Cross-Linked Polymers

Strong Means Slow: Dynamic Contributions to the Bulk Mechanical Properties of Supramolecular Networks**

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The desire to control rationally, through small-molecule synthesis, the properties of bulk materials has led to supramolecular approaches to, for example, polymers,[1,2] strong and weak organogels,[3] amphiphilic assemblies,[4] and liquid crystals.[5] In these materials, specific and well-defined interactions between molecules contribute to bulk material properties on two levels: structure and dynamics. Although the dynamic nature of the defining interactions is often the attribute that distinguishes supramolecular materials from their covalent counterparts,[6] direct mechanistic studies of the molecular contributions to the dynamic properties of materials are less abundant than structural studies.[7] Herein, we report that a simple structural variation in the networks of supramolecular sols and organogels provides a direct and quantitative measure of the relationship between molecular dynamics and macroscopic rheological properties. The approach is akin to a macromolecular "kinetic isotope effect", in that kinetic contributions to rate-determining processes are revealed by the differences in two isostructural systems. We find that it is the dynamics of molecular cross-links, much more so than their thermodynamics, which are specifically and quantitatively responsible for the bulk viscoelastic properties of the supramolecular networks.

The system under consideration is poly(4-vinylpyridine) (PVP) that is cross-linked by bis(M^{II}–pincer) compounds **1** (see Figure 2) derived from the work of van Koten[8] (M = Pd or Pt, Figure 1).[9] We recently reported that simple steric effects in the alkylamino ligands of **1** and related compounds change the rate of ligand exchange by approximately two orders of magnitude while leaving the thermodynamics of association effectively constant.[10] This independent control of dynamics is particularly significant; cross-linkers **1a** and **1b** (Figure 2) are structurally identical components within the network, and so their similar thermodynamics ensure that the extent and nature of cross-linking is essentially the same in the samples prepared from them. By extending the family of cross-linkers to the Pt^{II}–pincer molecules **1c** and **1d** (Figure 2) we are able to probe the effect of a wide range of molecular dynamics.

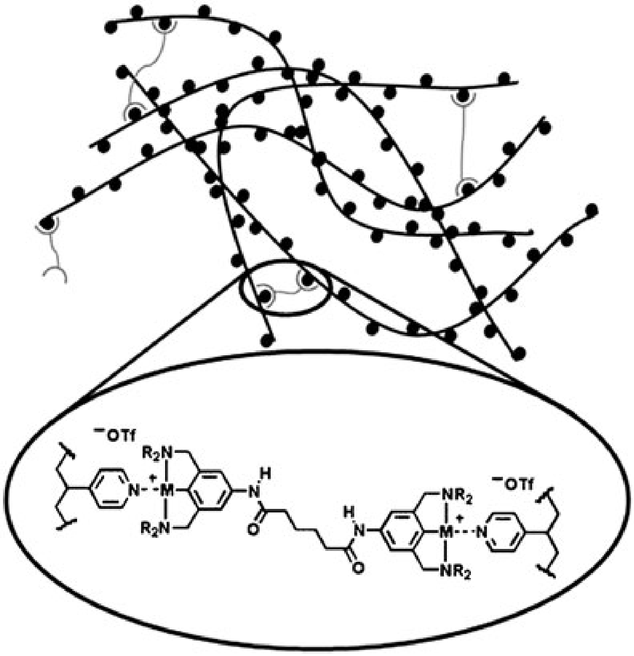

Figure 1. Schematic representation of reversible cross-links between poly(4-vinyl pyridine) through coordination with bis(M^{II}–pincer) complexes; OTf = $[CF_3SO_3]^-$.

The addition of 2% (by functional group) **1b** to a 100 $mg\,mL^{-1}$ DMSO solution of PVP (Aldrich, $M_r = 60\,000$) gives rise to a clear, thick, deep yellow solution whose viscosity is approximately 2000-times greater than that of PVP alone (33 Pa s vs. 0.016 Pa s). Two control experiments confirm that the viscosity increase is due to coordinative cross-linking of the PVP by **1b**. First, the viscosity does not increase upon the addition of the same quantity of monomeric

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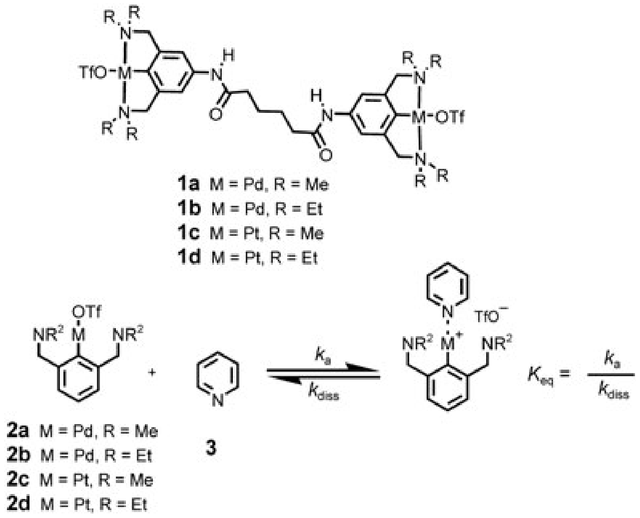

Figure 2. Structure of pincer-based dynamic cross-links **1a–d** and the model system **2** used to determine thermodynamic and kinetic parameters of pyridine coordination.

2b, so coordination to PVP alone is not responsible for the change in flow properties. Secondly, the viscosity of **1b**-PVP reverts back to that of a free-flowing solution with the addition of dimethylaminopyridine, which competes with the PVP side groups for the metal centers. The viscosity of the **1b**-PVP solutions depends on the concentration of **1b**. At constant total weight %, the solution viscosity increases monotonically with added **1b**, up to a viscosity of 550 Pa s at 5% functional group equivalents. These solutions are Newtonian, that is, their viscosities are independent of steady shear rate across the range examined (see Supporting Information).

The faster dynamics in cross-linker **1a** provide a mechanism by which to evaluate the dynamic contributions of ligand exchange to the properties of the network. The thermodynamics and kinetics in **1**-PVP are reported reliably by model system **2**-**3** (Figure 2; not accounting for cooperativity, the effects of which we assume to be equivalent in all systems),[10,11] and NMR spectroscopy measurements on **2a**-**3** and **2b**-**3** reveal nearly identical association constants of 35 M^{-1} (**2a**-**3**) and 29 M^{-1} (**2b**-**3**), in [D$_6$]DMSO. The effective concentration of pyridine in 100 mg mL^{-1} PVP is approximately 1 M, and so > 97% (higher if cross-linking is cooperative) of the metal sites are coordinated to PVP side groups. The ligand-exchange dynamics, however, are substantially different owing to increased steric bulk at the metal center of **2b**. For mixtures of 20 mM **3** and 10 mM **2**, the ^{1}H NMR spectrum of **2b**-**3** shows distinct signals corresponding to "free" (solvent-coordinated) and "bound" (pyridine-coordinated) metal centers, and the exchange between states is quantified by EXSY to be 15 ± 1 s^{-1}. We expect the rate of exchange to be 70–100-times faster in **2a**-**3**, and, consistent with that expectation, the corresponding NMR signals are coalesced owing to fast exchange. The coalescence places a lower limit of 200 s^{-1} on the exchange but does not permit an independent measurement. Thus the networks **1a**-PVP and **1b**-PVP are nearly identical in their equilibrium structure and extent of cross-linking, but they differ greatly in the dynamics of the interactions between the cross-linkers and the PVP backbone. The effect of those dynamics is dramatic. At 5% cross-linker, the viscosity of 100 mg mL^{-1} **1a**-PVP is only 6.7 Pa s—a factor of 80 less than that of the isostructural network **1b**-PVP. While the association constants are not identical, the effect of greater cross-linking in **1a**-PVP would be to increase the viscosity of **1a**-PVP relative to **1b**-PVP, the opposite effect to that observed. The dynamics dominate even the extent of cross-linking; 5% **1a**-PVP is less viscous, by a factor of 5, than 2% **1b**-PVP, despite having at least 2.5 times as many cross-links intact at any given instant.

The dynamic range of the experiments can be extended almost another five orders of magnitude by employing the platinum analogues **1c** and **1d** (Figure 2). The pyridine association constants of these compounds (again measured with the mononuclear analogues **2**) are greater than in **2a** and **2b** (8000 M^{-1} for **2c** and 4000 M^{-1} for **2d**), but more importantly the rate constants for ligand exchange are 3–5 orders of magnitude smaller (0.026 ± 0.05 s^{-1} for **2c** and 0.0006 ± 0.0001 s^{-1} for **2d**). These materials are gels at room temperature, and their viscosities are again correlated with molecular exchange dynamics, although absolute values for **1d**-PVP are outside the range accessible in our rheometer (Table 1).

Table 1: Absolute and relative thermodynamic, dynamic, and materials properties of pyridine coordination and the resulting supramolecular network solutions.[a]

Compound	K_{eq} [M^{-1}][b]	k_{ex} [s^{-1}][c]	η [Pa s][d]	K_{eq} [rel]	k_{ex}^{-1} [rel]	η [rel]
1a	35	≈1100[e]	6.7	1.2	0.014	0.012
1b	29	15[f]	550	1	1	1
1c	8000	0.026[f]	240000	280	600	440
1d	4000	0.0006[g]	> 240000[h]	140	25000	> 440

[a] 100 mg mL^{-1} of **1**-PVP in DMSO, 5% functional group equivalent relative to poly(4-vinyl pyridine)). [b] Taken from model system **2**-**3**; 298 K; uncertainty ±20%. [c] Taken from model system **2**-**3**; 298 K; unless otherwise stated, uncertainty ±10%. See Supporting Information for details. [d] Taken from low-frequency plateau in oscillatory shear measurements; 293 K. [e] Extrapolated relative to **1b** using ref. [10]; estimated relative uncertainty ±15%. [f] ^{1}H NMR EXSY spectroscopy; 298 K. [g] Ligand exchange monitored by ^{1}H NMR spectroscopy; 298 K. [h] more viscous than **1c**-PVP by inspection, value out of the range of the rheometer used.

The results offer mechanistic insights into the molecular origins of flow resistance in PVP supramolecular networks. The network responds to an applied stress through sequential, individual dissociation and re-association events, and these dynamics dominate over contributions from the intact supramolecular structure. It is noteworthy that the relationship appears to hold even when comparing **1b** and **1c**, where the association constants differ by a factor of approximately 300; relative viscosities are directly proportional to cross-link lifetime without considering the fraction of time for which the cross-links are dissociated. The entanglements that govern the viscoelastic response of these fluids are therefore specifically molecular in nature, rather than the result of increased friction owing to the size and/or physical entanglements of cross-link-induced aggregates. In this respect, the results described herein contrast with our previous study of linear polymeric assemblies defined by a similar coordination motif. In that work, the viscosities of the supramolecular polymer solutions reflected only the equilibrium structure of the assemblies without a measurable contribution from main-chain dissociation dynamics.[10]

van Esch and Feringa[12] and others[3] have described the importance of supramolecular organogels and the difficulty in probing the structural basis of their properties.[13] Reversible cross-linking, both specific[2,14] and nonspecific,[15] is well-known and is central to a range of fundamental and applied goals. In all cases, the intermolecular interactions contribute both to the equilibrium structure and the nonequilibrium dynamics of the materials. Herein we have shown that it is dynamics rather than the equilibrium structure that are paramount in determining the viscoelastic response of a family of cross-linked supramolecular polymers, a result that is in contrast to the behavior observed in linear analogues. The ability to address quantitatively the relative influence of dynamics and thermodynamics in supramolecular materials provides a mechanism to test the assumptions of old[16] and new[17] models of rheological behavior (e.g. transient network models, which appear to hold in this case) and to probe the role of cross-linking in important but challenging environments, such as grafted polymer brushes, thin films, composites and blends, and near the border of phase transitions. The results described above emphasize that under the nonequilibrium conditions of an applied mechanical stress, "strong" really means "slow". A quantitative understanding of when, where, and how molecular dynamics influence materials properties, therefore, provides an essential framework upon which organic chemists can contribute to materials engineering.

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