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Thermo-responsive properties of metallo-supramolecular block copolymer micellar hydrogels

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Metallo-supramolecular micellar hydrogels exhibiting thermo-mechanical responsiveness are prepared through the hierarchical assembly of a heterotelechelic associating copolymer. The copolymer consists of a linear thermo-sensitive water-soluble sequence terminated by a short hydrophobic sticker at one end, the other being functionalized by a chelating ligand. As the first level of assembly, the associating copolymer is dissolved in aqueous solution to yield micellar nanostructures, bearing coordinative motifs at the end of the coronal chains. The second level of assembly is achieved when transition metal ions are added to the micellar solutions, resulting in almost instantaneous gelation. The thermo-mechanical response of those materials is investigated in detail by rotational rheometry, showing abrupt changes within the temperature boundaries corresponding to the phase transition of the polymer block located in the micellar corona.

Introduction

Nowadays, smart polymer gels constitute one of the most studied categories of soft materials.[1] They undergo physico-chemical changes in response to small variations in environmental conditions, which usually alter their rheological properties. Stimuli can be classified depending on their nature. Physical stimuli typically involve light irradiation, temperature variation, or mechanical stress. On the other hand, chemical ones include changes in pH, redox potential, or ionic strength, as well as the addition of chemical species. In practice, complex structured materials potentially adapt to different signals and thus show multi-responsiveness.[2] In this respect, increasing the level of structural complexity is considered as a powerful tool since it allows targeting numerous constitutive elements of the system.

Conventional ways of bestowing responsive properties to polymer materials rely on the introduction of stimuli-sensitive sequences. Hence, thermo-sensitive poly(*N*-isopropylacryl-amide) (PNIPAAm) is a widely used polymer showing lower critical solution temperature behaviour. As a result, PNIPAAm-based hydrogels generally undergo a shrinking-type volume phase transition upon heating.[3] Practically, the lower critical solution temperature is generally reported around 32 °C,[4] but is affected by hydrophobic or hydrophilic comonomers,[5] as well as the presence of salts[6] or surfactants.[7] Another strategy to impart responsiveness to polymeric materials involves the use of secondary interactions, like metal coordination[8] or hydrogen bonding.[9] Indeed, they are usually weaker but dynamically more flexible than covalent bonds,[10] offering a way of imparting adaptive and self-healing properties to non-covalent assemblies.[11] Following those principles, scientists are able to build responsive and dynamic architectures through the hierarchical assembly of small building blocks at the molecular level.[12]

In the past few years, structuring transient micellar networks *via* an orthogonal combination of hydrophobic and coordinative interactions has appeared as a powerful approach to tune the rheological properties and responsiveness of soft materials. While the coordination complexes can be specifically addressed by *e.g.* adding a competitive ligand,[13] the morphology and softness of the hydrophobic cores can be readily tuned according to environmental conditions.[14] In addition, the strength and dynamics of transient cross-links can be controlled depending on the choice of metal ions and the length of the hydrophobic sequence.[15] Ultimately, further control over the rheological properties of the resulting networks can be achieved by multiplying the number or position of associating motifs along the macromolecular building blocks.[16] In parallel, temperature triggered gelation has been reported while using thermo-responsive polymer sequences as core forming units.[17]

Here, we report on the preparation and characterization of a supramolecular hydrogel from a thermo-sensitive associating copolymer consisting of a linear water-soluble sequence terminated by a short hydrophobic sticker at one end, the other being functionalized by a chelating ligand. As the first level of assembly, the copolymer is dissolved in aqueous solution to

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yield micelles bearing coordinative motifs at the end of the coronal chains. The second level of assembly is achieved upon the addition of metal ions to the micellar solution, resulting in gelation. The thermo-mechanical response of the accordingly obtained material is finally investigated under oscillatory shear, focusing on the adaptive properties that the thermo-sensitive sequence confers to the self-assembled material.

Experimental section

Materials

Terpyridine end-capped polystyrene-*block*-poly(*N*-isopropylacrylamide) diblock copolymer (PS_{27}-*b*-$PNIPAAm_{300}$-tpy; M_n (^{1}H-NMR) = 37 700 g mol^{-1}; $Đ$ (SEC) = 1.32) was synthesized *via* sequential reversible addition–fragmentation chain transfer (RAFT) control radical copolymerization, as described elsewhere.[15] Anhydrous cobalt chloride ($CoCl_2$, Aldrich, >98%) salts were kept in a glove box and weighed under an argon atmosphere.

Instrumentation

Differential scanning calorimetry (DSC) measurement was performed on a Mettler Toledo 821 calorimeter. The sample was placed in a sealed aluminium capsule (40 μL) in order to avoid water evaporation. The DSC instrument was calibrated using an indium standard. The sample was initially heated from 20 to 45 °C at 1 °C min^{-1} under a static air atmosphere, followed by cooling at the same rate immediately after heating. Shear rheological experiments were performed on a Kinexus Ultra (Malvern Instrument) rheometer equipped with a heat exchanger and modified with a solvent trap. Measurements were carried out at given temperatures, using a 20 mm plate–plate geometry, in a water-saturated atmosphere in order to minimize evaporation of the solvent. The gap was adjusted between 50 and 250 μm so that the geometry was completely filled. Normal forces were checked to be relaxed prior to any measurement.

Preparation of micellar hydrogels

Samples were prepared by dissolving a given amount of PS-*b*-PNIPAAm-tpy block copolymer in MilliQ water. The sealed reaction vessels were then placed in a fridge and shaken from time to time to form homogenous concentrated solutions. After that, the gels were readily obtained by adding half an equivalent of the transition metal ion (with respect to the terpyridine content) dissolved in a defined amount of MilliQ water to each concentrated solution. The reaction vessels were finally placed again in the fridge overnight to ensure homogenous gelation and stabilization of the gels. The final concentration of associating copolymers in the samples is 5% w/v.

Results and discussion

Self-assembly of PS-*b*-PNIPAAm-tpy into micellar gel

The hierarchical assembly of the PS_{27}-*b*-$PNIPAAm_{300}$-tpy associative copolymer into supramolecular hydrogels has been investigated. First, a concentrated micellar solution was prepared by directly dissolving the copolymer into MilliQ water. Given the water solubility of the PNIPAAm block under ambient conditions, micelles made of a PS core and PNIPAAm coronal chains, bearing a terpyridine moiety at their extremity were thus obtained (Fig. 1). Since the associating copolymer features a corona forming block much longer than the core-forming block, spherical micelles are expected to be formed. At this point, no gelation occurred at the investigated concentration, which can be explained by the lack of entanglement between coronal chains of neighbouring micelles. Instead, a free-flowing solution is obtained, that separates into two macroscopic phases upon heating (Fig. 2a). Then, half an equivalent of cobalt(II) ions, as their chloride salts, was added with respect to the terpyridine content to yield hydrogels with a final concentration in associating copolymers of 5% w/v (Fig. 1). Practically, an efficient gelation arising from inter-micellar complexations was evidenced by the tube inversion test (Fig. 2b).

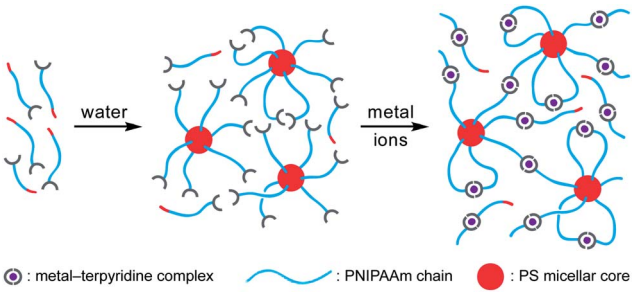

Fig. 1 Schematic representation of the hierarchical assembly of heterotelechelic associating copolymers into a metallo-supramolecular micellar gel.

The thermo-responsiveness of the accordingly obtained gel was visually demonstrated by immersing the sample into a heated water bath. Above a critical temperature, a mesoscopic phase separation is observed, the gel becoming cloudy, as illustrated in Fig. 2b. Surprisingly, no macroscopic phase separation arising from the deswelling and subsequent shrinkage of the gel occurred within the observation timescale. Indeed, poly(*N*-isopropylacrylamide) hydrogels are commonly characterized by a very sharp volume change upon heating,[18] unless stabilized by the presence of hydrophilic groups.[19] Hence, it is assumed that the positively charged metal–terpyridine junctions

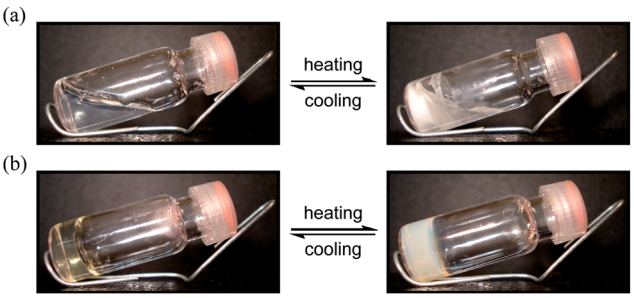

Fig. 2 Pictures showing the responsiveness of (a) a 5% w/v solution of PS_{27}-*b*-$PNIPAAm_{300}$-tpy copolymer and (b) a 5% w/v hydrogel prepared from the PS_{27}-*b*-$PNIPAAm_{300}$-tpy copolymer and Co(II) ions, at 20 °C and 35 °C.

ensure here a certain hydration of the gel and further prevent its collapse, mainly because of the inherent electrostatic repulsions between charged complexes.

Thermal characterisation of the PS-*b*-PNIPAAm-tpy gel

Differential scanning calorimetry was carried out on the self-assembled hydrogel prepared from the PS_{27}-*b*-$PNIPAAm_{300}$-tpy copolymers and Co(II) ions. In agreement with the turbidity observation (Fig. 2b), DSC measurements performed between 20 and 45 °C indicate that the sample undergoes a phase transition upon temperature rise (Fig. 3). This phenomenon is rationally attributed to the coil-to-globule transition of PNIPAAm chains from a swollen hydrated state to a shrunken dehydrated state when the LCST is crossed.[3]

Practically, the heat-induced phase transition of the investigated hydrogel is identified as an endotherm in the thermogram, while the reversibility of the process has been checked upon cooling (Fig. 3). The onset of the thermal transition was determined to be around 29.5 °C, from the intersection of the baseline and the leading edge of the endotherm. On the other hand, the phase separation temperature was taken at the maximum of the endotherm. The latter was evaluated at 32.5 °C, which is consistent with the reported value for the lower critical solution temperature of PNIPAAm.[4] The transition temperature upon cooling was however 1.5 °C lower than that in the heating process, clearly indicating a hysteresis, as usually observed for PNIPAAm.[20]

Rheological characterisation of the PS-*b*-PNIPAAm-tpy gel

The rheological behaviour of the PS_{27}-*b*-$PNIPAAm_{300}$-tpy hydrogel was investigated by rotational rheometry. At first, frequency sweeps were performed to probe the dynamic response of the sample, under ambient conditions and around the phase transition temperature determined by DSC. Precisely, the evolution of the elastic and viscous character of the gel was followed while varying the frequency of the oscillation. As an indication of the behaviour, solid- or liquid-like, that dominates the material under shear, the loss tangent ($\tan\delta$) was evaluated from the ratio between loss (G'') and storage (G') moduli. In practice, those measurements were performed under strain amplitudes that ensure a linear response from the material.

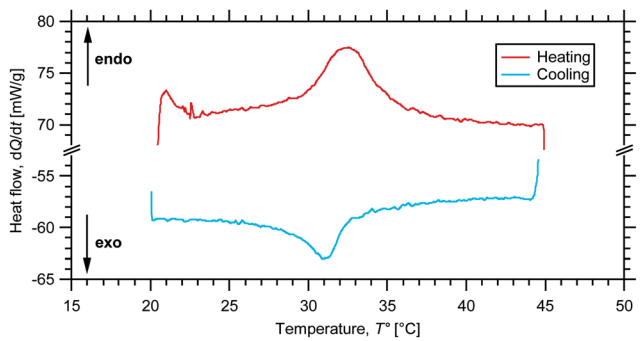

Fig. 3 DSC thermogram of a 5% w/v hydrogel prepared from the PS_{27}-*b*-$PNIPAAm_{300}$-tpy copolymer and Co(II) ions.

Then, the non-linear viscoelastic response of the gel under large amplitude shear was further investigated by amplitude strain sweeps, at a given oscillation frequency. Notably, particular attention is paid to the relationship between the applied stress (σ_0) and the resulting deformation (γ_0), along with the behaviour of the gel at the limit of destructuration. Indeed, the latter undergoes a shear-induced gel-to-sol transition when the stress applied on the sample overwhelms the yield strength of the material.

As illustrated in Fig. 4, a drastic change in the rheological behaviour of the gel is noticed in frequency sweeps when the external temperature is increased from 20 °C to 35 °C. Under ambient conditions, the material shows the characteristic features of a transient metallo-supramolecular micellar network.[15] At high frequencies, the non-covalent network appears intact since the supramolecular junctions do not dissociate on the experiment timescale. As the timescale of the oscillations increases, the material relaxes stress, both storage and loss modulus curves falling down as the frequency of the oscillations is decreased. In this respect, two relaxation timescales (τ) are distinguished at 20 °C, in agreement with our previous study.[15] The first mode (τ_1) corresponds to the dissociation of associating hydrophobic stickers and subsequent exchange of the polymer chains between hydrophobic nodes. On the other hand, the second mode (τ_2) is dictated by the dissociation kinetics of the metal–terpyridine bis-complexes tethering the network.

Above the LCST, a sudden transition from a gel to a flowing dispersion would be expected because of the collapse of the PNIPAAm coronal blocks. Inversely, the material considered here behaves more solid-like, similar to the covalently bound polymer network, in agreement with the visual observation

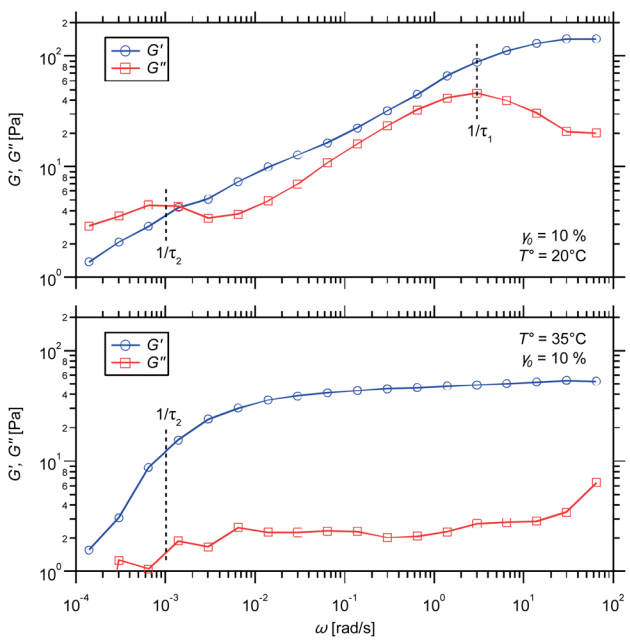

Fig. 4 Comparison between frequency sweeps performed on a hydrogel prepared from the PS_{27}-*b*-$PNIPAAm_{300}$-tpy copolymer and Co(II) ions, at 20 °C (top) and 35 °C (bottom).

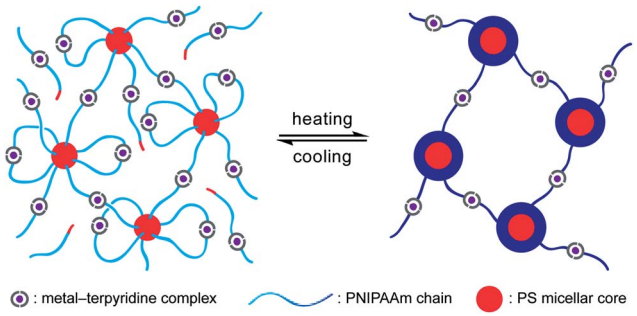

Fig. 5 Schematic representation of the thermo-response of a PS-*b*-PNIPAAm-tpy metallo-supramolecular micellar gel.

(Fig. 2b). Compared to 20 °C, elasticity indeed dominates more clearly over viscous effects even if a slight decrease of the high-frequency plateau modulus, indicating a diminution in the number of elastically active micellar bridges, is observed (Fig. 4). Compared to the situation at 20 °C, only a final relaxation is achieved at 35 °C, over a timescale that matches the one of metal–ligand bridge dissociation. Such an observation suggests that the escape of hydrophobic stickers from micellar cores has been frozen, which in turn would prevent the relaxation of the material over short timescale. Essentially, this consideration might be rationalized by taking into account the partial collapse of the thermo-sensitive chains onto the transient micellar cores, which results in turn in the shielding of the latter (Fig. 5). In this picture, the core–shell type structure of the hydrophobic nodes would indeed prevent the network integrity from being mechanically perturbed by shear forces.

From frequency sweep measurements (Fig. 4), a plausible contribution of inter-micellar interactions between collapsing coronal chains to the network elasticity is not apparent. Indeed, such additional cross-links would be accompanied by the emergence of a long relaxation process,[21] which was not evidenced here. Above the phase transition temperature, the presented hydrogel is characterized by a terminal flow behavior whose timescale (τ_2) attests to the presence of metal–ligand bridges between collapsed micellar objects (Fig. 5).

The change in the rheological properties of the gel in response to heat was further investigated by performing amplitude strain sweeps on the sample. Precisely, the evolution of storage and loss moduli was checked at a given oscillation frequency, under increasing amplitudes of deformation (1st run). At low strain, the micellar gel is characterized by a plateau in both moduli, which extends over the linear viscoelastic regime, *i.e.* the region where shear stress amplitude (σ_0) on the sample increases linearly with the amplitude of deformation (γ_0). In this region, the three-dimensional structure of the network is only weakly affected by mechanical forces and deforms elastically through entropic distortions. Due to its supramolecular character, the gel exhibits a gel-to-sol transition when stressed above the yield strength. At larger deformations, shear stress becomes almost independent of shear strain, meaning that the supramolecular network is mechanically disrupted, which corresponds to the non-linear regime. In practice, the critical shear strain and stress values (γ_0^c and σ_0^c) that separate the linear from the non-linear regime were determined from strain–stress curves, at the onset of breaking. In addition, the reversibility of the phenomenon occurring under large oscillatory shear was addressed by coming back to small oscillation amplitudes right after the first strain sweep (2nd run).

In the first set of experiments, strain sweeps were performed on the associating copolymer hydrogel at room temperature and at the phase transition temperature. As illustrated in Fig. 6,

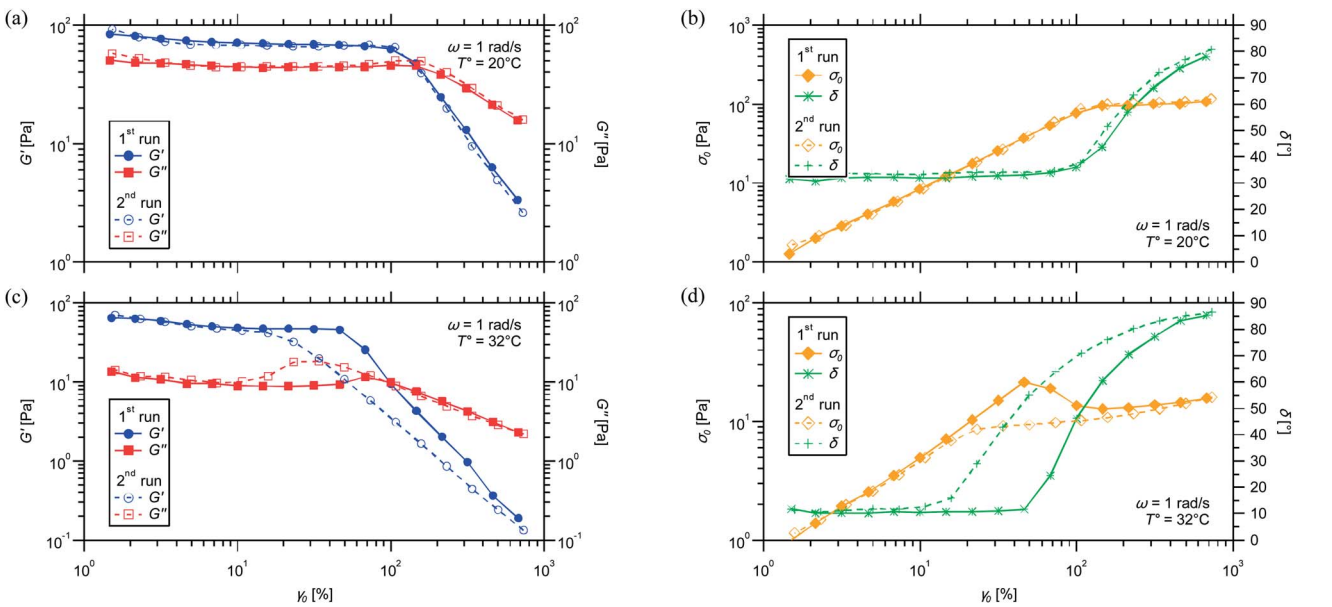

Fig. 6 Amplitude sweeps on a 5% w/v hydrogel prepared from the PS_{27}-*b*-$PNIPAAm_{300}$-tpy copolymer and Co(II) ions: evolution of the elastic and viscous moduli with an increasing (1st run) and decreasing (2nd run) strain amplitude at (a) 20 °C and (c) 32 °C; evolution of shear stress amplitude and phase angle with an increasing (1st run) and decreasing (2nd run) strain amplitude at (b) 20 °C and (d) 32 °C.

the plateau values for the storage modulus, at an oscillatory frequency of 1 rad s^{-1}, are comparable between 20 and 32 °C. However, the loss modulus was half an order of magnitude lower at 32 °C, lowering the proportion of energy that is dissipated through the irreversible flow of the network. In addition, the applied shear strain at which yield occurs was found to vary significantly. Precisely, the supramolecular hydrogel withstands larger deformations under ambient conditions (Fig. 6b – $\gamma_0^c \approx 100\%$) than at the phase transition temperature (Fig. 6d – $\gamma_0^c \approx 50\%$). Moreover, the stress–strain curve displays a maximum stress at a temperature of 32 °C (Fig. 6d – $\sigma_0^{c,max} \approx 20$ Pa), before reaching an equilibrium stress (Fig. 6d – $\sigma_0^{c,equi.} \approx 10$ Pa) that is one order of magnitude lower than the equilibrium stress at 20 °C (Fig. 6b – $\sigma_0^{c,equi.} \approx 100$ Pa). At larger deformations, the storage modulus progressively deviates from the linear to the non-linear viscoelastic regime, and strain softening is finally observed at both 20 °C (Fig. 6a) and 32 °C (Fig. 6c). Coming back to small deformations (2^{nd} run), full healing of the gel was observed at both temperatures, while storage and loss moduli recovered their original values. Compared to the situation at 20 °C, a peculiar hysteresis, that is particularly marked in G', is however observed at 32 °C during the healing process (Fig. 6c). This observation suggests that a certain proportion of the mechanical energy, that is reversibly stored in the entropic distortion of the polymeric network, is dissipated upon shear-induced flow of the gel. This proportion is known as the hysteresis loss and is given, with respect to the strain energy, by the area under the stress–strain loop.[22]

In essence, the rheological response of the investigated hydrogel is consistent with the thermo-responsive behaviour of poly(*N*-isopropylacrylamide) chains in aqueous solution. Below the LCST, favourable interactions allow the dissolution of the polymer in water *via* hydrogen bonding. In this respect, PNIPAAm chains are in a nearly extended conformation at 20 °C, which in turn allows them to reversibly bind *via* supramolecular links. Under those conditions, the release of mechanical stress proceeds *via* activated dissociation and subsequent exchange of the non-covalent bonds structuring the material, as illustrated in Fig. 7a. Above the phase transition temperature, the hydrogen bonds are disrupted and thus the polymer phase separates. From a structural point of view, free macromolecular chains are expected to undergo a coil-to-globule transition. Within the network, mechanical forces can however induces stretching of PNIPAAm chains up to a certain extend that is lowered in the range of the phase transition temperature (Fig. 6). Exceeding the yield strength of the material then allows stress release and collapse of the polymer chains (Fig. 7b). Once the network is mechanically disturbed, a certain proportion of stretched chains thus transits to the globule conformation, which is responsible for the hysteresis loss. At large strain, the conformation of the collapsed chains prevents the reformation

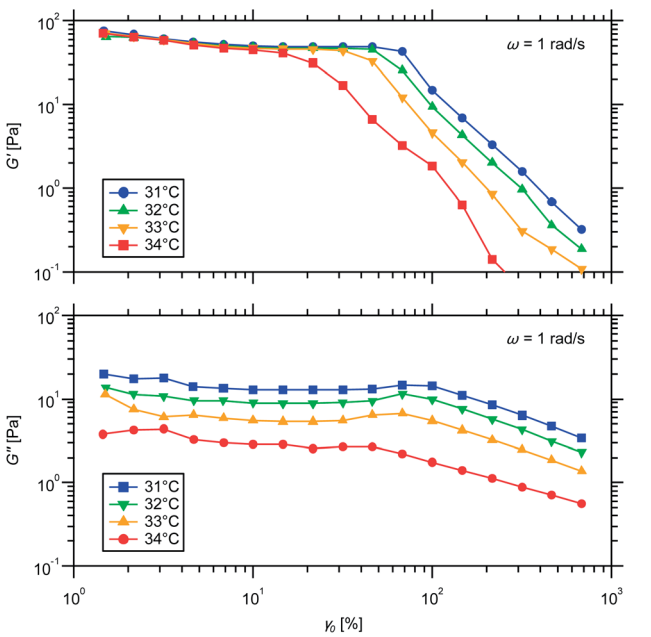

Fig. 8 Thermal dependence of the elastic and viscous moduli of a 5% w/v hydrogel prepared from the PS_{27}-*b*-$PNIPAAm_{300}$-tpy copolymer and Co(II) ions, in amplitude strain sweeps.

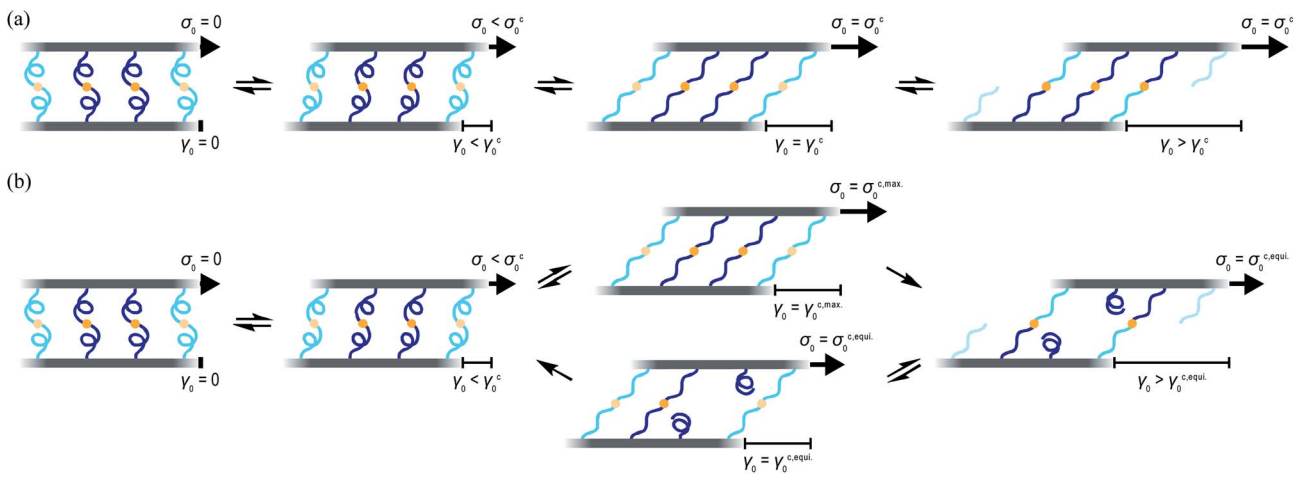

Fig. 7 Sketches featuring the behaviour of non-covalently bridged thermo-sensitive polymer chains under shear, (a) below and (b) above the LCST.

of elastically active cross-links. Complete healing of the gel is thus only observed when coming back to small deformations, which subsequently allows the reformation of elastically active junctions between polymer strands.

To further illustrate the thermo-sensitivity of the investigated material, its mechanical properties were investigated more deeply in the range of the phase transition temperature. In practice, isothermal amplitude strain sweeps were performed on the gel with an incremental temperature change. As shown in Fig. 8, the linear storage modulus shows a consistent value all over the transition temperature region, meaning that the number of mechanically active chains tethering the micellar network remains essentially constant. On the other hand, the equilibrium viscous modulus gradually decreases when temperature rises. As the PNIPAAm chains undergo a coil-to-globule transition, the volume fraction of polymer in solution is indeed reduced, as illustrated in Fig. 5, which lowers the proportion of mechanical energy dissipated through viscous effects.

The consistent number of stress carrying chains within the network was further supported by the invariance of the linear strain–stress relationships (Fig. 9). As noted above, the onset of network breaking is however shifted to lower strain amplitude when the temperature is increased. In the range of the phase transition, the yield strain of the material is progressively reduced by nearly one order of magnitude. Fundamentally, this observation reflects the will of PNIPAAm chains to adopt a globule conformation upon heating. In agreement, the hysteresis loss evaluated from strain–stress curves becomes drastically more pronounced (Fig. 10). Along with a decreasing yield strain, the stress value that marks the end of the linear viscoelastic response of the material gradually declines upon heating. On the whole, the phase transition is responsible for a nearly one decade decrease in the yield strength of the material.

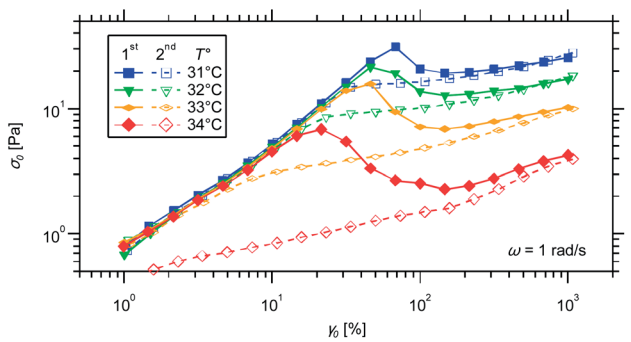

Fig. 9 Stress–strain relationships for a 5% w/v hydrogel prepared from the PS_{27}-*b*-$PNIPAAm_{300}$-tpy copolymer and Co(II) ions: stress amplitude with an increasing (1st run) and decreasing (2nd run) strain amplitude, at different temperatures.

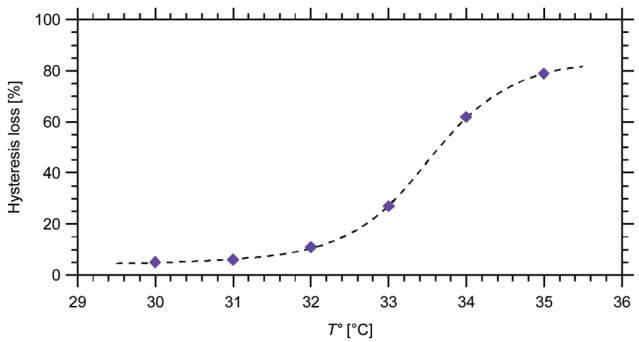

Fig. 10 Percentage of hysteresis loss for a 5% w/v hydrogel prepared from the PS_{27}-*b*-$PNIPAAm_{300}$-tpy copolymer and Co(II) ions, as a function of the temperature.

Conclusions

To summarize, a well-defined terpyridine end-functionalized polystyrene-*block*-poly(*N*-isopropylacrylamide) copolymer has been self-assembled to yield hydrogels exhibiting thermo-mechanical responsiveness. Below the lower critical solution temperature of PNIPAAm chains, the investigated material shows the characteristic features of a temporary micellar network, which is due to the dynamic exchange of polymer strands between the micellar aggregates. Above the phase transition temperature, the collapse of PNIPAAm chains causes the shielding of the transient micellar cores, which reinforces them kinetically. As a result, the rheological behaviour of the material changes from the one of a transient micellar gel to the one of a dynamically more stable coordination rubbery gel.

Even if a mesoscopic phase separation is observed, the mechanical integrity of the hydrogel is however preserved above the phase transition temperature. This unusual ability is attributed to the presence of charged metal–ligand complexes acting as non-covalent bridges between micelles. When stressed by mechanical forces, this self-assembled material exhibits a fully reversible gel-to-sol transition at the phase transition temperature as well as under ambient conditions. Self-healing of the material was however marked by a hysteresis at the phase transition temperature, which is rationally correlated with the conformational behaviour of the thermo-sensitive chains in aqueous solution. In this regard, heating the gel across the phase transition boundaries leads to a more pronounced hysteresis, along with a gradual decrease in the yield strength of the material. Given its remarkable thermo-mechanical responsiveness, we believe that our study will contribute to develop potential applications of self-assembled hydrogels, *e.g.* as sensors or actuators.

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