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Dissociating sticker dynamics from chain relaxation in supramolecular polymer networks—The importance of free partner!

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Abstract

Associating polymers constitute a fascinating class of materials because of the richness in their rheological behavior. Their rheology is known to be mainly dictated by the nature and intrinsic stabilities of transient associations. Here, we provide a direct observation of the importance of free associating sites in the macroscopic relaxation of supramolecular networks constructed from ultrahigh molecular weight polymers with sparsely distributed stickers of finite functionality. Their rheological signature affords evidence that the macroscopic relaxation of supramolecular networks can be apparently dissociated from the intrinsic lifetime of the associating units, provided that diffusion processes do not lead to successful chain relaxation at the microscopic level. © *2017 The Society of Rheology*.
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I. INTRODUCTION

Supramolecular polymers, i.e., macromolecules containing short chemical sequences interacting with each other via noncovalent associations, constitute a fascinating class of materials because of their rich rheological behavior [1,2]. Their rheology is mainly dictated by the nature and intrinsic stabilities of transient associations, which confer strength and dynamics to the self-assembled networks [3,4]. In particular, supramolecular polymer gels, whose rheological behavior falls between the limits of solid and liquid, have emerged as a major topic in this field. Due to diffusion of molecules in the amorphous gel phase, they indeed exhibit some of the characteristics of both of them, which further depend on the timescale and amplitude of strain [5].

At the base of supramolecular polymeric materials lie macromolecular building blocks that have been designed to carry functional groups. The latter can be of various characteristics and act as stickers, or "sticky points," for transient network formation, enabling connection and reconnection [6]. The strength and dynamics of sticky associations, i.e., the time by which the supramolecular moieties dissociate and recombine, constitute relevant issues to design associating polymers. In addition, dynamics of individual polymer chains must be sufficient to enable a certain mobility of the supramolecular groups and hence confer dynamic adaptive properties. A characteristic feature of supramolecular polymers is thus that their rheological behavior can reflect two characteristic timescales: one for the formation and breakage of temporary interchain associations; the other for the relaxation of chains or chain segments as captured by classical polymer physics [6,7].

Theoretical models have been developed for describing the dynamic and rheological properties of supramolecular polymer networks in accordance with their structural classification [1,2,8–18]. For transient networks formed by unentangled polymers with many pairwise associating stickers per chain, the sticky Rouse model developed by Rubinstein and Semenov predicts that the relaxation time of the chains is proportional to the renormalized bond lifetime times the square of the number of interchain sticky bonds per polymer [2,19]. Renormalization arises from the fact that a sticker needs to experience many breaking and reforming events with its old partner before finding another open sticker to associate with. At high bond energies, the most likely scenario is that the sticker, having unsuccessfully searched for a new partner, associates again with its old one, therefore prolonging the effective lifetime of the same bond.

In reversible networks where the stickers are able to aggregate into large clusters, the bond lifetime renormalization can be considered negligible within defined limits of sticker dissociation energy [11]. This is because the aggregates can accommodate varying numbers of stickers that undergo the hopping event by dissociating from one cluster and then associating into another. In the case of well-defined, like pairwise, associations of stickers of finite functionality, breaking a transient bond leads to rheological activation only if a new partner is found instead of reassociation with the old partner. While the bond opening may give rise to a local response, the partner exchange process is relevant

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for macroscopic rheological relaxation [20,21]. More precisely, stress relaxation requires the accompanying movement of chain segments attached to a specific cross-linking site after sticker dissociation [22].

In their unassociated state, stickers are allowed to diffuse within a given exploration volume of the supramolecular network. In the case of nonsaturating associations, stress relaxation implies that unassociated stickers cover the average distance between neighboring clusters before the reassociation event. In the case of finite associations, two distinct situations should be considered depending on the mechanism of sticker exchange. In a first configuration, the exchange proceeds via a concerted or stepwise substitution mechanism where the approach of an unassociated sticker results in the ejection and replacement of one of the associated partners from a complex. In essence, this situation is comparable to the one where the incorporation into the large clusters proceeds concurrently with the ejection of free stickers. In such transient networks, stress relaxation suggests that free stickers cover the path between neighboring complexes before reassociating. In a second configuration, the exchange between saturated complexes requires a breaking event that generates a vacant association site where the free sticker can associate. Therefore, the material relaxation implies that unassociated stickers cover the average distance between neighboring open stickers rather than complexes, which is intrinsically more restrictive.

In simulations, the spacers and thus the distance in between the stickers are kept relatively short, which limits the capacity of clearly identifying the contributions from segmental dynamics and its interplay with the sticker hopping process. Theoretically, the diffusion distance that has to be covered by the sticker is determined not only by the average distance between sticker clusters, complexes, or free partners but also by the lifetime of the association and topological constraints that arise from the chain connectivity. Despite significant progress in the description of relaxation mechanisms, the interplay between these critical parameters remains poorly updated experimentally. The experimental difficulties in maintaining a uniform chain length and sticker distribution in a wide range of molecular weights and degree of functionalization are the main obstacles for the application of experimental results in bringing prediction pieces together.

In particular, for long and sparsely associating chains combined with high bond strength, the equilibrium concentration of open stickers can be smaller than one per exploration volume. In this case, open stickers cannot bond by diffusion and other mechanisms can be postulated to govern the mobility of open stickers at longer timescales, which results in a different relaxation regime [20]. In this work, the focus is thus on transient networks constructed from ultrahigh molecular weight (UHMW) polymers via coordination of sparsely distributed ligands. These stickers of finite functionality form saturated *tris*-complexes in the presence of trivalent transition metal ions. Hence, we here provide a direct observation of the importance of free associating sites in the macroscopic relaxation of those supramolecular networks.

II. SYSTEM DESIGN

The adequate design of a supramolecular polymeric system is mandatory to provide a direct experimental observation of the crucial importance of partner exchange in the relaxation of supramolecular polymer networks. Such a polymeric system should incorporate sticky monomers (or stickers) of finite functionality so that their reversible bonding leads to the formation of finite-size complexes with well-defined stoichiometry, which in turn work as cross-links for network formation. In this study, high bonding energies are required so that a majority of stickers are fully associated and the fraction of open stickers is essentially negligible. However, the reversible association should be labile enough to allow dissociation events and therefore establish a dynamic binding equilibrium. Finally, a low sticker density would reduce the local number of free sticky sites so that open stickers most likely recombine with their old partners following a bond breaking event.

This approach is essential for providing a clear microscopic picture of the relationship between the dynamics of the cross-links and the viscoelastic behavior in the reversible networks of interconnected complexes. Our hypothesis is that the relaxation associated with the dynamic nature of the reversible interactions can be efficiently quenched in sparsely connected supramolecular networks. In this configuration, the conventional picture of a single sticker hopping from one complex to another is indeed very unlikely due to the large volume to explore to find a free partner. Fundamentally, this approach will allow dissociating the dynamics of stickers from the macroscopic relaxation of the materials. In turn, this will provide clear evidence that relaxations in supramolecular polymers are directly related to the molecular chain mobility, e.g., diffusion or fluctuations of the polymer backbone, rather than the reversible association and disassociation of sticker complexes.

The developed system will be composed of linear polymers that are able to associate by 1:3 metal–ligand interactions. These associations result in the formation of complexes whose stoichiometry is precisely defined by the coordination theory or steric constraint. Indeed, a metal ion in a given electronic configuration is assumed to have a fixed coordination number and geometry in combination with a given ligand. In the present study, coordinatively saturated octahedral complexes are expected for which dissociative ligand substitution is most favored. In this ligand exchange mechanism, the metal–ligand bond should be broken before a new ligand can bind the complexes, thereby avoiding an energetically unfavorable intermediate. Generally speaking, the coordinative interactions are also particularly interesting because the metal–ligand bonds are relatively strong (bond energy around 40–120 kJ/mol) and highly directional. Finally, significant changes in the kinetic and thermodynamic stability of the resulting assemblies can be readily achieved depending on the metal ion.

Our strategy relies on the incorporation of multiple ligand moieties as pendant groups distributed along the chain of linear hydrophilic polymers. In this study, UHMW associating copolymers with a low grafting density will be used so that

the average distance between stickers is relatively high. Highly stable complexes are targeted by the appropriated choice of metal ions in combination with chelating ligands that form saturated octahedral *tris*-complexes at the stoichiometry. In practice, the metal ions will be incorporated into the system during a mixing step via a solution process. The supramolecular polymeric system will be thus studied in solution, where metal–ligand complexes can provide efficient cross-links to generate a percolated network even at low concentrations. This strategy will avoid uncontrolled phase separation, crystallization, or stacking of the associating units, which generally occur when supramolecular polymers are studied in the bulk and complexify the interpretation of the results.

To introduce the coordination motif into the architecture of macromolecular chains, the envisaged strategy consists in the use of functional comonomers during the polymerization process. The building of structurally defined materials with reliable properties implies that block copolymers can be synthesized with well-defined molecular characteristic features, motivating the use of living or controlled polymerization techniques. Among them, the macromolecular design via reversible addition-fragmentation chain transfer (RAFT) or interchange of xanthates (MADIX) polymerization [23,24] is particularly attractive given the wide range of polymerizable monomers, the mild synthetic conditions, and the compatibility with various functional groups, including chelating ligands. Also, this polymerization technique was recently demonstrated to give access to controlled ultrahigh molar mass polymers via a gel process [25].

III. EXPERIMENTAL SECTION

A. Copolymers

The samples are linear UHMW narrowly dispersed water-soluble copolymers that are sparsely decorated with ligands in the side-chain. Their nature, composition, and synthetic route are reported elsewhere [26]. The chemical synthesis of the polymer skeleton is achieved through the macromolecular design via interchange of xanthate (MADIX) polymerization. This technique allows preparing polymers that are well-defined with respect to topology, molecular weight, and composition, further targeting very high molecular weight polymers using the MADIX-gel process [25]. For this purpose, highly polymerizable hydrophilic monomers are used in combination with a functional comonomer bearing a ligand moiety.

In practice, all polymerizations are conducted adiabatically in oxygen-free homogenous concentrated aqueous media, with the increase in temperature being monitored during the reaction. The chain growth is initiated by decomposition of very low concentrations of a water-soluble redox initiator pair at room temperature. Precisely, the generation of primary radicals is ensured by the decomposition of a persulfate salt, which is promoted by the presence of a reductant. In parallel, a hydrophobic xanthate is used as a reversible chain transfer agent to control the polymerization batch process, in the presence of the minimum amount of cosolvent to ensure its solubility.

Fast and nearly quantitative gel polymerizations of comonomers can be conducted in a controlled manner by following previously established procedures [25]. Molecular weights of 500, 1000, and 2000 kg/mol are targeted for the polymer chains according to the initial ratio between the monomers and the chain transfer agent. In parallel, the number of incorporated ligand moieties, and hence the number of associating points along the chain, is controlled by the initial feed in functional comonomers, which is adjusted to 1, 3, or 5 wt. %.

Size exclusion chromatography (SEC) analyses on associating copolymers reveal narrow symmetrical molar mass distributions for all copolymers. Accordingly, low dispersities (<1.3) are obtained irrespective of the targeted molecular weights, thereby attesting to the decent control over the polymerization process. As shown in Fig. 1, the increase in molar masses with the targeted chain length is clearly evidenced by the shift of SEC traces to lower elution times. Using multiangle light scattering detection, absolute values of average molecular weights are found to be in very good agreement with theoretical expectations for the whole range of targets.

B. Sample preparation

Different solutions of UHMW associating copolymers are prepared by diluting the raw polymer material in purified water, at different concentrations. When necessary, the *p*H of the media is adjusted to neutral by the addition of either hydrochloric acid or sodium hydroxide. Then, defined amounts of trivalent metal salts dissolved in a defined amount of purified water are added to the viscous polymer solutions under vigorous shaking. At this step, the amount of metal ions can be varied with respect to the ligand content in order to adjust the cross-link density between associating chains. In parallel, the nature of the metallic cation can be varied in order to tune the molecular dynamics of the self-assembled network. The two selected metallic ions are the chloride salts of iron(III) and aluminum(III). The first cation has a particularly stable half-filled *d* electronic sublevel that gives rise to substitutionally labile complexes in solution. The second is even more labile in regard to coordination thanks to a pseudonoble-gas electron configuration. At the end of the preparation protocol, the samples are allowed to

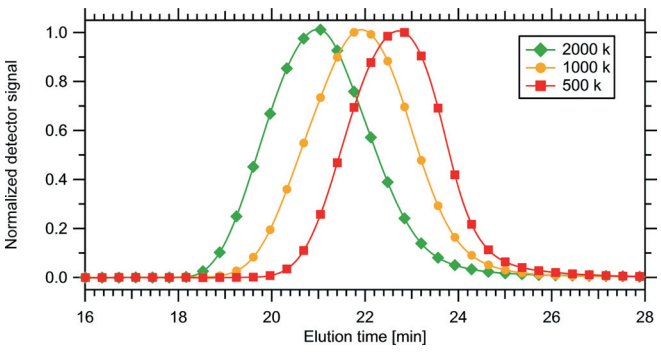

FIG. 1. SEC elugrams of UHMW associating copolymers of various lengths.

rest over one week to ensure homogeneous gelation and stabilization of the hydrogels.

C. Rheology

Rheological measurements are performed using a TA Instruments ARES-G2 strain-controlled rheometer with concentric cylinder geometry of inner and outer diameters of 14 and 15 mm, respectively, and a gap size of 4500 μm. The rheometer is equipped with a solvent trap and the atmosphere saturated with water in order to minimize evaporation of the sample. The effects of sample loading are reduced by applying small amplitude oscillatory shear until a steady-state response, i.e., time-independent storage (G') and loss (G'') moduli are observed. Equilibration times range from few minutes for low viscous solutions and weakly percolated gels to few hours for strongly associated gels. Normal forces are checked to be relaxed to <0.1 N prior to any rheological measurement.

The time-temperature superposition principle is not used here because a thermorheologically complex behavior is a priori expected for supramolecular systems. All curves are recorded at a given temperature, with time limitations at the low frequencies. Data are associated with a confidence interval of 10% estimated from repeated loadings and batch-to-batch variations.

IV. RESULTS AND DISCUSSION

In the following, the rheological behavior of UHMW associating copolymers is investigated in aqueous solutions via rotational shear rheometry, with emphasis on the effect of numerous experimental variables and parameters. The samples consist of monodisperse linear water-soluble copolymers sparsely decorated with ligands in the side-chain. At first, the addition of selected metal ions to their aqueous solutions is tested to drive the formation of metallo-supramolecular networks (Fig. 2). Both the quantities and the nature of the metal ions can be varied in order to control the cross-link density and dynamics of the resulting metallo-supramolecular networks. Then, the thermo-rheological signature of the samples is studied within the boundaries defined by water melting and boiling points. Then, the influence of the concentration, chain length, and number of stickers on the cross-linking density and relaxation phenomenon is investigated. Finally, the nonlinear behavior of the samples is tested under large amplitude oscillatory shear.

A. Influence of the metal ions

Aqueous solutions of the UHMW associating copolymers are prepared by diluting the raw polymer materials in purified water. These solutions can be turned into supramolecular hydrogels upon adding trivalent metal ions, i.e., that can accommodate up to three ligands. While metal-free polymer solutions behave as viscous liquids, soft gels withstanding the inversed tube test are readily obtained depending on environmental conditions. This mixing process indeed creates metal–ligand associations between polymer chains toward the formation of percolated three-dimensional networks, as schematized in Fig. 2.

In this regard, the cross-linking density of the supramolecular networks and the number of free sticky coordination sites can be hypothetically controlled by the amount of metal ions added to the system, with respect to the total ligand content. In turn, this offers the possibility for tuning both the organization and the dynamic response of the supramolecular hydrogels, therefore requiring an in-depth study of their complex behavior. This will be the first step in tackling the role of the combined effect of the dynamics of the associating units and the internal dynamics of the building blocks in the macroscopic relaxation of supramolecular polymer materials.

Experimentally, the evolution of the dynamic mechanical properties of the material is monitored by frequency sweeps performed under strain control and at room temperature. Varying the frequency of the oscillatory shear allows capturing the timescale, τ, of stress relaxation in the supramolecular networks. On short observation timescales ($t_{exp} < \tau$), motions of the supramolecular network are restricted around the noncovalent associations acting as sticky points between chains [27,28]. When increasing the oscillation timescale ($t_{exp} > \tau$), interchain cross-links may dissociate, thereby allowing chain segments to diffuse through the solvating media. An onset of material flow might be thus expected when lowering oscillation frequency.

As a reference sample, the rheological characterization is first conducted on metal-free solutions of UHMW associating copolymers by performing frequency sweep measurements at room temperature. In the investigated concentration range, these solutions behave as free flowing liquids that

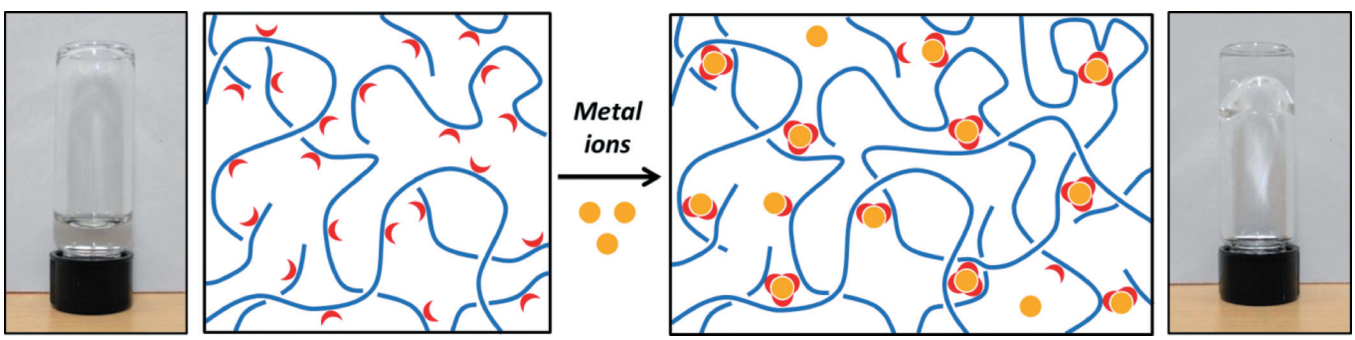

FIG. 2. Schematic and pictures showing the metallo-induced gelation of a solution of UHMW associating copolymers decorated with ligands in the side-chain.

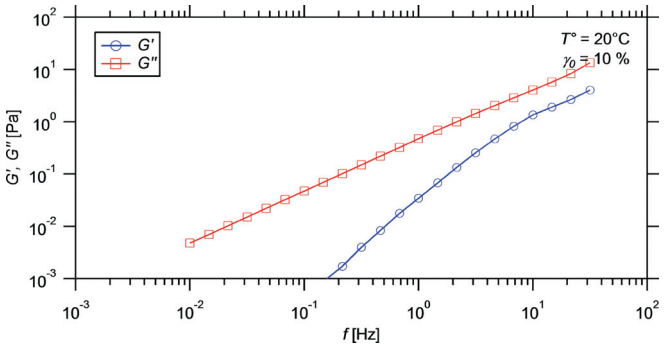

FIG. 3. Frequency sweeps monitoring the dynamic mechanical properties of a ligand-decorated UHMW copolymer (2000 kg/mol) metal-free solution (1 wt. %).

lack connectivity between polymer strands. A careful analysis of the rheological signature of these polymer solutions however shows that the dynamic moduli obey a scaling law in the high-frequency regime, with a slope equal to 2/3 (Fig. 3). This characteristic signature evidences important hydrodynamic frictions between the UHMW coils that restrict the flow of the solution. This rheological behavior can be described in the context of the Zimm model, with a spectrum of relaxation in the high-frequency range and a terminal relaxation time which corresponds to the onset of Newtonian flow. Beyond this, the linear viscoelastic response at the low-frequencies reflects that of fully relaxed polymer chains, with characteristic frequency power law dependencies of 1 and 2 (Fig. 3).

In a next series of experiments (Fig. 4), selected metal ions are added to polymer solutions and their amount is varied below and above the metal-to-ligand stoichiometry of 1:3, which corresponds to $^1/_3$ eq. of metal ions with respect to the total ligand content. Frequency sweep measurements are systematically conducted under strain control that ensures a linear response, as estimated below from strain sweeps. In the presence of 0.1 eq. of given cations, an essentially liquidlike behavior is evidenced by the scaling of both

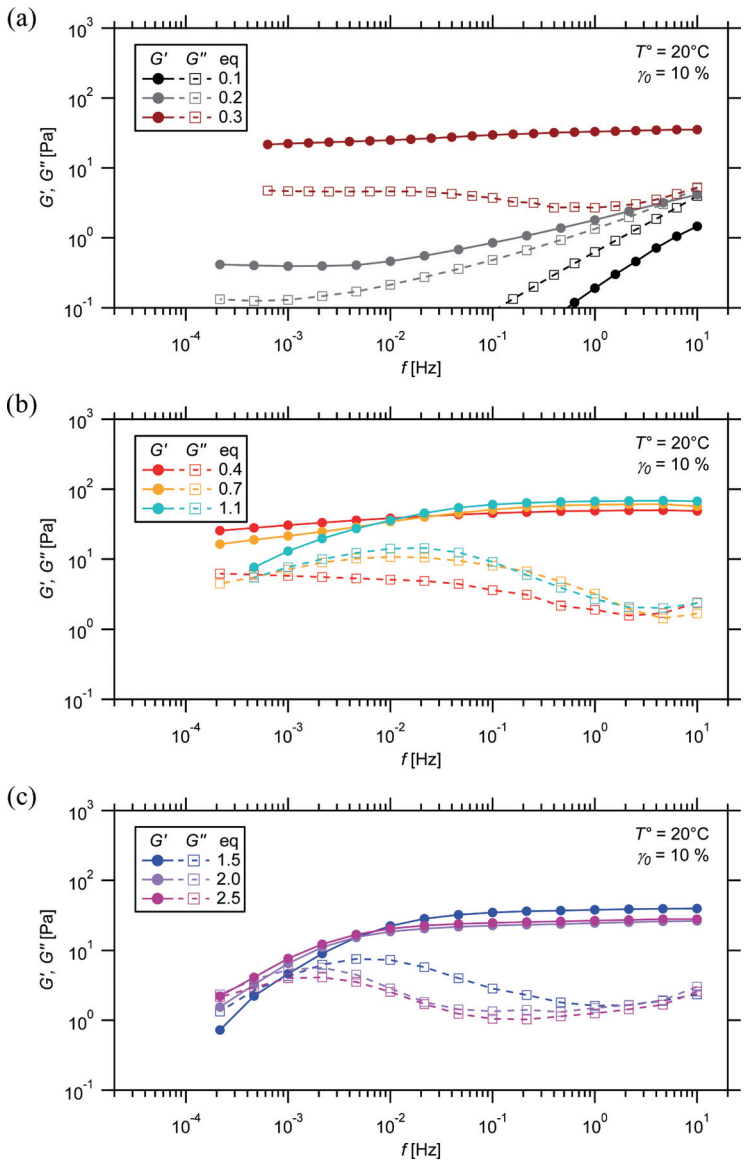

FIG. 4. Frequency sweeps monitoring the dynamic mechanical properties of ligand-decorated UHMW copolymer solutions (1000 kg/mol; 5% stickers; 1.25 wt. %) in the presence of different amounts of Fe(III) trivalent metal salt given in equivalents with respect to the ligand groups.

moduli with oscillation frequency and a clear dominance of viscous effects [Fig. 4(a)]. This situation is indicative of a low cross-linking density that is due to the insufficient number of interchain metal–ligand associations. Indeed, 0.1 eq. corresponds already to a few tens of ions per chain, which is theoretically sufficient to generate a percolated network. However, a large proportion of the metal ions is expected to be involved in the formation of intrachain bonds due to the low polymer concentration in solution. Therefore, this fraction does not contribute to the network formation at the expense of elastically active intermolecular bonds.

As the amount of metal ions is increased in the solution to reach the stoichiometry, low frequency plateaus progressively rise in accordance with the establishment of active cross-links between neighboring polymer chains. In this regime, a control over the cross-linking density in the system is thus possible depending on the ratio between the metal and ligands. Approaching the 1:3 stoichiometry of metal–ligand complexes [Fig. 4(a)], nearly parallel moduli are ultimately achieved over the entire frequency decades, resulting in an almost frequency-independent phase angle. The binding of three ligands is thus clearly evidenced by the equivalence attained at around $^1/_3$ eq. of metal ions per ligand. If the coordination was sterically limited to two ligands, then 0.5 eq. of metal ions would have been required in order to bind all the chain segments and hence achieve the plateau in modulus. In addition, the elastic response is nearly 1 order of magnitude higher than its viscous counterpart, at least in the investigated frequency range. In a rheological point of view, these features are the trademark of permanently cross-linked hydrogels. The absence of the relaxation process indeed indicates that segmental motions of the chains are restricted around the metal center, even under substoichiometric conditions. In this picture, the metal–ligand complexes provide efficient bridges between UHMW polymer chains to form a three-dimensional network.

At this point, the absence of material relaxation can be still perceived as a consequence of an intrinsic frozen character for the metal–ligand associations, i.e., the absence of bond breaking events, rather than the impossibility for dissociated ligands to find free coordination sites in their near surrounding, i.e., the absence of the ligand exchange event. However, it can be concluded from experimental observations that neither the reversible nature of the interaction nor the motions of the polymer backbone itself contribute to the relaxation of the material, at least on the timescale of the observation. The model of permanent rubbery gels, whose cross-link density depends on the amount of metal ions as cross-linkers, can be conveniently used to describe the rheological signature of the material.

When the amount of metal ions is further increased above the 1:3 metal–ligand complex stoichiometry, the rheological behavior of the material progressively deviates from that of permanent gels to that of transiently cross-linked gels. The latter are dominated by elasticity on a short timescale (high frequency) and by viscosity on a long timescale (low frequency), as shown in Fig. 4(c). For fast oscillations, the largest part of the deformation energy is indeed still stored in entropic distortions of the polymer network. Below a certain frequency of oscillation, the elastic modulus starts to drop, while the viscous modulus goes through a local maximum so that both moduli cross each other at the cross-over frequency. In practice, this cross-over is a signature of the material relaxation occurring at a characteristic timescale, $\tau = 1/f$. Although the viscoelastic material is dominated by elasticity before the modulus cross-over, a liquidlike behavior tends to govern the sample at low oscillation frequencies.

On the whole, the presence of metal ions in the system has therefore an impact on both the cross-linking density and the dynamic properties of the supramolecular networks. The first variable is controlled by the amount of metal with respect to the ligand until the complex stoichiometry is reached. In this respect, increasing the metal concentration leads to an increased cross-link density in accordance with the formation of metal–ligand bridges between chains in solution. At a low metal content, only a few active cross-links lead to a weakly percolated network structure, as illustrated in Fig. 5(a). When the complex stoichiometry is reached, the cross-link density of the materials is maximized with all ligand moieties being coordinated around the different metal centers [Fig. 5(b)]. When exceeding the stoichiometry, only a small decrease in the elastic plateau modulus is observed [Figs. 4(b) and 4(c)], which might be ascribed to the formation of *bis*- or *mono*-complexes which reduces the cross-link density and hence the number of elastically active polymer segments [Fig. 5(c)].

On the other hand, the dynamic properties of the materials remain macroscopically unexpressed as long as the amount of metal ions remains substoichiometric [Fig. 4(a)]. However, doping the hydrogels with an excess of metal ions leads to an activation of the material relaxation. In particular, the modulus cross-over provides clear evidence of the lability of the metal–ligand bonds, which otherwise would prevent the flow of the material. Indeed, the ligands need to reversibly dissociate from the metal center in order to temporally liberate a chain segment from its anchorage. In the

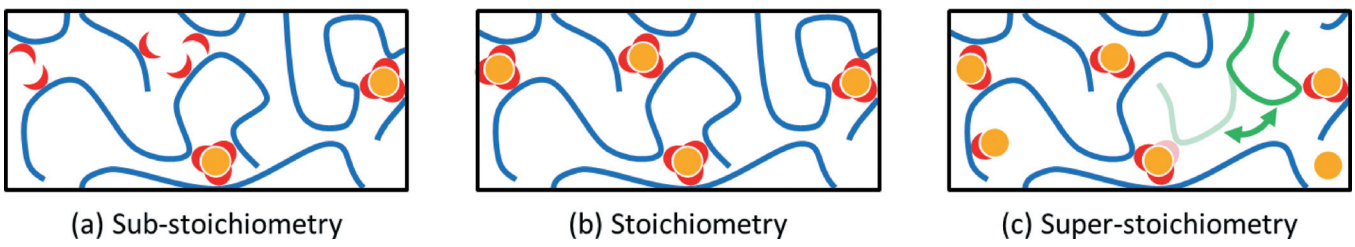

FIG. 5. Schematic representations of metallo-supramolecular networks built from ligand-decorated UHMW copolymers in combination with different amounts of trivalent metal ions.

broad field of supramolecular networks, this dissociation process is generally accompanied by stress release due to permitted segmental diffusions followed by reassociation of the stickers with a different partner [7,22,29]. Given the high stability constants for the formation of metal–ligand complexes, the association kinetics is supposed to be extremely fast, which prompts the need of vacant association sites in the near surrounding environment.

Under stoichiometric conditions, the exchange of ligands around different metal centers is thus inhibited by the presence of stable, saturated *tris*-complexes that are sparsely dispersed in the media [Fig. 5(b)]. Whatever the frequency of dissociation events, the high binding affinity combined with the lack of vacant association sites forces temporary dissociated ligands to reversibly reassociate on the same coordination site instead of elsewhere. The topological structures of these networks are therefore fixed by preventing any existing sticky bonds from hopping to a neighbor. In turn, the absence of net structural displacement results in an apparently negligible constraint release for the chain segments, from the micro- to the macroscopic level. Overall, the relaxation of the material is thus a locally diffusion-limited process that is hindered by the absence of free coordination sites as supramolecular anchorage for ligands, irrespective of their dissociation dynamics.

Under substoichiometric conditions, free ligands additionally act as spectators in competition for absent vacant coordination sites [Fig. 5(a)]. However, when an excess of metal ions is added to the associating copolymer solutions, vacant coordination sites are inevitably created due to the presence unsaturated *mono*- or *bis*-complexes or free cations. In turn, it is believed that these coordination holes enable the creep of the material through segmental diffusion via a thermally activated hopping mechanism, i.e., successive dissociations/associations of ligand stickers [Fig. 5(c)], widely reported in the scientific literature [22,29]. As evidenced by the weak decrease in the elastic plateau modulus, the cross-linking density of the network however remains almost unaltered by the excess of transition metal ions in the system.

In theory, this relaxation phenomenon can be correlated with the dynamics of metallo-supramolecular associations tethering the polymer network. In the context of transiently connected polymer networks, the dissociation of ligands from coordination sites indeed generally constitutes the rate limiting step for material creep. Accordingly, the characteristic relaxation time of the investigated materials is here finely tuned depending on the choice of the metal cations, which can be further related to the kinetic stability of the metal–ligand complexes. In practice, faster relaxations are obtained when faster-dissociating aluminum(III) ions are used in place of the slower-dissociating iron(III) ions (Fig. 6), with the first forming more labile coordination complexes compared to the second. Hence, the material relaxation is effectively changed from a diffusion-limited to a kinetically limited process controlled by the nature of the supramolecular associations.

B. Thermo-rheological behavior

The thermal dependence of the dynamic mechanical properties of metallo-supramolecular networks is further

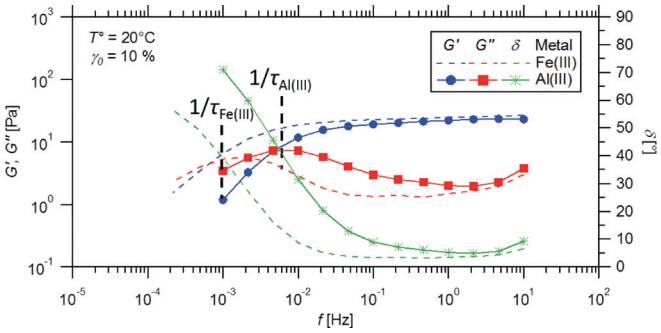

FIG. 6. Frequency sweeps monitoring the relaxation of the same ligand-decorated UHMW copolymer solution (1000 kg/mol; 5% stickers; 1.25 wt. %) in the presence of 2 eq. of two different trivalent metal salts: Fe(III) and Al(III).

investigated to demonstrate the crucial importance of vacant coordination sites in their relaxation mechanism. To this aim, frequency sweeps are carried out on gels under strain control by recording the evolution of dynamic moduli at decreasing frequency at various temperatures. In this respect, higher temperatures should enhance the relaxation dynamics due to sticker dissociation, which is classically a thermally activated process.

Experimentally, a sharp distinction is observed when comparing the thermo-mechanical behaviors of hydrogels prepared with a stoichiometric amount or an excess of metal ion. As mentioned above, their rheological signatures are identified as those of permanently and transiently cross-linked networks (Fig. 4), respectively. Accordingly, only a weak thermal dependence of the viscoelastic responses of the hydrogels prepared with a stoichiometric amount of metal ions is monitored when increasing the temperature up to 80 °C (Fig. 7). These results are characteristic of strong covalent or chemically cross-linked networks although the latter are tethered by noncovalent or physical interactions, namely, the coordination bonds. Even if thermal energy is provided to overcome the energy barrier for ligand dissociation and allows multiple dissociation events, the macroscopic relaxation of the material is inhibited by the absence of intermolecular exchange at the microscopic levels. Given the very low sticker density and large volume to explore for each chain segment, the timescale needed for a chain relaxation would require an infinite number of scissions and formations of the same bond between two old partners.

The situation, however, is different in the case of transient hydrogels prepared with an excess of metal ions, for which a relaxation occurs on the timescale of the experiment. As illustrated in Fig. 8, a diminution in the apparent relaxation frequency of dynamic networks is observed upon heating, with the local maximum in G'' and modulus cross-over monotonously shifting to higher frequencies. If the swallow slopes of moduli in the low frequency regime are related to the amount of metal ions as shown in Fig. 4, a clear deviation is observed at high temperature, which can be ascribed to significant evaporation of the sample. In transient networks, stress relaxation occurs via the dissociation of elastically active transient cross-links and the subsequent motion of the polymer chains. In this respect, providing thermal energy to

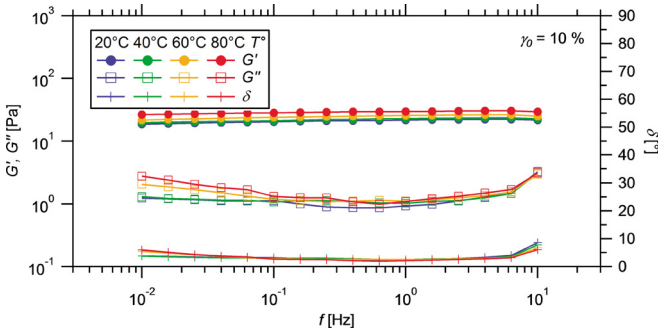

FIG. 7. Frequency sweeps monitoring the dynamic mechanical properties of a ligand-decorated UHMW copolymer solution (2000 kg/mol; 5% stickers; 1 wt. %) in the presence of the stoichiometric amount of Fe(III) trivalent metal salt at different temperatures.

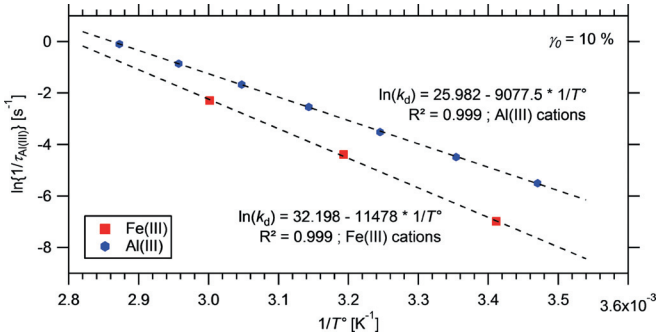

FIG. 9. Arrhenius plot of the apparent relaxation rate of a ligand-decorated UHMW copolymer solution (1000 kg/mol; 5% stickers; 1.25 wt. %) in the presence of 2 eq. of two different trivalent metal salts: Fe(III) and Al(III).

the system accelerates the dissociation of ligands from metal-complexes, which is the rate-limiting step. In turn, this enhanced chain relaxation leads to a decrease in the apparent relaxation time characterizing the material under shear. On the other hand, the plateau elastic modulus remains almost unaffected at high frequency, therefore attesting the thermal stability of the supramolecular assembly.

When plotted against temperature, the apparent relaxation time of the transient networks—estimated from the local maximum in G''—shows an exponential decrease in accordance with the Arrhenius law (Fig. 9). Accordingly, the slope is related to the activation energy for this relaxation mode, which corresponds to the exchange of ligands between cross-link nodes. From the temperature dependences of relaxation times, activation energies of around 75 and 95 kJ/mol were determined for the breaking and exchange of the polymer chains when aluminum(III) and iron(III) ions were used, respectively. Such activation energies match reversible processes and can be tuned in the stability order of the metal–ligand association.

C. Influence of the concentration

A control over the network cross-linking density is obviously gained by varying the concentration of associating copolymers in solution, as probed by frequency sweep measurements (Fig. 10). In the diluted regime, associating chains are well separated in solution and intermolecular associations are limited, resulting in no gelation. In practice, the Newtonian flow of the material at a low concentration is evidenced by the power law frequency dependence of around 2 and 1 for storage and loss modulus, respectively. Above a critical gel concentration, the formation of active intermolecular bridges between overlapping chains generates a percolated network, as illustrated in Fig. 12(a).

The resulting hydrogel shows the characteristic features of covalently bound materials, provided that the stoichiometric amount of metal ions is used with respect to ligands. A comparison with the blank shown in Fig. 3 provides clear evidence that the effects observed upon increasing polymer concentration are not due to plausible entanglements but well to elastically active metal–ligand bridges between the UHMW polymer chains. Further increasing the concentration in associating copolymer enhances the formation of bridges at the expense of intramolecular loops, resulting in a net increase in the density of elastically active chains. In practice, strengthening of the viscoelastic response can be monitored by an increase in both dynamic storage and loss moduli with concentrations (Fig. 10).

To provide a more quantitative analysis of the results, the number-average molecular weight of a polymer strand between two cross-linking nodes, M_x, can be assessed at different concentrations. These values can be estimated from the measured plateau modulus relative to the thermal

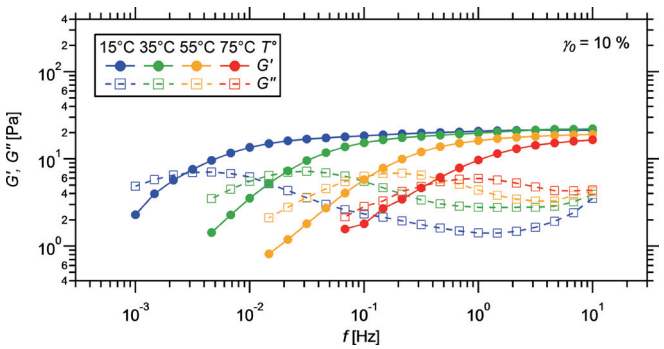

FIG. 8. Frequency sweeps monitoring the dynamic mechanical properties of a ligand-decorated UHMW copolymer solution (1000 kg/mol; 5% stickers; 1.25 wt. %) in the presence of 2 eq. of Al(III) trivalent metal salt at different temperatures.

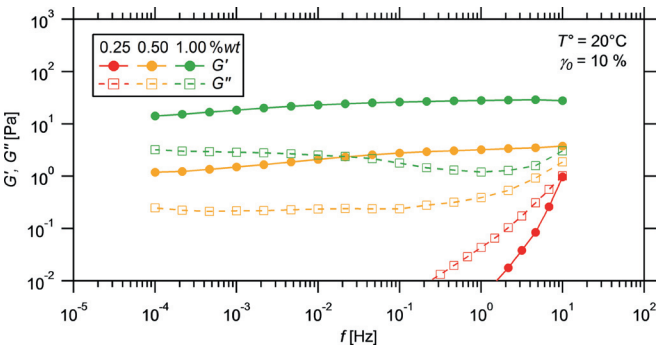

FIG. 10. Frequency sweeps monitoring the cross-link density of ligand-decorated UHMW copolymer solutions (2000 kg/mol; 5% stickers) of different concentrations in the presence of the stoichiometric amount of Fe(III) trivalent metal salt.

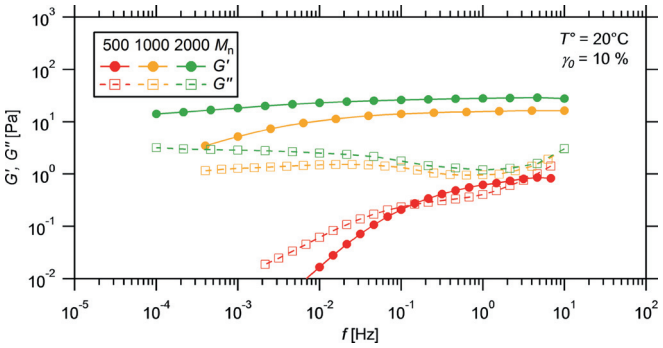

FIG. 11. Frequency sweeps monitoring the dynamic mechanical properties of solutions of ligand-decorated UHMW copolymers (5% stickers; 1 wt. %) of various lengths in combination with the stoichiometric amount of Fe(III) trivalent metal salt.

agitation energy via $M_x = cRT^\circ/G'$, where c is the concentration of polymer. At all concentrations, the average molecular weights of the network strands are found to be very high, precisely M_x (1%) ≈ 800 kg/mol and M_x (0.5%) ≈ 3500 kg/mol, for the ligand-decorated UHMW copolymer solutions (2000 kg/mol; 5% stickers) in the presence of the stoichiometric amount of iron(III) cations (Fig. 10). In particular, the calculated values largely exceed the number average molecular weight between ligands placed along the chain, which is theoretically expected for an ideally percolated network.

These results give credit to the fact that many metallo-ligand bonds are involved in intrachain complexation rather than elastically active bridges between the UHMW polymers. At a concentration of 1 wt. %, very long subchain segments are trapped into the network architecture, which indicates that the concentration of polymer approaches the percolation threshold. At a concentration of 0.5 wt. %, the calculated number-average molecular weight of a network strand is larger than the number-average molar mass of the UHMW chains. In this concentration regime, the density of cross-links is so low that a significant fraction of the chains is either not incorporated into the supramolecular network or only acts as extenders between network nodes. The proximity to the critical gelation concentration is validated by the frequency sweep measurement performed at a concentration of 0.25 wt. %, indicating a pure Newtonian behavior for the solution.

D. Influence of the chain length

The effect of the chain length is additionally tested by comparing the dynamic mechanical properties of metallo-supramolecular hydrogels prepared from associating copolymers of different average molecular weights, 500, 1000, and 2000 kg/mol, at a given concentration. As shown in Fig. 11, decreasing the chain length of the associating copolymers leads to a dramatic drop in both elastic and viscous responses to oscillatory shear. This drop is more pronounced in the low frequency regime so that a modulus cross-over is observed for the low molecular weight polymer. Even at the stoichiometry of the metal–ligand complexes, the macroscopic relaxation of the materials becomes thus possible, which highlights the role of network topology in relaxation mechanisms.

When shortening the length of the associating copolymers, the number of dangling chain ends in the architecture of the gels increases inevitably as illustrated Fig. 12(b). These mobile extremities are not trapped into the network scaffold and thus facilitate stress relaxation via fluctuation mechanisms. The chains gradually reorganize themselves in space, moving in relation to each other and liberating the constraints created during deformation. In turn, this reorganization locally enhances the degree of freedom of neighboring segments, which may ultimately open the way for the diffusive relaxation process of the entire chain. This is notably observed for the low molecular weight copolymer gels, where a terminal flow regime is clearly evidenced by the frequency-dependence of both moduli (Fig. 11).

For short associating copolymers, the number of ligands and thus anchoring points per single chain is indeed reduced so that segmental motions are less restricted. According to theoretical predictions [2], the relaxation time of the chains will decrease proportionally with the square of the number of interchain sticky bonds per polymer. On the other hand, the diffusional motions of high molecular weight copolymers are dramatically restricted by the cooperative effect of multiple stickers, which is apparently irrespective of their dissociation dynamics at the metal–ligand stoichiometry. Again, these results demonstrate that the macroscopic relaxation of this particular class of supramolecular materials is rather a diffusion-limited process that should be dissociated from the dynamics of the associating units themselves.

E. Influence of the density of the ligand

The number of ligands incorporated along the chain can be easily tuned during the synthesis by varying the ratio between the different comonomers, while keeping the chain length constant. Precisely, the initial feed in functional comonomers is adjusted to 1, 3, or 5 wt. % during the synthesis of the copolymer. This allows investigating the effect of

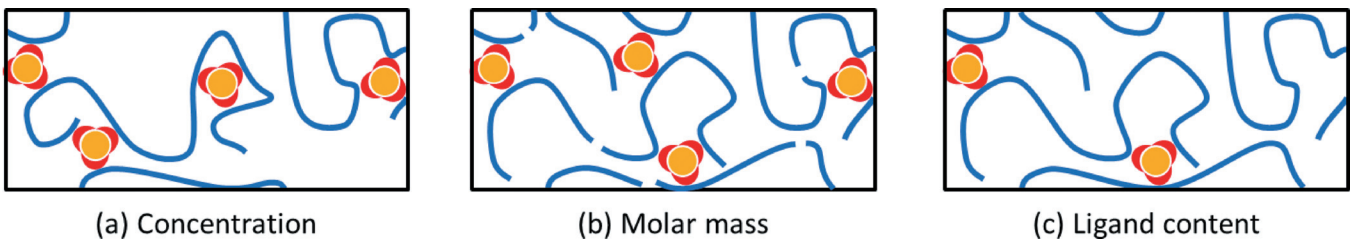

FIG. 12. Schematic representations of metallo-supramolecular networks built from ligand-decorated UHMW copolymers and trivalent metal ions according to different parameters.

the number of anchoring groups per chain on the rheological properties of the self-assembled hydrogels [Fig. 12(c)]. If the relaxation is governed by the life-time of transient associations, decreasing their concentration should lead to renormalized stress relaxation dynamics that is shifted to a longer timescale [2]. This renormalization is due to the lower probability for a dissociated chain segment to find a free coordination site in the near environment for ligand exchange. On the other hand, the relaxation dynamics of the material should be enhanced as the number of anchoring ligands per chain is reduced [2].

Experimentally, the macroscopic relaxation of the material is accelerated at low sticker contents, as attested by frequency sweep measurements (Fig. 13). Again, this observation indicates that the segmental dynamics of the building blocks plays a major role in the material relaxation. These long range motions are indeed exalted as the number of anchoring stickers is reduced along the chain. On the other hand, no direct correlation can be established with the lifetime of the transient metal–ligand bonds, which is dictated by the kinetic stability of the complexes. At low sticker density, the formation of a percolated network is also compromised by the lack of interchain connections. In accordance with a decreased cross-link density illustrated in Fig. 12(c), a weakening of the viscoelastic response of the gels is also recorded when lowering the number of associating stickers. In essence, the rheological signature of the material can be thus gradually varied from that of an essentially highly elastic polymer gel to that of a viscous polymer solution.

F. Nonlinear response

The influence of the strain amplitude on the rheological properties of the metallo-supramolecular hydrogels is investigated by sweeping amplitudes of oscillation in the dynamic test. At low deformations, both storage and loss modulus remain constant with the strain amplitude, which corresponds to the linear viscoelastic regime. Under those conditions, strain on the sample increases linearly with the stress amplitude and elasticity dominates over viscous effects. At a certain point, deviations from linearity are observed beyond which the material structure becomes affected by mechanical forces. A crucial but still not well understood aspect of supramolecular gels is their behavior under such a large amplitude

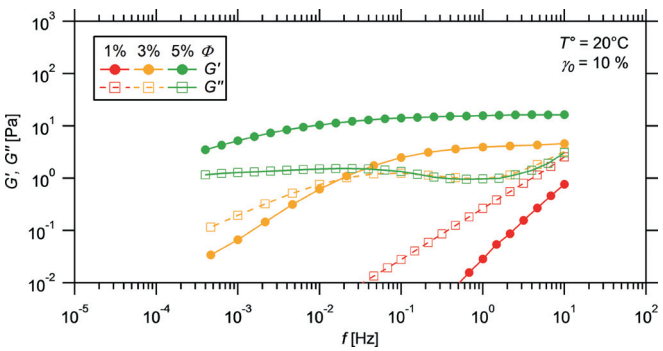

FIG. 13. Frequency sweeps monitoring the dynamic mechanical properties of solutions of ligand-decorated UHMW copolymers (1000 kg/mol; 1 wt. %) of various ligand contents with the stoichiometric amount of Fe(III) trivalent metal salt.

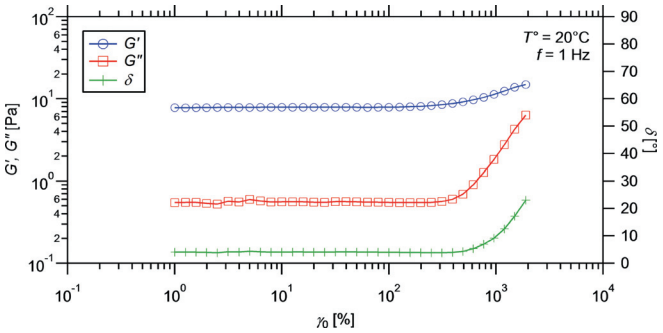

FIG. 14. Strain sweep monitoring the yield of a ligand-decorated UHMW copolymer solution (1000 kg/mol; 5% stickers; 1 wt. %) in the presence of the stoichiometric amount of Fe(III) trivalent metal salt.

oscillatory shear. In this regime, the interactions between associating polymer chains are mechanically altered by shear forces, which complexify the analysis of their rheological signature.

When the deformation exceeds a critical value, huge shear forces on samples are generally responsible for the apparent yielding of the materials. In this regard, the behavior of networks built in the presence of the stoichiometric amount of metal, with respect to ligands, can be distinguished from their transient analogs that contain an excess of metal ions. In practice, the firsts show strain hardening before being ejected from the geometry gap as a consequence of very high stress (Fig. 14). This large amplitude oscillatory shear response is typically observed for chemically cross-linked or permanent networks. In transient networks, strain hardening is also generally attributed to network reorganization, leading to mechano-induced reinforcement by a shear-induced conversion of intramolecular bonds into intermolecular associations [30–32]. Other mechanisms may also be invoked such as repulsive interactions between the chains that are forced to interpenetrate one another by the shear flow [15].

On the other hand, the second category of hydrogels suffers from strain softening, that is both moduli decrease with increasing strain (Fig. 15). In this case, the reversibility of the phenomenon occurring under large oscillatory amplitude shear is addressed by coming back to small oscillation amplitudes right after the first strain sweep. In practice, both storage and loss modulus recover their original values under decreasing strain. Moreover, the same cycle can be repeated multiple times without deviation or loss in properties, therefore evidencing efficient and autonomous healing of gels. A pronounced hysteresis is however systematically observed when coming back to small deformations. This observation suggests that a certain proportion of the mechanical energy, that is, reversibly otherwise stored in the entropic distortion of the polymeric network, is dissipated during shear-induced flow of the gel. At the limit of linearity, an overshoot, i.e., a local increase in the response of gels followed by softening, is observed in the viscous modulus before material rupture. This observation might be rationalized in terms of creation and loss of the network junctions, which are continually created and destroyed due to flow energy [33,34].

Although an abrupt drop in the viscoelastic response of the gel is achieved upon increasing deformation, a smoother

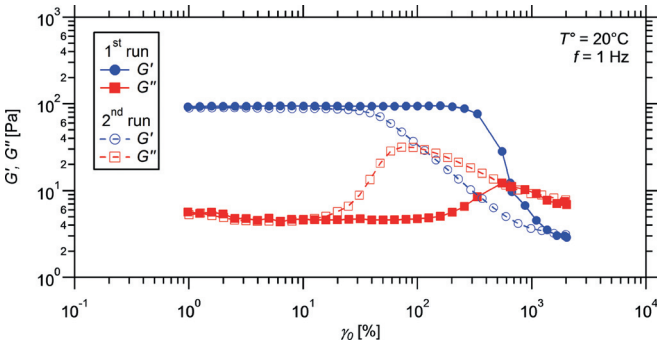

FIG. 15. Strain sweep monitoring the yield of a ligand-decorated UHMW copolymer solution (1000 kg/mol; 5% stickers; 1.25 wt. %) in the presence of an excess of Fe(III) trivalent metal salt (first run under increasing strain and second run under decreasing strain).

transition is then observed upon recovery with G' following a power law strain dependence of 1. However, the analysis of these nonlinear data must be taken with care and requires more advanced rheological characterization tools. Indeed, many inhomogeneous flows in the measuring geometries, such as shear banding [35,36], wall slip [37], elastic instability [38,39], and secondary flows [40], are susceptible to occur under a large amplitude of deformation. In addition to imperfect mechanical excitations, these nonlinear irregularities can violate the mathematical assumptions describing the stress and strain inputs. In this regard, these phenomena might be more marked for the destructuring material (first run) compared to the rebuilding network (second run). Indeed, the initial network structure confers a strong cohesion to the material that is pushed out of equilibrium under large amplitude oscillatory shear beyond its yield point. On the other, the restructuring polymer solution might show less flow heterogeneities, like shear banding, due to the lack of structuration. In turn, this could give rise to a quasiequilibrium viscoelastic response to large amplitude deformations.

V. CONCLUSIONS

In this study, the rheological behavior of UHMW linear polymers sparsely decorated with chelating ligands was investigated in aqueous solutions. The addition of selected metal ions to these systems resulted in the formation of percolated network structures whose characteristics were modulated in a controllable fashion. The influence of several parameters was tested on their relaxation dynamics, which are the nature and amount of metal ions, the concentration and length of the associating copolymers, the density of the ligand along the chains, and the temperature. The rheological signature of the gels was varied from that of a permanent rubbery gel to that of a transient swollen network by doping the system with an excess of metal ions or decreasing the number of ligands per single chain.

Hence, the results afford a direct observation that the macroscopic relaxation of strongly associated supramolecular networks can be apparently dissociated from the intrinsic lifetime of the associating units, provided that diffusion processes do not lead to successful chain relaxation at the microscopic level. This study also highlights the primary importance of the number of anchoring stickers, as topological constraints, and free associating sites, as prerequisites for sticker exchange, in the diffusional dynamics of the polymer chains. These conclusions are in line with the traditional picture of single sticker hopping where each sticky chain needs to dissociate by breaking all existing bonds in order to relax. These findings can be applied to understand the dynamics in supramolecular polymer networks where the stickers form well defined associations and also allow for the examination of assumptions made in the related theoretical models.

ACKNOWLEDGMENTS

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