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Rheological Behavior of Shear-Responsive Metallo-Supramolecular Gels

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Stimuli-responsive polymers (SRPs) exhibit a change in properties upon application of an external stimulus, such as a change in temperature, ionic strength, pH, or electric, magnetic, or mechanical fields or by chemical or biological analytes. Examples include liquid crystal polymers,[1] polymer solutions and gels, which undergo a change in phase morphology,[2] electro- and magnetorheological fluids,[3] and electroactive polymers (EAPs).[4] SRPs have potential applications as smart films in sensors, actuators, electrooptic devices, etc., where the rheological properties become important. Specifically, it is advantageous to have thixotropic character, i.e., under high shear stresses, typical of processing conditions, the film behaves as a free-flowing liquid, whereas at low stresses, relevant to postprocessing conditions, it exhibits high viscosity or gellike properties. One possible mechanism to achieve thixotropic properties is to utilize self-assembling monomers in which binding sites are incorporated to promote formation of a supramolecular (noncovalent) network, weak enough to be destroyed under high stresses and yet able to re-form upon removal of stress.[5,6]

Recently, some of us reported[7] the synthesis of a new class of responsive metallo-supramolecular polymers[8] based on the use of metal−ligand interactions. The tridentate ligand, bis(2,6-bis(1′-methylbenzimidazolyl)-4-hydroxypyridine (HO−BIP) was used to create a bis-ligand functionalized compound, **1**, by reaction of HO−BIP with diiodopentaethylene glycol.[7] Since the BIP ligand can bind transition metal ions in a 2:1 ratio, and lanthanoid ions in a 3:1 ratio, it is possible to create gels by mixing compound **1** with combination of lanthanoid (cross-linker) and transition metal (chain extender) ions (Figure 1).[7] Addition of 3 mol % La(III) nitrate to a $CHCl_3/CH_3CN$ solution of **1** followed by 97 mol % Zn(II) perchlorate, relative to the total number of BIP ligands, results in spontaneous formation of a gel. Thus, the metallo-supramolecular gel, **1:Zn/La**, can be prepared and, upon removal of solvent, can be reswollen with pure CH_3CN. These metallo-supramolecular polymer gels are thixotropic, since, on shaking, they form a free-flowing liquid, which, upon standing, re-forms the gel state. In this communication, we report the first rheological analysis of the thixotropic properties of a typical metallo-supramolecular gel, namely **1:Zn/La**.

A dynamic controlled stress sweep was performed[9] on a **1:Zn/La** gel (11 wt % solid swollen in acetonitrile). The stress was ramped at a frequency of 1.0 Hz, from 80 to 330 Pa, during a time period of 7 min, and the storage and loss moduli, G' and G'', were monitored. The storage modulus is a measure of elasticity and the loss modulus a measure of viscous behavior. Figure 2a shows the variation of G' and G'', as well as the shear strain, γ. At small stresses, the material exhibits the properties of a strong gel, i.e., $G' \gg G''$, with a storage modulus of 1.2×10^4 Pa. As the stress is increased, the strain increases linearly, i.e., G' remains constant, emblematic of linear viscoelastic behavior. The gel is highly responsive in the sense that, after only a small amount of creep, when the stress reaches ∼155 Pa, a catastrophic yield event occurs, the storage modulus drops to essentially zero, and the strain increases dramatically (to ∼40 000%). The stress and strain at which the stress−strain relationship begins to deviate from linearity are defined as the yield stress ($\sigma_c = 155.4$ Pa), and yield strain, ($\gamma_c = 1.3\%$), respectively. Beyond the yield event, the strain increases linearly, indicative that the gel has transformed to a Newtonian sol. The dynamic viscosity falls (Figure 2b) to a steady-state value of $\eta^* = 0.0095$ Pa s, corresponding to a reduced specific viscosity η_{sp}/c = 250 mL/g, indicative that the network has been degraded to non-cross-linked fragments.[10]

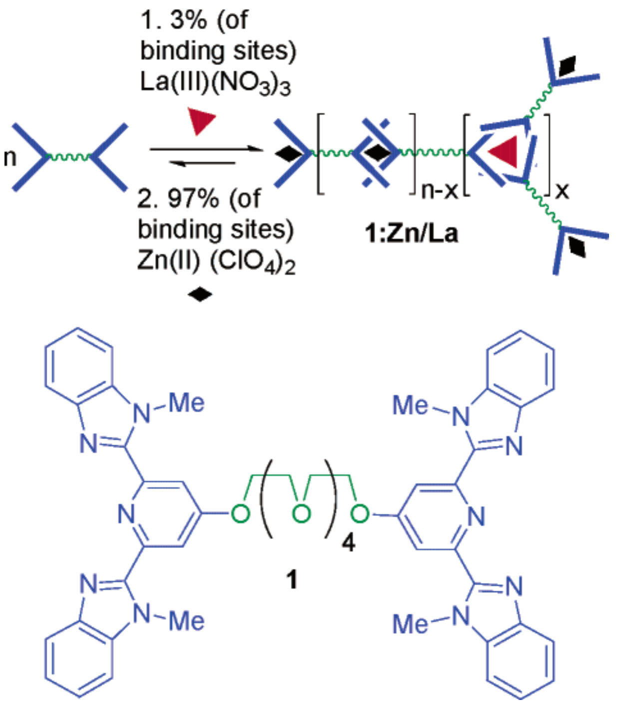

Figure 1. Schematic representation of the formation of a metallo-supramolecular gel using a combination of lanthanoid and transition metal ions mixed with monomer **1**.

It is interesting to compare the experimental value of the storage modulus, $G' = 1.2 \times 10^4$ Pa, against that calculated using the classical theory of rubber elasticity. For the latter, we may select the result obtained, assuming affine deformation of junction points:[11]

$$G'_{\mathrm{affine}} = RT\nu\phi^{-1/3} \tag{1}$$

where R is the gas constant, T is absolute temperature, ν is the number of elastically effective network strands per unit volume of the dry network, and ϕ is the volume fraction of the network at swelling equilibrium. Alter-

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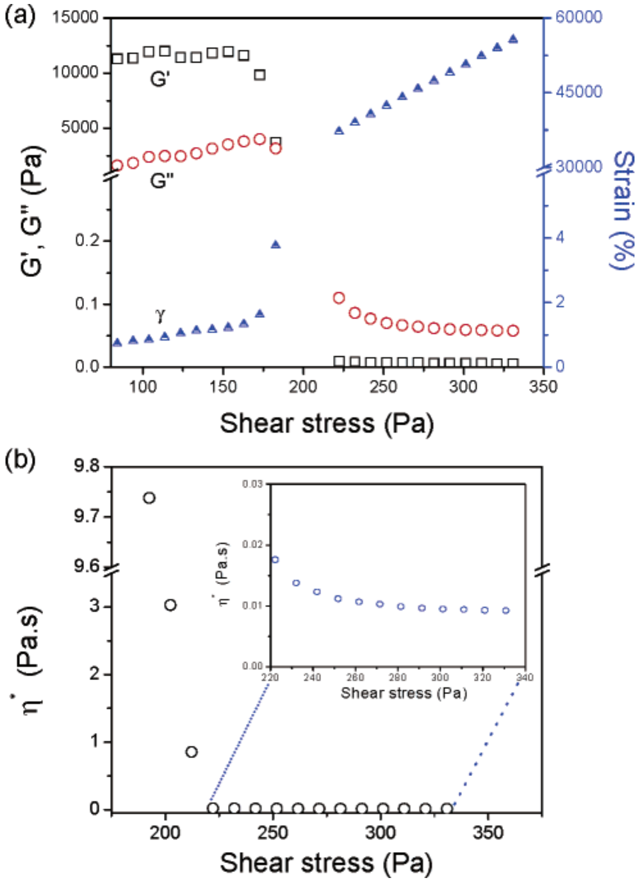

Figure 2. (a) Oscillatory shear stress sweep of the 11 wt % **1:Zn/La** gel annealed in acetonitrile for 40 min after preshearing into the sol state. The storage and loss moduli, and shear strain are monitored as a function of applied stress; (b) Viscous flow beyond the yield point for the gel. The dynamic viscosiy is plotted vs applied shear stress. The inset highlights the decrease of η^* toward steady-state Newtonian flow.

natively, we may use the result derived for mobile cross-links:[12,13]

$$G'_{\text{phantom}} = RT(\nu - \mu)\phi^{-1/3} \qquad (2)$$

where μ is the number of network junction points.

From the composition of the system, which is 0.0757 M in **1** and realizing that the number of cross-links amounts to 2% of the molar concentration of [**1**], we compute the theoretical cross-link density, $\mu = 1.515 \times 10^{-3}$ M. Moreover, since each junction point is trifunctional, and each network strand is anchored at a junction point, it follows that there are 1.5 network strands per junction point. Thus, $\nu = 1.5 \times \mu = 2.273 \times 10^{-3}$ M. We compute the volume fraction of the swollen network to be $\phi = 0.086$. Using these results, we obtain $G'_{\text{affine}} = 2.74 \times 10^4$ Pa, and $G'_{\text{phantom}} = 0.915 \times 10^4$ Pa. Thus, the experimental result falls between the two theoretical values, consistent with a previous study of end-linked poly(ethylene oxide) networks.[10] In fact, at the small deformations used in our experiments, it is expected that the networks will deform affinely. The discrepancy indicates there are fewer elastically effective chains than predicted for a perfect network. In general, this can be assigned to elastic losses because of incomplete reaction, giving rise to dangling ends, or the formation of loop structures, due to intramolecular binding events,[14] which are more likely to occur at low volume fractions. Often, however, such effects are offset by increases due to chain interaction or topological entanglements.[13,14] In the present study, we deduce that the low modulus may arise because a substantial fraction of metal ions are not fully complexed, and/or because of elastic losses through macrocycle formation.

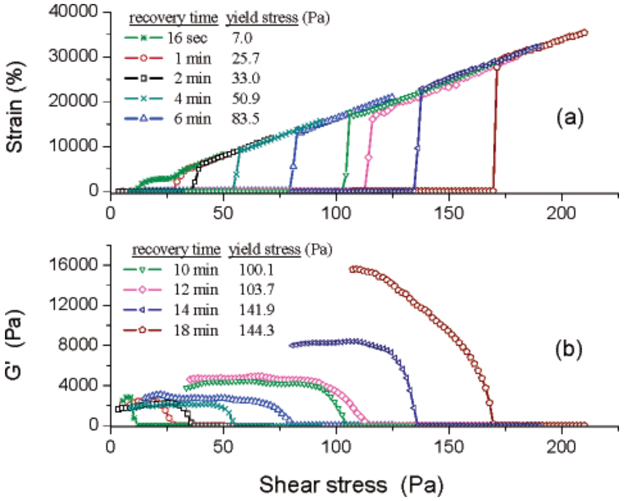

Figure 3. Reconstitution of the presheared 11 wt % **1:Zn/La** gel after yield is monitored by repeated oscillatory shear stress sweep as a function of increasing recovery time: (a) linear strain dependence indicates Newtonian flow after yield point; (b) the storage modulus increases with increased recovery time.

The recovery of the gel state was monitored by subjecting the presheared gel to repeated dynamic shear sweeps, performed after increasing recovery periods, as shown in Figure 3. Network reconstitution begins almost instantaneously, since G' reaches a substantial value after only 16 s, at which point, moreover, $G' \gg G''$. The results suggest two further regimes of structural recovery, depicted in Figure 4, which summarizes the dependence on recovery time of G' and G'', η^*, σ_c, and γ_c, estimated as discussed for Figure 2a. Initially, up to ca. 5 min, G' and G'' change very little, whereas σ_c increases monotonically, because of an increase in yield strain, γ_c, since $\sigma_c = G^*\gamma_c$. Subsequently, G' increases strongly, the yield stress also increases, while the yield strain decreases. As noted above, theory suggests $G' \sim \nu kT$, where ν is the number density of elastically effective strands. The yield stress is affected not only by ν but also by the ductility as measured by γ_c. Apparently, therefore, the cross-link density of the initially re-formed network remains approximately constant during the first phase, but the ductility increases with extent of reaction. This suggests the formation of a relatively loose network, with dangling ends rather than cross-links, in contact with a relatively large sol fraction. The sol phase may consist of molecules with free BIP ligands and/or some higher order self-assembled species. The next step involves incorporation of these elementary species from the sol phase into the network primarily via an increase in the number and length of the dangling ends, the number of elastically effective network strands remaining essentially constant. Subsequently, the cross-link density increases steeply, which involves binding of the dangling ends into the network. We note that the modulus of the fully reconstituted gel (measured after 18 min recovery period) is slightly higher than the freshly formed gel (1.5×10^4 vs 1.2×10^4 Pa). This presumably reflects some loss of solvent through evaporation during this relatively protracted experiment (5 h), coupled to an

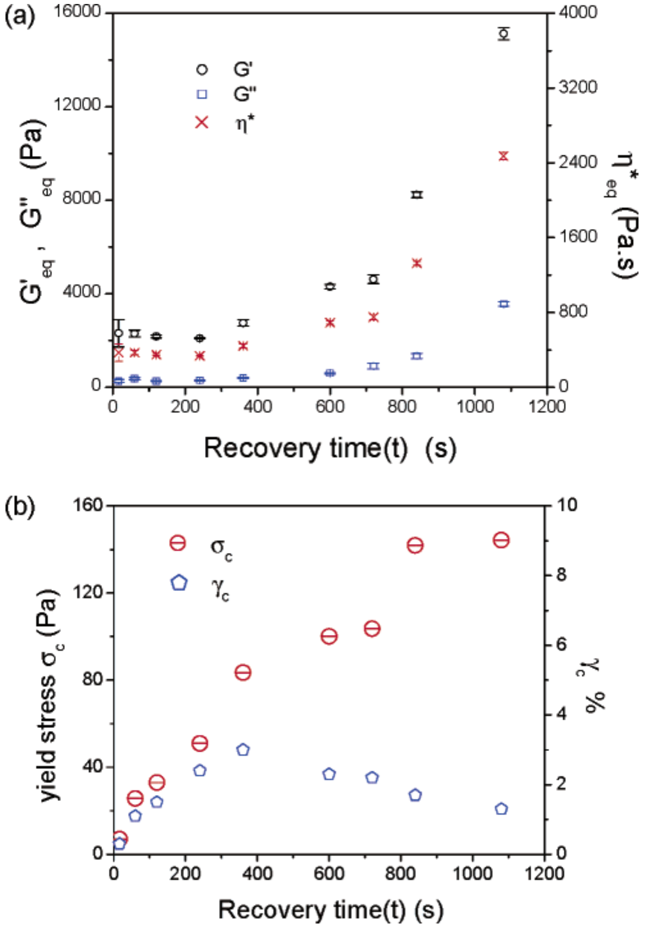

Figure 4. Dependence on recovery time of (a) storage and loss moduli G' and G'' and dynamic viscosity η^* and (b) yield stress σ_c and yield strain γ_c for the 11 wt %. **1:Zn/La** gel prior to yield (data extracted from stress sweep curves shown in Figure 3).

increase in the number of elastically effective strands. Thus, we do not extend the experiment further.

To summarize, rheological analysis was performed on a metallosupramolecular gel formed via sequential binding of monomer **1** with 3 mol % La(III) nitrate followed by 97 mol % Zn(II) perchlorate and swollen in acetonitrile. The system **1:Zn/La** at a concentration of 11 wt %, forms a shear-responsive gel, with a well-defined yield point at which it forms a Newtonian sol. Partial reconstitution of the network takes place instantaneously (within 16 s), but complete regeneration of the preexisting gel requires ~18 min. Reassembly appears to be a three-step process. After initial formation of a loose gel, the storage modulus remains essentially constant but the yield stress and strain increase linearly. Subsequently, the storage modulus increases strongly and the yield strain decreases. A possible interpretation is that the initial loose network is formed primarily via 2:1 ligand:Ln(II) or ligand:Zn(II) complex formation, with many dangling chain ends. The final phase could involve conversion of the 2:1 Ln(II) complexes into 3:1 cross-linking sites and/or the formation 2:1 Zn(II) complexes which tie up the loose chain ends. An alternative mechanism could involve the metal ion induced self-assembly of **1** into hierarchical cross-linked species that subsequently form the gel upon aggregation. We are currently looking into these two possible mechanisms in more detail.

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