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Main-chain dynamics in metallo-supramolecular polymers: from solution to elastomeric fibres‡

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Main-chain reversible coordination polymers were formed from bis-platinum pincer complexes **2** and bis-pyridine-terminated poly-THF-bis-Py **1**. The properties of the polymers, both in solution and in fibres drawn from solution, are characterised. Structural perturbations that influence the ligand exchange (dissociation) rate of the defining metal–ligand bond have no measurable impact on either the viscosity of the polymer solutions or the ultimate yield behaviour of the fibres.

Keywords: supramolecular polymers; metal–ligand coordination; dynamics

1. Background and introduction

Main-chain reversible polymers (RPs) consist of molecular building blocks that comprise two or more molecular recognition end groups that are covalently linked (*1–12*). At equilibrium, reversible association of the end groups defines the main chain of linear polymers (*5–12*). The structure and properties of an RP depend on the strength and specificity of the association, the conformational flexibility of the molecule, the concentration of the monomer and the chemical and physical environment of the system. Because of their reversible nature, RPs offer promise as environmentally benign materials due to the ease of processing and recycling and the absence of a polymerisation catalyst. RPs are furthermore unique relative to their covalent analogues in that fracture at the reversible junctions along the main chain can be repaired, because end-group dissociation and reassociation is a dynamic equilibrium process (*7*, *13*). Reported RPs encompass a range of structural motifs, phase behaviour (*7*, *9*, *11*, *14–16*) solution and solid-state mechanical properties (*8*, *17*, *18*) and environmental responsiveness (*18*). In the light of this themed journal issue, it is particularly appropriate to highlight Dmitry Rudkevich's early contributions in the areas of polymeric encapsulation complexes, work that was performed in collaboration with Ron Castellano and Julius Rebek and that, as well as any, illustrates the rich potential of the supramolecular blend of molecular and material response (*9*).

Under non-equilibrium conditions such as those imposed by mechanical stress or concentration gradients, the dynamic nature of the association/dissociation along the main chain might contribute to the bulk properties of RPs. In order to probe the influence of main-chain reversibility on the dynamic response of an RP, it is desirable to separate the contributions from main-chain dissociation (given by the kinetic rate constant k_d, Figure 1) from the effect of thermodynamics (K_{eq}). This delineation is often complicated, especially in systems where association occurs at or near the diffusion rate, by the fact that K_{eq} and k_d are anti-correlated. In mechanistic studies of RPs, the inverse correlation of k_d and K_{eq} creates a persistent frustration; high K_{eq} leads to higher RP molecular weights and slower *equilibrium* polymeric dynamics, while lower k_d leads to slower *reversible* dynamics along the main chain. The response of the RP, whether controlled by the action of an intact equilibrium structure or by reversibility along the main chain, is slowed by both mechanisms.

In order to directly probe the contributions of main-chain reversibility to RP properties, we recently reported that the equivalent of a 'macromolecular kinetic isotope effect' could be used to vary k_d while keeping K_{eq} effectively constant. In this strategy, isotopic substitutions are not actually employed, but molecular contributions to rate-determining material processes are revealed by kinetic differences in two isostructural systems. The independent control of k_d relative to K_{eq} is accomplished through simple

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‡Dedicated to the memory of Dmitry Rudkevich.

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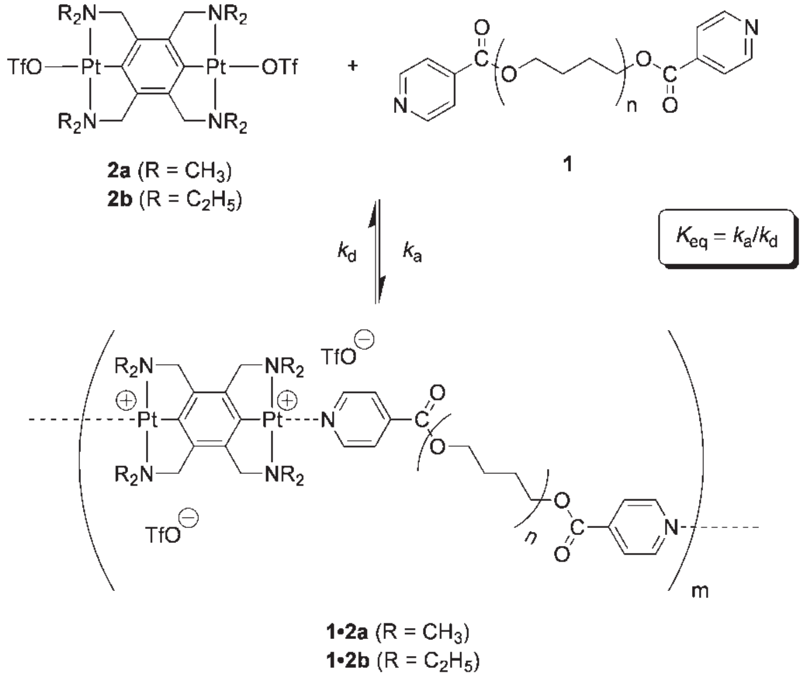

Figure 1. Main-chain RP formed by reversible metal coordination between 1,4-phenylene-bridged bis-platinum complexes **2** and poly-THF-bis-Py **1**. The association constant K_{eq} is effectively identical for **1·2a** and **1·2b**, but k_d is ~50 times faster for **1·2a**.

steric effects at the metal of square planar Pd(II) and Pt(II) complexes. Ligand exchange at square planar Pd(II) and Pt(II) typically occurs through an associative process, in which the attacking nucleophile associates to the metal centre prior to the departure of the original ligand. Because the pentacoordinate transition state is crowded relative to the reactant and product metal–ligand complexes, steric effects in the spectator ligands of the complex have a significant effect on the rate of ligand exchange, while having a minimal effect (by comparison to the transition state) on the stability of the isosteric endpoints. Pincer motifs such as those investigated extensively by van Koten and co-workers (*19*) have proven to be attractive in this regard (Figure 1) (*20*, *21*). The *N*,*C*,*N*-pincer complexes are synthetically accessible, stable and the sterics of the alkylamino ligands are easily manipulated (*22*). Substitution of R = Et for R = Me in the Pt(II) complexes (**2b** vs. **2a**, Figure 1(c)), for example, changes the rate of ligand exchange by a factor of ~50 (*23*).

We report here the incorporation of **2a** and **2b** into the main chain of RPs, and we examine the effect of changing the rate of reversibility on the mechanical properties of RP solutions and those of fibres drawn from RP solutions. The fibres are elastomeric (strains at break of up to 70%) and they support weights of up to 2.03 g for an 11 μm fibre. Across a range of concentrations, and in the solid state, the two effectively isostructural RPs exhibit indistinguishable mechanical properties. The results demonstrate that reversibility along the main chain need not imply a sacrifice in the strength of polymeric materials.

2. Experimental section

2.1 Materials

Dimethyl sulphoxide (Acros, Geel, Belgium), 1,2-dichlorobenzene (Acros) and methyl isonicotinoate (Sigma-Aldrich, St. Louis, MO, USA) were used as received. NMR solvents, DMSO-d_6, 1,2-dichlorobenzene-d_4, dichloromethane-d_2 and chloroform-d_1 were used as received from Cambridge Isotope Laboratories (Andover, MA, USA). The poly-THF-bis-pyridine compound was synthesised from the coupling reaction of Terathane (polytetrahydrofuran Mn = 2900, Aldrich) and isonicotinoyl chloride hydrochloride (Acros). Compounds **2** were synthesised as previously reported (*23*).

2.2 Measurement of Pt–pyridine association constants

The association constants K_a of metal–ligand coordination were determined by ^{1}H NMR spectroscopy using a Varian 400 MHz NMR spectrometer. For example, **2a** (3.6 mM) and substituted pyridine **3** (3.6 mM) were dissolved in DMSO-d_6. The integrations of the free and bound species were used to calculate the equilibrium constant of the complex, which is calculated in terms of the concentration of the functional groups (twice the concentration of the monomer **2a**).

2.3 Quasi-elastic light scattering

Solutions of **1** and **2** in 5/95 DMSO/1,2-dichlorobenzene were combined in a 1:1 molar ratio, verified by viscosity titration, at the desired concentration. The solutions were then filtered through a nanofilter system (0.1 μm, Whatman). Data were obtained using a Wyatt Dawn EOS with a QELS detector. The data were processed with QELS Batch software (Wyatt Technology, Santa Barbara, CA, USA). The samples were diluted to the desired concentrations for subsequent measurements.

2.4 Viscometry

All viscosity data were obtained using a Bohlin VOR rheometer with a concentric cylinder geometry (fixed bob and rotating cup). The inner cylinder diameter was 25 mm with an outer cylinder diameter of 26 mm, a bob height of 21.4 mm and a cone angle of 2.3°. The sample (~ 2 ml) was loaded into the cup, with heating when necessary to allow the material to flow into the geometry, and the bob was lowered into the cup. The sample was allowed to equilibrate to 20°C. Torque bars (98.72, 10.42 and 0.245 g cm) were chosen so that the recorded stress moduli were within 10–90% of the dynamic range of the detector.

2.5 Fibre strength

Fibres were drawn by hand from concentrated (80 wt%) solutions of **1·2** in dichloromethane using a small glass rod. Once drawn, the fibres were allowed to air dry for 2 h. The diameter of the fibre was determined by optical microscopy, using an elastomeric grid with 2 μm features as a reference background. The fibre was then wrapped around a small lock, and the lock was placed on an analytical balance. The fibre was pulled by hand at a rate of approximately 1 cm/s, and an observer noted the change in weight displayed on the analytical balance as the fibre transferred an upward force to the lock. The minimum weight (largest negative value) was recorded, and its absolute value was taken as the force at break. The force at break was divided by the cross-sectional area of the fibre, calculated from the measured diameter by assuming a cylindrical geometry.

Table 1. Ligand association constants (25°C) for bis-platinum complexes **2** with poly-THF-bis-Py **1** in DMSO-d_6.

Complex	K_{eq} (M^{-1})
1·2a	3.2×10^2
1·2b	2.4×10^2

Note: Association constants are calculated on a functional group basis (two per molecule) and the independent coordination is assumed at each Pt and pyridine site. Uncertainties: K_{eq} (± 20%).

3. Results and discussion

3.1 Solution studies

The association constants K_{eq} of metal–ligand coordination were determined by ^{1}H NMR spectroscopy in DMSO-d_6, and they are calculated and reported in terms of functional group concentration (which is twice that of monomer concentration for compounds **1** and **2**). The association constants of bis-platinum complexes **2** with polymer-tethered pyridine **1** are $3.2 \times 10^2\,M^{-1}$ and $2.4 \times 10^2\,M^{-1}$ for **1·2a** and **1·2b**, respectively, in DMSO-d_6 (Table 1). These values are similar to our previous results for coordination of substituted pyridines to bis-palladium and bis-platinum pincer complexes (*23*).

One of the main considerations in the preparation of coordination polymers with a high degree of polymerisation (DP) is to obtain a nearly exact stoichiometry between ligand and metal, because an excess of either component can act as a chain terminator for reversible polymerisation. To compensate for small uncertainties in the molecular weight of **1**, the purity of the compounds, or the measured weights of the samples, the stoichiometric ratio of ligand to metal was optimised by viscosimetric titration of **2** vs. **1** at 25°C. The resulting titration curves for **2a** and **2b**, shown in Figure 2, reflect similar behaviour.

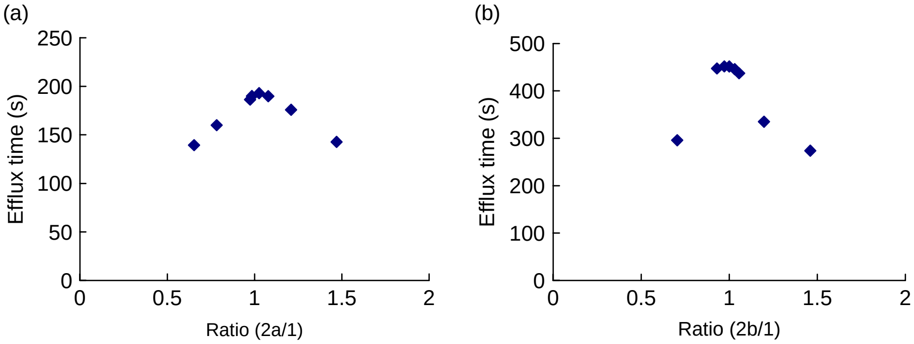

Figure 2. (a) Titration curve of 3.5 wt% poly-THF-bis-Py **1** (w/w, *1,2*-dichlorobenzene/DMSO = 50/50) by 3.5 wt% PtMeOTf **2a** (DMSO). (b) Titration curve of 5 wt% poly-THF-bis-Py **1** (w/w, *1,2*-dichlorobenzene/DMSO = 97/3) by 5 wt% PtEtOTf **2b** (1,2-dichlorobenzene).

As **2** is added to **1**, the viscosity increases until maximising at a ratio of 0.97–1.03. The increased viscosity is attributed to the formation of RPs, because the viscosity drops upon the addition of additional **2**. The maximum viscosity is obtained at nominal ratios of 1.03 for **2a**:**1** and 0.97:1 for **2b**:**1**. These samples were taken to be 'true' 1:1 samples and the stoichiometry that gave the maximum viscosity was used in subsequent experiments.

Yount et al. (*20*) recently reported that the viscosities of similar main-chain reversible coordination polymers depended only on the equilibrium structure of the RPs, and differences in dissociation rates along the polymer backbone did not contribute. To test this relationship for the **1·2** polymers, two 20 wt% solutions of 1:1 **1·2a** and **1·2b** were prepared in 1,2-dichlorobenzene/DMSO (w/w, 95/5). The viscosities of the RP solutions were measured with a Bohlin VOR rheometer (25°C), as were the viscosities of each of several samples prepared by serial dilution (15, 10, 5, 2.5 and 1.25 wt%, Table 2). The viscosities of 20 wt% **1·2a** and **1·2b** solutions were 4.7 and 3.5 Pa s, respectively, and each decreased upon dilution, reaching respective values of 4.0×10^{-3} and 4.5×10^{-3} Pa s at 1.25 wt%, respectively.

The range of concentrations and viscosities examined here is far greater than that in a previous study on related Pd coordination polymers. In the previous work, the maximum concentration studied was 7.2% by weight in DMSO, corresponding to a viscosity of 5.06 cSt (mm^2/s). These solutions were in the dilute regime, where interactions between polymers were negligible. In the present experiments, scaling laws suggest that the RPs are clearly in the semi-dilute regime above 15 wt% (data not shown), and hence, overlap between polymers contributes to the viscosity of the solutions; the chains must move through and around each other under flow. As with the Pd-based system of Yount et al., however, the viscosity of the RP solutions remains effectively independent of main-chain dissociation kinetics (Figure 3). The increased viscosity is therefore attributed to the hydrodynamics of intact, equilibrium RP structures. The equilibrium size of the RPs is expected to be essentially identical, because the association constants for pyridine coordination to **2** are similar for **2a** and **2b**.

Table 2. Viscosities of solutions of RPs **1·2a** and **1·2b** as a function of concentration in 1,2-dichlorobenzene.

	Viscosity (Pa s)	
Wt%	**1·2a**	**1·2b**
20	4.7	3.5
15	8.0×10^{-1}	4.0×10^{-1}
10	9.6×10^{-2}	8.0×10^{-2}
5	1.5×10^{-2}	1.5×10^{-2}
2.5	4.5×10^{-3}	5.0×10^{-3}
1.25	4.0×10^{-3}	4.5×10^{-3}

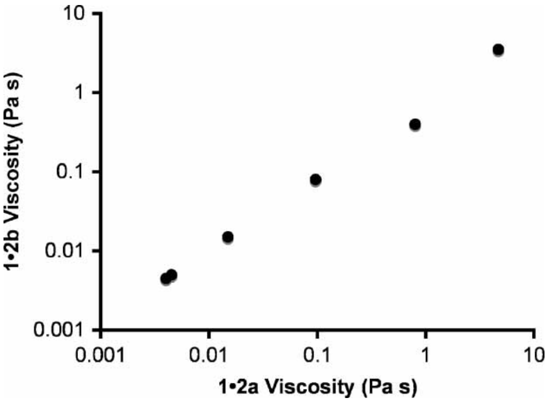

Figure 3. Relative viscosities of RP solutions **1·2a** vs. **1·2b** at different wt% in 1,2-dichlorobenzene with a small portion of DMSO (w/w, 95/5).

This expectation is supported by quasi-elastic light scattering of **1·2a** and **1·2b** in the dilute regime. The hydrodynamic radii of the two RPs, measured by QELS in 1,2-dichlorobenzene/DMSO co-solvent (w/w = 95/5), are shown in Table 3. The two RPs are indistinguishable at 0.56 wt%, with average R_h values of 37 nm for **1·2a** and 36 nm for **1·2b**. At 1.48 wt%, R_h values increased to 49 nm for **1·2a** and 47 nm for **1·2b**.

These results demonstrate that *N*,*C*,*N*-pincer Pt(II) complexes with pyridine form high molecular weight, soluble polymers in 95/5 1,2-dichlorobenzene/DMSO co-solvent. The association constant of the Pt-pincer complex in the co-solvent was not measured directly, but it can be inferred from the viscosimetric titrations. When the relative concentration of the two RP constituent monomers is sufficiently far from unity, the molecular weight of the **1·2** RPs is determined by their ratio. Thus, for both **1·2a** and **1·2b**, empirical scaling laws relating viscosity to average RP DP can be determined. The maximum viscosity of each sample, presumably obtained at effectively exact stoichiometry of the two components, can then be related to the DP of the polymer at that concentration. Under these conditions, the RP molecular weight is limited, not by the stoichiometry of the monomers, but by the association constant K_a of the Pt–pyridine complex. For high degrees of association,

Table 3. Hydrodynamic radii of RPs **1·2a** and **1·2b**, as measured by quasi-elastic light scattering (Wyatt QELS).

	R_h (nm)	
Solute	0.56 wt%	1.48 wt%
1·2a	36	47
1·2b	37	49

the DP is found according to Equation (1) (where C is the concentration of monomers) (*24*):

$$\mathrm{DP} = (2K_{\mathrm{a}}C)^{1/2} + 1. \tag{1}$$

The association constants satisfying the viscosimetric titrations and Equation (1) are $9.2 \times 10^4\,\mathrm{M}^{-1}$ for **1·2a** at 16.8 mM solution, and $1.1 \times 10^5\,\mathrm{M}^{-1}$ for **1·2b** at 23.7 mM solution. These values are greater than those of RPs **1·2a** and **1·2b** in DMSO ($3.2 \times 10^2\,\mathrm{M}^{-1}$ and $2.4 \times 10^2\,\mathrm{M}^{-1}$ for **1·2a** and **1·2b**, respectively), consistent with the relatively poor coordinating ability of 1,2-dichlorobenzene relative to DMSO.

The **1·2a** and **1·2b** RPs add to a growing list of soluble metallo-supramolecular RPs. The first soluble metallo-supramolecular RPs were reported by Rehahn (*25*), including RPs in which solubility was imparted by functionalising a rigid ligand with long alkyl groups (*25a*). The present work has greater similarity with the approach of Schubert and co-workers (*26*), who generated bisfunctionalised telechelics such as poly(THF) or PEG end-capped with terpyridine ligands. The addition of octahedral coordinating transition-metal ions to terpyridine-modified prepolymers leads to a spontaneous self-assembly of two terpyridine units and therefore to polymerisation. The formation of the complexes can be reversed, for example, by changing the pH value (*26b*) or applying electrochemical (*26c*) or thermal stimuli (*26d*), and numerous examples of metallo-supramolecular interactions have recently been reported (*27–29*). Work by Meijer and Sijbesma has shown that supramolecular polymers, when formed by sufficiently strong interaction, may possess properties that are similar to traditional covalent polymers while still being reversible along their main-chain on reasonable timescales (~ seconds) (*8*, *15*). Well-ordered non-covalent polymer fibres have been shown to possess tensile strengths that approach those of commercial fibres. RPs assemble with minimal imperfections and repair themselves on useful timescales, and hence, their long-term integrity may even surpass that of covalent polymers.

The distinguishing feature of the RPs reported here is that the two effectively isostructural RPs have significantly different dissociation kinetics along the reversibly assembled polymer backbone. The pseudo-independent variation in main-chain kinetics provides a mechanistic probe of the molecular dynamics that underlie RP properties. For example, the solution viscosity of the RPs across a range of concentrations is essentially independent of the kinetics of the metal–ligand coordination bond in the two systems at hand. The solution properties are determined not by the reversibility of the polymer main chain, but by the average structure of the intact RPs.

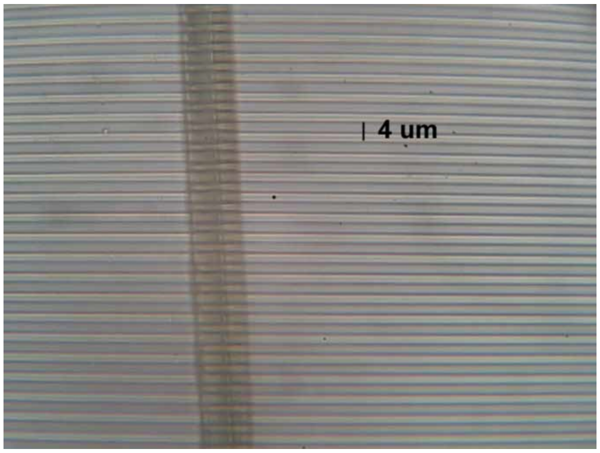

Figure 4. Microscopy image of a **1·2b** fibre drawn by hand from a CH_2Cl_2/CH_3OH (v/v, 9/1) solution. Fibre diameters are calculated using the 4 μm background grid as an internal reference.

3.2 Fibre formation and properties

To investigate whether the Pt–pyridine coordination in these complexes is sufficiently strong to bear load in the solid state, fibres of **1·2** were drawn by hand from a CH_2Cl_2/CH_3OH (v/v, 9/1) solution. The fibres had considerable elasticity immediately after drawing (strain at break $\gg$ 100%), and maintained much of that elasticity after drying for 24 h under vacuum (strain at break ~50%; see movie in the Supporting Information, available online). The fibre widths were determined by optical microscopy (1.5–16 μm, Figure 4), and their strength at break was measured by hand. True to their reversible nature, the fibres could be redissolved, redrawn and tested multiple times with no apparent difference in performance.

The fibres are reasonably strong and quite tough. For example, an 8.5 μM **1·2b** fibre maintained a load of 0.67 g at ~70% elongation before breaking. The calculated tensile strength of 120 MPa (load at break divided by fibre cross-sectional area) is within an order of magnitude of optimised, covalent polymeric fibres that are common in textiles and other material applications (typically of the order of ~5 g for a 10 μm fibre) (*30*). The **1·2** RP fibres, however, are sufficiently elastic that the toughness, or total work necessary to stretch and break the **1·2b** RP fibre, is therefore far greater than for polyamide-imide fibres, and similar properties are observed across numerous fibres, despite the crude drawing and characterisation techniques employed (Figure 5).

Good solid-state mechanical properties are known for other metallo-supramolecular polymers. Paulusse and Sijbesma have shown that coordination polymers of bifunctional phosphorus ligands and palladium dichloride can also be given into fibres, and their coordination

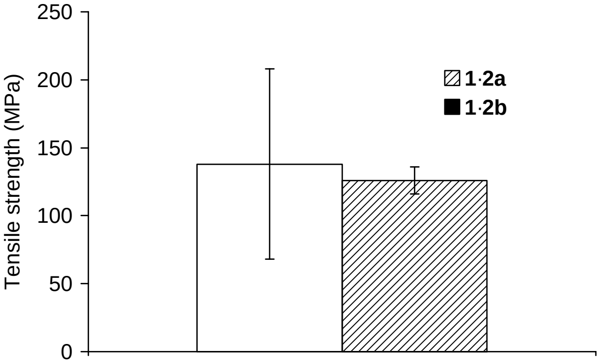

Figure 5. Calculated tensile strength (load at break divided by fibre cross-sectional area) for hand-drawn fibres of **1·2a** and **1·2b**. Standard deviations reflect measurements on $n = 5$ and $n = 3$ fibres for **1·2a** and **1·2b**, respectively.

polymers have shown the polymeric nature based on the presence of T_g (glass transition temperature) and the fibre-forming properties of the melt (*31*). Rowan and Beck (*29b*) have shown that metallo-supramolecular polymers of 2,6-bis(benzimidazolyl)-4-oxypyridine-terminated poly(THF) and metal(II) perchlorate salts can be formed into thermoplastic elastomeric films in which the ionic blocks and soft (tetrahydrofuran) segments are phase separated. More generally, it has been shown previously that relatively weak association constants are sufficient to generate impressive mechanical properties. Rowan and Sivakova (*29c*), for example, have studied the synthesis of nucleobase-terminated low molecular weight poly(THF) macromonomers, and have also demonstrated that a combination of phase segregation between the hard nucleobase chain ends and the soft poly(THF) core combined with aromatic amide hydrogen bonding is utilised to yield the highly thermosensitive supramolecular polymeric materials. They have suggested that the rheology of these systems is strongly dependent on the end groups' dissociation frequency from the 'hard' segments; therefore, the rate of decomplexation of the ends groups, T_g of the hard segment, and the compatibility of the hard and soft segments can all be tailored to alter this dissociation rate. In our system, we can easily control the dissociation rate by changing the substituents on bimetallic pincer compounds **2**.

The molecular-level environment within an elastomeric fibre undergoing mechanical deformation is undoubtedly quite different from that in an RP solution. One advantage of the 'macromolecular kinetic isotope effect' is that it is readily portable to such environments, even if the effect of the environment on the absolute rates of the individual processes is not known. One can imagine, for example, that the ultimate failure of the fibres is initiated by chain rupture that involves metal–ligand displacement within the fibre – a triflate counterion, residual solvent or ambient water molecule, or even a free pyridine end group from elsewhere in the fibre, could serve as a nucleophile that displaces a coordinated pyridine from its position along a polymer backbone. Such a displacement could create a microscopic defect that leads to propagation and failure of the fibre under stress. While nucleophilic displacements govern the mechanical properties of polymer networks cross-linked by **2** and related compounds, however, they do not appear to dictate the failure of the elastomeric fibres. We acknowledge that this analysis is highly phenomenological, and that we assume that the many effects known to influence fibre tensile strength (crystallinity, chain-end segregation and molecular weight and molecular weight distribution (*32*)) are conserved in the two systems due to the structural homology and nearly identical association constants for pyridine coordination in **2a** and **2b**. The tensile strength of **1·2a** fibres and that of **1·2b** are identical within experimental error (Figure 5), providing compelling evidence that the nucleophilic displacement mechanism that governs failure under load in solution (as measured by single-molecule force spectroscopy (*33*)) is not operative in the solid state. The absence of the typical associative ligand displacement pathway in the fibres is likely tied to their significant tensile strength, since the likely alternative failure mechanisms (chain disentanglement and/or purely dissociative scission of the coordination bond) would be comparable to those in conventional, covalent polymers. At the same time, advantages of reversible polymerisation are retained: the broken fibres are easily dissolved and drawn again from solution.

4. Conclusions

Main-chain RPs with high DP and good solubility in organic solvents have been prepared from ligand coordination between 1,4-bis-platinum complexes **2** with poly-THF-bis-pyridine **1**. Steric effects in the bis-platinum complexes provide a simple but effective mechanism for probing the contributions of ligand exchange along the polymer backbone to the solution properties of the RPs. The viscosity of the polymer solutions reflects only the equilibrium size of the polymer, and not its dissociation kinetics. Strong, elastomeric fibres were pulled from concentrated solutions. As in the polymer solutions, nucleophilic ligand displacement mechanisms do not appear to limit the mechanical properties of the polymer fibres in the solid state. Thus, the coordination polymers retain the advantages of high molecular weight and useful mechanical properties along with the ease of processing and recycling that come with main-chain reversibility.

Supporting Information

A movie showing elastomeric character of a fibre is available for download from the journal website.

Acknowledgements

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