dissolved in MilliQ water (with respect to the average amount of terpyridine groups) were then added to the micellar solutions at room temperature in order to form gels with the final concentrations of 3, 4, 5, 6, and 10 wt% (w/v) (see Fig. 4).

In the concentrated regime, intermicellar interactions between terpyridine groups from different micelles are possible when the coronal chains start to overlap. In the case of a 3 wt% micellar solution, no notable gelation occurred. It is assumed that 4 wt% represents the critical gelation concentration for the micellar solution (see Fig. 5). Below that concentration, the number of micelles might be too low to ensure an overlap of the coronal chains which is mandatory for the formation of elastically active intermicellar coordinative bonds. The formation of stable Ni(II) complexes can be monitored from the characteristic absorption by UV/Vis spectroscopy as previously demonstrated.[15]

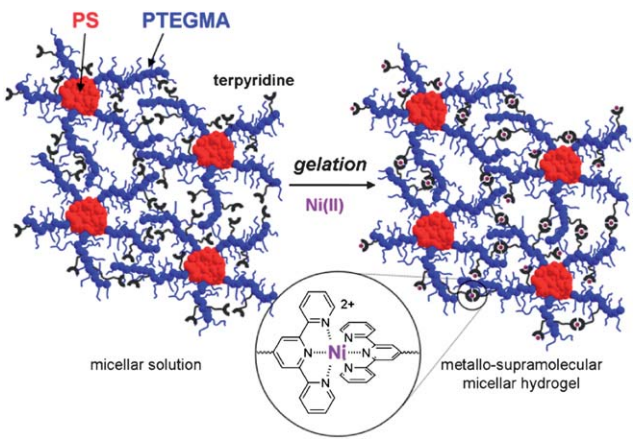


Fig. 4 Schematic illustration of the preparation of micellar gels from concentrated PTEGMA-*b*-PS aqueous solutions.

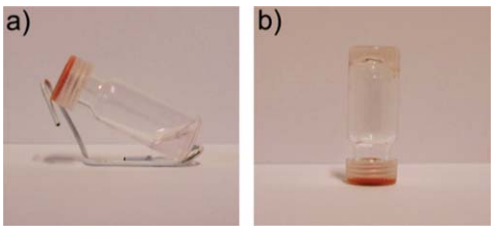


Fig. 5 Pictures of a PTEGMA-*b*-PS solution (a) before and (b) after the addition of Ni(II) to give a hydrogel at a final concentration of 4 wt%.

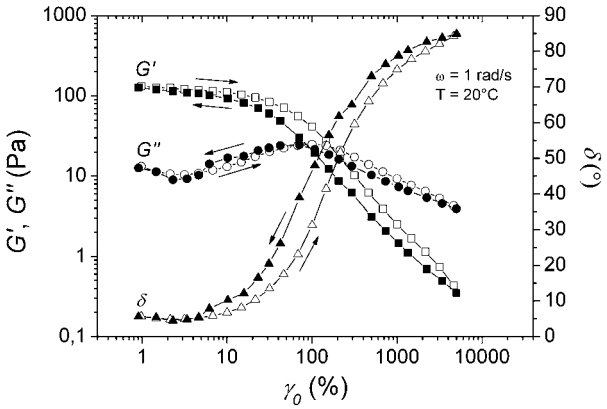


Fig. 6 Amplitude sweep of a 6 wt% (w/v) micellar hydrogel of PTEGMA-*b*-PS ($\omega = 1$ rad s^{-1}, $T = 20$ °C).

The prepared micellar hydrogels were further characterized by dynamic rheology measurements. At first, a strain sweep experiment was performed by measuring the evolution of the moduli while increasing the deformation of the gel. The micellar gels show a reversible mechanical-responsive gel–sol transition when the shear strain amplitude (γ_0) is increased (see Fig. 6).

During the measurement of each micellar gel, the storage (G') and the loss (G'') moduli show a plateau up to a deformation of approximately 10%. Although the amplitude of the strain is increased, both moduli remain almost constant. At higher strains (above 10%), the hydrogels show a gel-to-sol transition. The initial values for both moduli and the phase lag (δ) are

Table 1 Values of G' and G'' of different PTEGMA-*b*-PS micellar gels as well as for the PTEGMA gel at 10 wt% (w/v), in the viscoelastic linear regime

	PTEGMA-*b*-PS				PTEGMA
	4 wt%	5 wt%	6 wt%	10 wt%	10 wt%
G'^a/Pa	21	52	180	1760	6
G''^a/Pa	4	6	30	103	1

[a] $\omega = 1$ rad s^{-1}, $T = 20$ °C.

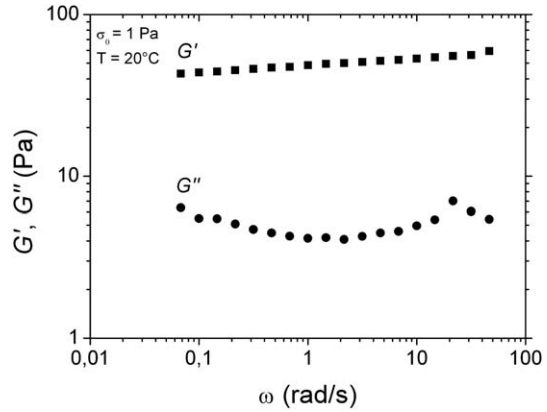


Fig. 7 Frequency sweep of a 5 wt% (w/v) micellar hydrogel of PTEGMA-*b*-PS ($\sigma_0 = 1$ Pa, $T = 20$ °C).

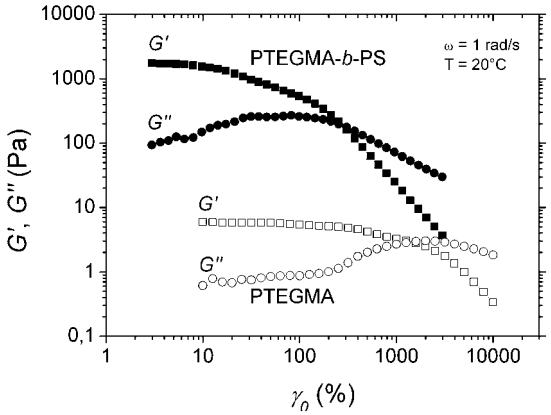


Fig. 8 Amplitude sweep measurements of a 10 wt% (w/v) PTEGMA-*b*-PS gel (filled symbols) and of a 10 wt% (w/v) PTEGMA gel (open symbols).

recovered for each micellar gel once the strain amplitude (γ_0) is reduced. Clearly, this is characteristic of a self-healing process that can be explained by the capability of the supramolecular gels to reform intermicellar connections (metal–ligand bonds) once the strain is removed (see Fig. 6). The initial values of G' and G'' of the different concentrated micellar gels are presented in Table 1.

The dynamic properties of the gels were then investigated in the linear viscoelastic regime by frequency sweep measurements. In the investigated frequency range, the elastic moduli were constant and about one order of magnitude higher than the loss moduli at the different concentrations (see Fig. 7). This suggests that the dynamic properties of the gels are determined by both the Rouse relaxation process and metal–ligand dissociation which is relatively slow in the case of bis(terpyridine) nickel(II) complex.[16] In addition, no significant influence of the temperature on the amplitude of both elastic and viscous moduli was observed.

Effect of the micellar core on gelation

As already mentioned, the amphiphilic PTEGMA-*b*-PS block copolymer self-assembles into spherical micelles. These structures then act as three-dimensional linkers to form an intermicellar network through supramolecular interactions of the terpyridine groups within the coronal chains when Ni(II) ions are added.

The influence of the PS micellar core can be investigated by comparing the critical gelation concentration of the gels obtained from PTEGMA-*b*-PS and PTEGMA solutions. In contrast to the PTEGMA-*b*-PS, the aqueous solutions of PTEGMA appear less viscous even at concentrations above 20 wt% (w/v). Different concentrated solutions of both polymers were prepared and compared in order to determine the concentration needed for a successful gelation. In the case of micellar solutions of PTEGMA-*b*-PS, gels are obtained above a critical concentration of 4 wt% (w/v) after the addition of Ni(II) ions. In sharp contrast, a minimum concentration of 10 wt% (w/v) is required to produce gels from PTEGMA. These results validate the use of amphiphilic block copolymers with terpyridine moieties within the water-soluble block to produce hydrogels. The intermediate self-assembly process of PTEGMA-*b*-PS to form spherical micelles provides additional cross-linking points within the system. Consequently, the final concentration needed to form a network is much less than in the case of non-micellar structures (PTEGMA). The rheological behaviour of a PTEGMA gel at 10 wt% was further investigated by rheology. The mechanical behaviour was then compared to a micellar gel of PTEGMA-*b*-PS at the same polymer concentration. The amplitude sweep measurements of the PTEGMA and PTEGMA-*b*-PS hydrogels are plotted in Fig. 8.

The differences in the mechanical properties between PTEGMA-*b*-PS micellar gels and PETGMA homopolymer gels are obvious. The moduli of the micellar gels originating from PTEGMA-*b*-PS are much higher than the moduli of the PTEGMA gels. Interestingly, the transition between the linear and the

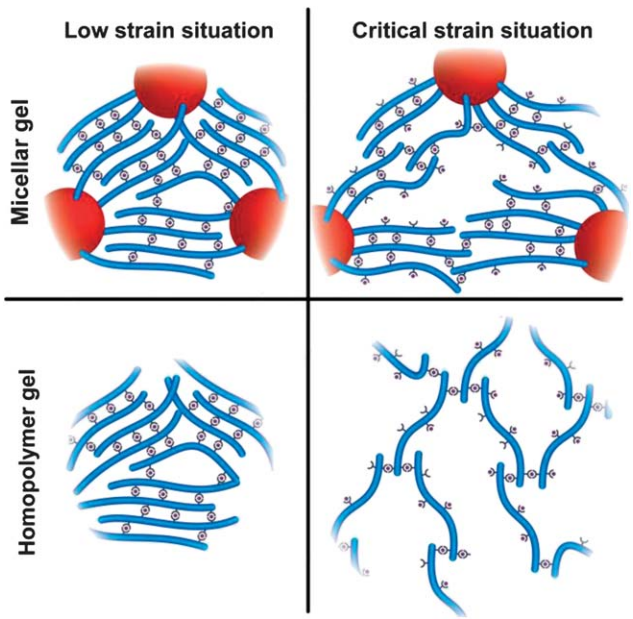


Fig. 9 Sketches of the deformation of hydrogels made from PTEGMA-*b*-PS (up) and PTEGMA (down) at low strains (left) and at critical strains (right). The PTEGMA gel would withstand higher strains before network breaking.

non-linear viscoelastic regimes is shifted to higher strain amplitudes for the non-micellar PTEGMA gels, indicating that they can withstand higher deformations. For these gels, the mechanical deformation is not restricted by the micellar cores. Consequently, a higher deformation of the network through the elongation of the polymer chains is therefore possible. Following this hypothesis the critical strain situation would be different for both gels, depending on the structure of the network formed as depicted in Fig. 9.

Conclusions

In summary, a well-defined PTEGMA-*b*-PS block copolymer was synthesized by RAFT copolymerization. The block copolymer consisted of a water-soluble PTEGMA block having terpyridine groups randomly distributed and a hydrophobic PS block. Due to its amphiphilic character, the PTEGMA-*b*-PS block copolymer was able to form spherical micelles in aqueous solution. This first level of self-assembly (*i.e.* the formation of micelles) was observed in the dilute regime and investigated by DLS. Upon addition of Ni(II) ions, metallo-supramolecular micellar gels were obtained in the concentrated regime. This second level of self-assembly was explained by the formation of bis-complexes between the terpyridine groups of the coronal chains of the micelles and the Ni(II) ions. A critical concentration (4 wt%) for the formation of micellar gels was found. The properties of the obtained gels were further investigated by rheology. PTEGMA-*b*-PS block copolymers formed gels at much lower concentrations than the corresponding PTEGMA polymers. The effect of the PS core was explained by the capability of the block copolymer to form micelles, which provide additional crosslinking points within the network. The rheological properties of PTEGMA and PTEGMA-*b*-PS based gels were investigated and compared for gels having a 10 wt% polymer content. A clear effect of the hydrophobic PS junctions was evidenced while both moduli shifted to higher values for the micellar gel. Moreover, the hydrogels made from PTEGMA could withstand higher strains.

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