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Supplementary Information

Main Chain Metallopolymers at the Static-Dynamic Boundary Based on Nickelocene

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1. Materials and Equipment

All reactions were carried out using standard Schlenk line techniques under an inert atmosphere of dinitrogen or argon using standard Schlenk line or glovebox techniques (MBraun glovebox MB150G-B maintained at < 0.1 ppm H₂O and < 0.1 ppm O₂), unless otherwise stated. Dry and degassed THF was distilled from Na/benzophenone prior to use. Dry hexanes, toluene and dichloromethane were obtained from a Grubbs-type solvent system employing alumina and supported copper columns.¹ 1,2-Difluorobenzene and *d*₆-benzene were purchased from Sigma-Aldrich and stored over molecular sieves. Pyridine and *d*₅-pyridine were purchased from Fluka and Sigma-Aldrich respectively and distilled from CaH₂ prior to use. Silica gel (for flash chromatography, CAS: 63231-67-4, was purchased from VWR and used as received. Celite 521 was obtained from Sigma-Aldrich and heated to 200 °C for 16 h prior to use. Anhydrous NiCl₂ was used as supplied by Sigma-Aldrich. The fly-trap ligand Li₂[(C₅H₄)₂(CH₂)₃] was prepared as described in the literature.^{2,3}

2. Cyclic Oligomers (6_x)

The cyclic oligomers **6_x** observed by ¹H NMR spectroscopy and ESI mass spectrometry during the synthesis of polymer **7_c** bear resemblance to similar cyclics based on ferrocene (which however feature strong, static Fe–Cp bonds).^{4,5} Oligoferrocene rings (with direct C–C links between Cp rings) have recently been synthesised by Albrecht, Long et al.,⁴ and oligoferrocenylsilane cyclic species with 2–7 repeat units were isolated by our group in 2009 from the polymerisation of a sila[1]ferrocenophane monomer in the presence of substitutionally-labile Lewis base initiators.⁵ This polymerisation draws resemblance to that of monomer **5**, where pyridine may act as the substitutionally-labile Lewis base initiator in this case (see postulated mechanisms in Supplementary Figs 9 and 10). Significant effort has been committed to isolation of cyclic species **6_x**, but unfortunately, due to the dynamic

equilibrium involving monomer **5**, cyclics **6_x** and polymer **7**, attempts to crystallise **6_x** from the supernatant of the polymerisation (by altering the solvent composition, or the temperature) simply resulted in re-equilibration. The isolation and purification of the aforementioned ferrocene cyclic oligomers relies on column chromatography, and in addition to re-equilibration of **6_x** in dilute solution, the highly air- and moisture-sensitive nature of nickelocene vs. ferrocene renders this type of purification unsuitable.

3. Mass Spectrometry

Electrospray ionisation (ESI) mass spectra were recorded on a Bruker Daltonics micrOTOF focus II time-of-flight mass spectrometer. Cone potentials between 50 and 150 V were used and optimised for each sample to maximise signal quality. Samples were dissolved at 0.1 mg mL⁻¹ in THF/acetonitrile (50%) and infused from a syringe pump.

4. NMR Spectroscopy

NMR spectra were recorded on a 500 MHz Varian System NMR spectrometer fitted with a Varian OneProbe. All spectra were recorded at 25 °C unless otherwise stated, and are reported relative to external TMS with reference to the most downfield residual solvent resonance (C_6D_6 : δ_{H} 7.16 ppm; d_5 -pyridine: δ_{H} 8.74 ppm).

General ^1H NMR spectra of paramagnetic $[n]$ nickelocenophane and polynickelocene species were recorded in deuterated solvents, and spectra were collected between +310 and –310 ppm to observe signals at both low and high field (number of scans = 2048, receiver gain = 50, relaxation delay = 0.1 s and acquisition time = 0.8389 s). The pulse angle was set to 90° and the transmitter offset to the centre of the spectral width. In all cases, backward linear prediction from 0 to 15 data points was employed to remove baseline distortion, phase correction was addressed manually, and a Bernstein Polynomial Fit was applied as a baseline correction (polynomial order = 10). For depolymerisation kinetic ^1H NMR experiments, protic solvents (1,2-difluorobenzene, dichloromethane, benzene, THF, pyridine and toluene) were used, and spectra were collected between –230 and –310 ppm to observe signals corresponding to the Cp protons of the monomer **5** and the polymer **7** (number of scans = 2048, receiver gain = 10, relaxation delay = 0.1 s and acquisition time = 0.328 s).

Regarding the integration of cyclopentadienyl resonances in NMR spectra taken at different temperatures, integration between two fixed chemical shift values was not feasible, as the position of these paramagnetic resonances shifted with temperature. In these cases, integration was performed across a set chemical shift range with the resonance(s) in question in the centre of this range (13 ppm for the monomer β -Cp resonance, and 26 ppm for the combination of monomer α -Cp and polymer Cp resonances). The error associated with the integration was assumed to be 5%.

5. Dynamic Light Scattering Size Measurements

(i) Experimental Details

Dynamic Light Scattering (DLS) experiments were performed to determine hydrodynamic radii of polymer solutions. Samples (2 mL) of different polymer concentrations (1 and 2 mg mL⁻¹) in toluene were filtered through a 0.45 µm membrane filter into an optical glass cuvette (10.0 mm path length). The measurements were performed on a Malvern Instruments Zetasizer Nano S using a 5 mW He-Ne laser (633 nm) at 20 °C. The correlation function was acquired in real time and analysed with a function capable of modelling multiple exponentials. This process enabled the diffusion coefficients for the component particles to be extracted, and these were subsequently expressed as effective hydrodynamic radius, by volume, using the Stokes-Einstein relationship.

(ii) Discussion

Polymer **7c** was fully soluble in toluene but both polymers **7a** and **7b** were only partially soluble, and some insoluble material, presumably of high molar mass, was removed by filtration prior to the DLS experiments. Consistent with toluene being a marginal solvent for **7**, aggregation of the polymer is observed in all samples (**7c**, **7b** and **7a**, 1 mg mL⁻¹) and is clearly visualized in the size distribution by intensity (Supplementary Figures 11, 12 and 13). The intensity distribution is weighted according to the scattering intensity of each particle (which scales with radius as 10⁶), and therefore the contribution of very few large particles to the total light scattered will be significant. As a result, these aggregates dominate the overall scattering intensity, and the 'size distribution by intensity' exaggerates their representation in solution. However, the scattering intensity by volume (the relative proportion of multiple components based on their mass, or volume) for the aggregates is much smaller, providing a more practical interpretation of the mass distribution.

Due to the uncontrolled nature of the polymerization, the material is likely very polydisperse, and the toluene used for the experiment is selectively dissolving the lower molecular weight material up to a cut-off point. Therefore above this point the material of higher molar mass is being removed via filtration in both cases (**7_b** and **7_a**).

Although we expect M_w of **7_a** to be greater than that of **7_b**, the difference in observed R_h between the two samples was not significant given the limited resolution of the DLS method at these particle sizes. The likely polydispersity of the material means that higher molecular weight polymer fractions are probably being removed via filtration in both cases (**7_b** and **7_a**), which may account for the observation of similar values of R_h for these samples.

6. Small Angle X-ray Scattering

(i) Background

The solution X-ray diffraction data were taken using a Ganesha small-angle X-ray scattering apparatus (SAXSLAB, Denmark). The instrument uses copper K α radiation (1.5 Å) and the scattering pattern is detected on a 2-dimensional Pilatus 300K X-Ray detector (Dectris, Switzerland). Prior to measurement, the absolute intensity scale was calibrated using a sample of deionized water. Samples were prepared at known concentrations in toluene and sealed into 1.5 mm diameter quartz capillary tubes (Capillary Tube Supplies, Cornwall, UK) with epoxy resin under an inert atmosphere. The thickness of each capillary was measured exactly by scanning the X-ray beam across the sample and observing the full-width at half-maximum of the transmitted intensity using a pin diode. All samples were then measured at two sample-to-detector distances (1400 mm and 350 mm) and measurements of the corresponding empty capillary and solvent background were subtracted prior to fitting. The instrument was evacuated during measurements to reduce air scattering.

At concentrations well below the critical concentration for the overlap of polymer coils, one can determine the radius of gyration (R_g), weight-averaged molecular weight (M_w) and polydispersity index (M_w/M_n) of polymers in solution using SAXS. Three different regions are apparent in a plot of the scattered intensity, I , versus the magnitude of the scattering vector, Q (log-log plot). At low Q , (the Guinier region) the radiation is probing large distances, so the X-ray scattering is sensitive to the overall dimension of the polymer coil. The intensity as Q tends to zero ($I(0)$) depends on the contrast between the scattering length density of the polymer and that of the solvent ($\Delta\rho$), the densities of the polymer at the solvent (D_P and D_S respectively), the weight-average degree of polymerization (z_w), and the concentration as weight fraction (w) (N_A = Avogadro constant, M_m = molar mass of monomer unit). It is therefore possible to determine the degree of polymerization of the polymer from

$I(0)$, given all other quantities are known (equation 5). For polydisperse polymers (of which **7** is a likely example), the weight-average degree of polymerization (z_w) is determined in a model-free way from $I(0)$).

$$z_w = \frac{N_A D_P^2}{\Delta \rho^2 D_S M_m} \frac{I(0)}{w} \quad (5)$$

The second region of I versus Q (the intermediate region) has a negative slope, where P is the particle scattering function (equation 6). The distances probed by the radiation in this region correspond to the interior of the polymer coil, so the scattering is sensitive to chain statistics, in particular the polymer conformation and interaction with solvent. Scattering at larger Q -values can provide information regarding the local structure of the molecule, however this will not be discussed here.

$$I(Q) = I(0)P(Q^2 R_g^2) \quad (6)$$

An empirical function is used to represent the shape of the scattering in the Guinier, intermediate and crossover regions, for a polymer in a good solvent (R_g = radius of gyration of polymer chain). Polydispersity (PDI) can be taken into account by averaging $P(Q^2 R_g^2)$ over the molecular weight distribution, but is better in this case modelled by the Schultz-Zimm distribution (equations 7 and 8):⁶

$$f(z) \propto \left(\frac{z}{\langle z \rangle_n} \right)^{k-1} \exp \left(- \frac{kz}{\langle z \rangle_n} \right) \quad (7)$$

$$k = \frac{1}{[(M_w/M_n) - 1]} \quad (8)$$

where the shape of the distribution (k) is determined by the PDI (M_w/M_n), affording more control over the modelling of the distribution. Two of the polymer samples, **7c** and **7b**, were investigated via SAXS. As mentioned above in the discussion of DLS data, the solubility of the samples decreases from **7c** to **7a**, and in this case the solubility of **7a** in toluene was too

low to allow for sufficient scattering intensity and accurate determination of the concentration of the solution samples.

(ii) Experimental Details

The data was fitted using a model for Gaussian-coil polymers as the gradient of the slope is recreated well with Schultz-Zimm polydispersity, and the PDI was limited to a maximum value of 5 (Supplementary Figure 16). The Guinier region for **7c** (Supplementary Figure 14) plateaus at low Q , which is indicative of solvated polymer chains, whereas we see a sharp increase in the same region for **7b** (Supplementary Figure 15) as the concentration of the toluene sample increases, which is indicative of aggregation of the polymer chains in solution. The fitted data shows the $I(0)/w$ value for sample **7b** (15.92), is about three times larger than that of **7c** (5.10), indicating that the weight-average degree of polymerization, z_w , is also three times larger. This supports the hypothesis that the molecular weight of the material increases as the concentration of the pyridine solution for polymerization increases. Using the calculated density ($D_P = 1.26 \text{ g cm}^{-3}$), the molecular weights of **7b** and **7c** respectively were 20,000 and 6,400 g mol^{-1} : significantly lower than those predicted from R_h in THF.⁷ This is perhaps not surprising, as the molecular weight from R_h was a relative value, calculated using monodisperse poly(ferrocenyldimethylsilane) standards.⁸ The molecular weight from R_h was also calculated using values for monodisperse polystyrenes in toluene, and this gave a similar discrepancy (see Supplementary Table 1).

7. Density Measurements

The density of polymer **7** was determined using a principle previously used to calculate the densities of a variety of metallopolymers,⁹ where the Van der Waals volume (V_W) of ferrocene in poly(ferrocenylmethylphenylsilane) was determined from experimental density values. This was adjusted for nickelocene (by comparing the densities of the tricarba[3]ferrocenophane and tricarba[3]nickelocenophane monomers) and V_W values were summed for nickelocene and the trimethylene component of the repeat unit using a tabulation of V_W provided for common organic structural groups.¹⁰ Two extreme scenarios were considered, incorporating either amorphous ($V_W(-CH_2-) = 16.37 \text{ cm}^3 \text{ mol}^{-1}$) or crystalline ($V_W(-CH_2-) = 14.68 \text{ cm}^3 \text{ mol}^{-1}$) trimethylene linkers.

The relationship between V_W and V_P is linear and reproducible ($V_M/V_W = 1.60 \pm 0.045$), allowing us to calculate the density of polymer **7** using equation 9 as follows:

$$D_P = \frac{M_P}{V_P} \quad (9)$$

Where V_P is the molar volume of the polymer repeat unit. The two extreme cases of amorphous and crystalline $-CH_2-$ groups (derived from amorphous and crystalline polyethylene) give densities of 1.21 g cm^{-3} and 1.26 g cm^{-3} respectively. Due to the semicrystalline nature of polymer **7** (see Supplementary Section 12 and Supplementary Figure 22), we expect the true density to lie between these two values. Experimental data of the density of **7** were measured using the oscillating U-tube principle with a Parr density meter. Measurements were made on THF solutions with polymer weight fractions between 1 and 5%. The density of the polymer was averaged across the concentration range to indicate that the experimental density, D_P is ca. $1.30 \pm 0.07 \text{ g cm}^{-3}$ (the large error is a result of the sensitive nature of the polymer).

Given the large experimental value and the semicrystalline nature of **7**, it is likely that the true density lies at the upper end of the range (between 1.21 g cm^{-3} and 1.26 g cm^{-3}). A value of $D_P = 1.26 \text{ g cm}^{-3}$ was therefore used to calculate absolute molecular weight (M_w) from the SAXS data (Table 1 and Supplementary Table 1).

8. Ceiling Temperatures

Equation 1 (an adaption of the Van't Hoff equation) allows for the determination of ΔH^0_{ROP} and ΔS^0_{ROP} , by plotting experimental data for the equilibrium monomer concentration $[M]_c$ in pyridine at various temperatures (T) (Supplementary Table 3, Figure 5a).

$$\ln[M]_c = \frac{\Delta H^0_{\text{ROP}}}{RT} - \frac{\Delta S^0_{\text{ROP}}}{R} \quad (1)$$

This provides a good estimation of the true ΔH^0_{ROP} and ΔS^0_{ROP} values, although the calculation includes a number of assumptions:

1. Flory's assumption that the reactivity of an active centre, located on a sufficiently long macromolecular chain, does not depend on the degree of polymerization.¹⁰
2. $[M]_c$ is calculated by the integration of Cp protons assigned to "polymer" and "monomer" respectively, and does not take into account the presence of small quantities of other species (e.g. cyclic oligomers, **6x**).

Equation 3 allowed us to determine the ceiling temperature (T_c) for the polymerization (at 0.44 M). In this case, $T_c = 365 \text{ K}$ (92 °C), but clearly this temperature will change as a function of the equilibrium monomer concentration.

$$T_c = \frac{\Delta H^0_{\text{ROP}}}{\Delta S^0_{\text{ROP}} + R \ln[M]_c} \quad (3)$$

Ceiling temperatures were calculated at different concentrations by inserting values of $[M]_c$ into equation 3, with $\Delta H^0_{\text{ROP}} = -10 \text{ kJ mol}^{-1}$, $\Delta S^0_{\text{ROP}} = -20 \text{ J K}^{-1} \text{ mol}^{-1}$ (Supplementary Table 5). The calculated ceiling temperatures increase as the concentration of the polymerization solution increases. For the bulk monomer **5** (in the solid state), the theoretical value is 1090 °C (taking the difference in ΔS^0_{ROP} at different standard states into account):

The values of both ΔH_{ROP} and ΔS_{ROP} depend on the monomer and polymer states. In particular, ΔS_{ROP}^0 values determined for different standard states (e.g. 1 mol L⁻¹ and weight fraction = 1) cannot be compared directly, and the experimental value of ΔS_{ROP}^0 was recalculated using equation 10:¹⁰

$$\Delta S_{\text{ROP}}^0(\text{mol L}^{-1}) = \Delta S_{\text{ROP}}^0(\text{wt. fraction}) + R \ln \frac{x/\text{wt. fraction}}{y/\text{mol L}^{-1}} \quad (10)$$

where x denotes a weight fraction corresponding to a monomer concentration of y mol L⁻¹.

0.44 M monomer solution:

Density of pyridine = 0.9832 g mL⁻¹ (at 20 °C)

Mass of **5** in 1 mL of 0.44 M pyridine solution = 0.101 g

Total mass of 1 mL of 0.44 M pyridine solution = 1.0832 g

Weight fraction of **5** (x) = 0.0932

$\Delta H_{\text{ROP}}^0(\text{mol L}^{-1}) = -9.86 \text{ kJ mol}^{-1}$

$\Delta S_{\text{ROP}}^0(\text{mol L}^{-1}) = -20.1 \text{ J K}^{-1} \text{ mol}^{-1}$

Therefore, $\Delta S_{\text{ROP}}^0(\text{wt. fraction}) = -7.23 \text{ J K}^{-1} \text{ mol}^{-1}$

Bulk monomer:

Using the value for $\Delta S_{\text{ROP}}^0(\text{wt. fraction})$ as calculated above, equation 11 (derived from equation 3 with adaption for wt. fraction vs. molar concentration) was used to calculate the ceiling temperature for the bulk monomer (assuming $\Delta H_{\text{ROP}}^0(\text{mol L}^{-1})$ and $\Delta H_{\text{ROP}}^0(\text{wt. fraction})$ are similar in value):

$$T_c = \frac{\Delta H_{\text{ROP}}^0(\text{wt. fraction})}{\Delta S_{\text{ROP}}^0(\text{wt. fraction}) + R \ln x} \quad (11)$$

Where the bulk monomer weight fraction (x) = 1.0, and both the monomer and polymer are assumed to be in amorphous states:

$$T_c^{\text{bulk}} = 1363 \text{ K}$$

$$= 1090 \text{ }^\circ\text{C}$$

9. Computational Chemistry

Calculations regarding the tilt/energy relationship for ferrocene and nickelocene (Figure 4b, Supplementary Table 2): density functional calculations were carried out using the Amsterdam Density Functional program suite ADF 2010.2.¹²⁻¹⁴ Scalar relativistic corrections were included via the ZORA method for all calculations.¹⁵⁻¹⁸ The generalized gradient approximation was employed, using the local density approximation of Vosko, Wilk, and Nusair¹⁹ together with nonlocal exchange correction by Becke^{20, 21} and nonlocal correlation corrections by Perdew.²² TZP basis sets were used with triple- ζ accuracy sets of Slater type orbitals and polarization functions added to the main group atoms. The cores of the atoms were frozen up to 1s for C and 2p for nickel.

On bending the Cp rings in ferrocene from D_{5h} to C_{2v} symmetry, destructive interference occurs between the metal d orbitals and the ring $p\pi$ orbitals, resulting in an overall increase in energy.²³ In this report by Green, discussion is limited to these three orbitals which are principally metal 3d in character, and some occupied Cp orbitals of lower energy.²³ In nickelocene, the bonding description is somewhat different due to the occupation of the $e_1''^*$ antibonding orbitals. On bending, the antibonding character of these orbitals decreases so the overall increase in energy is reduced from that in ferrocene.

10. Thermal Diffusion Microrheology

(iii) Experimental Details

Dynamic Light Scattering (DLS) microrheology experiments were performed on polymer solutions containing trimethylsilyl-modified silica tracer particles of ca. 200 nm diameter (sicastar[®], micromod Partikeltechnologie GmbH) using a Malvern Instruments Zetasizer Nano ZS equipped with a 5 mW He-Ne laser (633 nm) at 25 °C. The correlation function was acquired in real time and considered to solely represent the diffusion of the tracer particle in the polymer solution. The size of the tracer particles in pyridine solution was determined prior to microrheology experiments using DLS size measurements at two different concentrations (2.5 and 5.0 mg/mL).

A solution of monomer **5** in pyridine (0.98 M) was allowed to equilibrate at room temperature for 48 h, and the resulting green solution (1 mL) was transferred into an optical glass cuvette (10.0 mm path length). The tracer particles (5 mg) were added to the polymer solution, which was then stirred for 2 h. A microrheology measurement was performed, and 0.1 mL of pyridine was then added to the sample (new concentration = 0.87 M), which was stirred at room temperature for 24 h and subjected to a further microrheology measurement. This process of dilution/equilibration/measurement was repeated five more times, resulting in seven total sets of rheological data at increasingly dilute concentration (0.98, 0.87, 0.79, 0.71, 0.66, 0.60 and 0.56 M), summarised in Supplementary Table 6.

(iv) Theory

In general, rheology is the study of the deformation and flow of materials under stress. Newtonian fluids exhibit viscosity and negligible elasticity, and Hookean solids have an elastic modulus but do not flow. Viscoelastic materials fall between these two extreme examples, and exhibit a combination of both features: they are capable of both energy storage

(elastic behaviour) and energy dissipation (viscous behaviour) depending on the timescale of the applied deformation.

DLS microrheology is a passive rheological technique suitable for measuring low viscosity and weakly structured samples: it does not rely on the application of mechanical stress, and instead the colloidal probe particles (tracers) undergo thermal fluctuations in a polymer solution at thermal equilibrium.²⁴ It is particularly useful for characterising the viscoelastic properties of air- and moisture-sensitive polymers. The mean square displacement (MSD) of the tracers is measured by DLS, and from this the rheological properties were subsequently evaluated using the generalized Stokes-Einstein relation.

The frequency-dependent complex viscosity, η^* (shown in Supplementary Figure 17 for polymer **7**), is derived from viscoelastic moduli, and is related to shear viscosity using the Cox-Merz rule (assuming angular frequency is analogous to shear rate, and complex viscosity is analogous to shear viscosity). The shear modulus (G^*) can be separated into two components; elastic modulus, G' and viscous modulus, G'' , which are measures of the stored energy (the elastic portion), and the energy dissipated as heat (viscous portion) respectively (shown in Supplementary Figure 18). If $G' > G''$, then the elastic properties dominate (the polymer exhibits solid-like behaviour), whereas if $G' < G''$, then viscous properties dominate (the polymer exhibits liquid-like behaviour). The crossover point at which $G' = G''$ (between the terminal and rubbery plateau regions) is used to determine the relaxation time of the polymer, τ , using equation 12, and is often at very high frequency for low viscosity, non-Newtonian materials.

$$\frac{G'}{G''} = \omega\tau \quad (12)$$

For a particular polymer sample, with decreasing concentration the crossover point ($G' = G''$) occurs at higher frequency, as the rubbery region is less extensive due to a reduction in the number of chain entanglements.

The reptation time (τ_{rep}) of polymers in general describes the time necessary for an entangled polymer chain to diffuse out of an imaginary tube, the dimensions of which are defined by the network of neighbouring chains. Considering dynamic polymers, which can undergo chain scission, there is another relaxation process to be considered: the characteristic breaking time (τ_{break}), defined as the lifetime of a polymer chain of mean length before breaking occurs (anywhere along its length) to yield two individual chains.²⁵ The relationship between τ_{rep} and τ_{break} is commonly discussed as ζ (equation 13).

$$\zeta = \frac{\tau_{\text{break}}}{\tau_{\text{rep}}} \quad (13)$$

$$\tau \sim C^A \quad (4)$$

$$\alpha = \frac{l_e}{\underline{L}} \quad (14)$$

The total relaxation time (τ) scales with concentration (C) by an exponent, A (equation 4). In the reptative regime (where $\tau_{\text{break}} \gg \tau_{\text{rep}}$), $\alpha \leq \zeta \leq 1$ and $A = 1.2$ (α is defined in equation 14), where l_e = the mean curvilinear length between entanglement point and $\underline{L}$ is the mean chain length). On the other hand, “unbreakable chains” ($\tau_{\text{break}} \geq \tau_{\text{rep}}$) are characterised by $\zeta \geq 1$ and $A = 3.4$.

Sources of error between bulk rheology and DLS microrheology:²⁶

- Tracer-matrix interactions (physical or chemical) may alter the local environment and affect diffusivity. The extent of interaction is measured by the difference in zeta potential between the solvated tracer particles in the presence and absence of the polymer sample. Zeta potential measurements could not be performed on **7** due to the

air/moisture-sensitive nature of the polymer, but our expectation is that interactions are minimal due to the inert trimethylsilyl surface chemistry of the tracer particles.

- The size of the tracer particle (ca. 200 nm) should be larger than the microstructural length scale of the polymer network in order to probe the bulk response. As the molecular weight of **7** changes with dilution, the relative length scales of the tracer/polymer network may also change. Relative to polymer **7_a** (formed by polymerisation of **5** in pyridine at 1.31 M) the size of the tracer is sufficiently large (35x larger).

11. Cyclic Voltammetry

(i) Experimental Details

Cyclic voltammetry (CV) studies were carried out using an EG&G model 273A potentiostat linked to a PC using EG&G model 270 Research Electrochemistry software in conjunction with a BASi Epsilon electrochemical workstation. The working electrode was a glassy carbon disc (3.0 mm diameter), and the auxiliary electrode a platinum wire. The reference electrode was a saturated calomel electrode separated from the test solution by a fine porosity frit and an agar bridge saturated with KCl. Cyclic voltammograms were obtained in CH₂Cl₂ or THF with 0.05 M [*n*Bu₄N][B(C₆F₅)₄] as supporting electrolyte at scan rates of 200 mV s⁻¹ and 1 mM analyte. Cyclic voltammograms were referenced to the [Fe(C₅H₅)₂]/[Fe(C₅H₅)₂]⁺ redox couple using [Fe(C₅H₅)₂] as an internal standard.

(ii) Electrochemistry of tricarba[3]nickelocenophane **5**

The redox properties of tricarba[3]nickelocenophane **5** were investigated using cyclic voltammetry (CV) in the presence of the non-coordinating supporting electrolyte [*n*Bu₄N][B(C₆F₅)₄] and in non-coordinating solvents (*E*_{1/2} values given for CH₂Cl₂), and compared to the results previously obtained for nickelocene.²⁷ Dichloromethane was selected as the solvent in order to allow for the greatest possible electrochemical window. An electrochemically reversible oxidation to monocation [**5**]⁺ was observed (*E*_{1/2}(1) = -0.75 V vs. FcH), appearing at lower potential in the cyclic voltammogram (Supplementary Figure 20) than that observed in the analysis of nickelocene.²⁷ The second oxidation to the dication [**5**]²⁺ (*E*_{1/2}(2) = ca. 1.10 V vs. FcH) was found to be only partially electrochemically reversible as a result of the high electrophilicity of the dication. This irreversibility of the second oxidation is similar to that reported for a naphthalene-bridged [3]nickelocenophane,²⁸ and a tetracarba-bridged [4]nickelocenophane.²⁹

(iii) Electrochemistry of polynickelocene **7b**

Analysis of the redox properties of the polymer **7b** was conducted by CV, and the results compared to those obtained for the parent monomer **5** (see Supplementary Figure 20). Due to fast depolymerization of the polymer in dichloromethane (see Supplementary Figure 8), THF was instead employed as the solvent in this case, but the same non-coordinating supporting electrolyte $[n\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ was used. In contrast to monomer **5**, polymer **7b** displayed a more complex response (Supplementary Figure 21), with two overlapping waves ($E_{1/2} = -0.65$ V, $E_{1/2} = -0.51$ V) in the region expected for the first oxidation of **7b** to $[\text{7b}]^{n+}$ (n = number of repeat units).

This observation of two overlapping waves is similar to previous reports on the redox chemistry of polymetalloenes, and may be assignable to the first wave corresponding to oxidation of the metallocene units at alternating sites along the backbone, and the second wave to oxidation of the remaining metallocene units.^{5, 30} The degree of separation between the two waves ($\Delta E_{1/2} = 0.14$ V) is relatively small, indicating a possible weak intrachain metallocene interaction, resulting from the separation of the metallocene units with a relatively long, non-polarizable C_3 linker. We tentatively attribute the presence of detectable interaction despite the presence of the relatively long C_3 spacer to the use of the non-coordinating $[n\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ electrolyte, which enhances electrostatic repulsion effects.³⁰ In contrast to monomer **5**, the second oxidation could not be detected for **7b** despite increasing the scan range to the potential limit of the solvent (THF). We attribute this to the relative difficulty associated with the removal of an additional electron from a positively charged Ni centre in proximity to two other cationic Ni centres in the polymer chain; a situation that does not exist for the mononuclear Ni complex **5**.

12. Wide Angle X-ray Scattering

Wide angle X-ray scattering (WAXS) experiments were carried out on a D8 Advance diffractometer fitted with an 0.6 mm fixed divergence slit, knife-edge collimator and a LynxEye area detector using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Data was collected between 5 and 50 degrees 2θ in $\theta/2\theta$ mode with a step width of 0.5° . Samples were prepared by the loading of solid polymer sample (ca. 30 mg) onto a silicon wafer prior to analysis.

Supplementary Figure 1. *In situ* ¹H NMR spectrum (500 MHz, *d*₅-pyridine) of polymerization of monomer **5** (concentration = 0.79 M, t = 48 h).

Supplementary Figure 2. Positive mode ESI mass spectrum of supernatant after 1st precipitation of polymer **7c** into hexanes, showing monomer **5** and cyclic oligomers **6₂–6₄**.

Supplementary Figure 3. High resolution positive mode ESI mass spectrum (black) of supernatant after first precipitation of polymer **7c** into hexanes, showing monomer **5**. The theoretical isotopic distribution of peaks due to nickel isotopes is shown mirrored, in green.

Supplementary Figure 4. High resolution positive mode ESI mass spectrum of supernatant after first precipitation of polymer **7c** into hexanes, showing cyclic dimer **62**. The theoretical isotopic distribution of peaks due to nickel isotopes is shown mirrored, in green.

Supplementary Figure 5. High resolution positive mode ESI mass spectrum of supernatant after first precipitation of polymer **7c** into hexanes, showing cyclic trimer **63**. The theoretical isotopic distribution of peaks due to nickel isotopes is shown mirrored, in green.

Supplementary Figure 6. High resolution positive mode ESI mass spectrum of supernatant after first precipitation of polymer **7**_c into hexanes, showing cyclic tetramer **6**₄. The theoretical isotopic distribution of peaks due to nickel isotopes is shown mirrored, in green.

Supplementary Figure 7. *In situ* ^1H NMR spectrum (500 MHz) of polymerization of monomer **5** in pyridine, CH_2Cl_2 and THF (20 $^\circ\text{C}$, concentration = 0.79 M, t = 48 h).

Supplementary Figure 8. Depolymerisation of polymer **7** (solutions of ca. 3 mg mL $^{-1}$) to monomer **5** in a range of solvents over time.

Supplementary Figure 9. Proposed chain growth mechanism involving ring-opening of monomer **5** with via coordination of two pyridine molecules, propagation and backbiting/macrocyclization step.

Supplementary Figure 10. Proposed step growth mechanism involving ring-opening of monomer **5** via coordination of two pyridine molecules, and illustrative formation of cyclic species **6₂**.

Supplementary Figure 11. DLS size distribution by volume (dark) and intensity (light) for **7c** (toluene, 25 °C, 1 mg mL⁻¹). Size distribution by intensity (light) shows presence of material at large R_h values, assigned to small quantities of aggregated polymer.

Supplementary Figure 12. DLS size distribution by volume (dark) and intensity (light) for **7b** (toluene, 25 °C, 1 mg mL⁻¹). Size distribution by intensity (light) shows presence of material at large R_h values, assigned to small quantities of aggregated polymer.

Supplementary Figure 13. DLS size distribution by volume (dark) and intensity (light) for **7a** (toluene, 25 °C, 1 mg mL⁻¹). Size distribution by intensity (light) shows presence of material at large R_h values, assigned to small quantities of aggregated polymer.

Supplementary Figure 14. Small angle X-ray scattering data: log-log plot of the scattered intensity (I) versus the magnitude of the scattering vector, Q , for polymer **7c** at various concentrations in toluene.

Supplementary Figure 15. Small angle X-ray scattering data: log-log plot of the scattered intensity (I) versus the magnitude of the scattering vector, Q , for polymer **7b** at various concentrations in toluene.

Supplementary Figure 16. Small angle X-ray scattering data: Fits of the scattered intensity (I) versus the magnitude of the scattering vector, Q , for polymer **7c** (blue) and **7b** (red) at various concentrations in toluene.

Supplementary Figure 17. Plots of complex viscosity vs. angular frequency of polymer **7** at various concentrations in pyridine (obtained by DLS microrheology).

Supplementary Figure 18. Plots of elastic and viscous moduli (G' and G'' respectively) vs. angular frequency (ω) of polymer **7** at various concentrations in pyridine.

Supplementary Figure 19. Plot of τ (obtained from the cross-over point of G' and G'') vs. concentration for polymer **7** in pyridine.

Supplementary Figure 20. Cyclic voltammogram for monomer **5** (1 mM) in 0.05 M $[n\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{CH}_2\text{Cl}_2$, scan rate 200 mV s^{-1} , $T = 298 \text{ K}$.

Supplementary Figure 21. Cyclic voltammogram for monomer **7b** (1 mM) in 0.05 M $[n\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{THF}$, scan rate 200 mV s^{-1} , $T = 298 \text{ K}$.

Supplementary Figure 22. WAXS data for polymer **7b**.

Sample	Conc. (M)	Yield of 7 (%) ^a (at 32 h)	R_h (nm)	σ^e	DLS ^f		SAXS ⁱ
					M_w (g mol ⁻¹) (PFS/THF standard)	M_w (g mol ⁻¹) (PS/toluene standard)	M_w (g mol ⁻¹) ^j
7_a	1.31	62	5.7 ^c	3.8	50,900 ^g	56,000 ^h	^k
7_b	0.79	30	6.3 ^c	5.0	61,200 ^g	66,700 ^h	20,000 ^l
7_c	0.44	21	3.2 ^d	2.9	17,600 ^g	20,500 ^h	6,400 ^l
7_d	0.22	^b	—	—	—	—	—
7_e	0.11	^b	—	—	—	—	—
7_f	0.04	^b	—	—	—	—	—

Supplementary Table 1. Effect of concentration on conversion of monomer **5** to polymer **7** in d₅-pyridine. ^aIsolated yield (via two precipitations of polymer solution into hexanes, then drying in vacuo). ^bNo polymer could be isolated via precipitation into hexanes. ^cPolymer only partially soluble in toluene at 1 mg mL⁻¹. ^dPolymer fully soluble in toluene at 1 mg mL⁻¹. ^eStandard deviation across DLS measurements. ^fDLS experiments carried out on toluene solutions of polymers. ^gEstimated by means of calibration with R_h/M_w correlations for poly(ferrocenyldimethylsilane) in THF. ^hEstimated by means of calibration with R_h/M_w correlations for polystyrene in toluene.³¹ ⁱScattering experiments carried out on toluene solutions of polymers. ^jCalculated using polymer density, $D_P = 1.26$ g cm⁻³. ^kSolubility of **7_a** in toluene too low to allow for sufficient scattering intensity. ^lAbsolute value of M_w determined in toluene.

Temperature (°C)	% polymer (NMR)	ΔG (kJ mol ⁻¹)
60	29.3	-0.74
55	31.9	-0.80
50	34.4	-0.84
45	37.7	-0.93
40	39.4	-0.94
35	44.1	-1.10
30	49.5	-1.29
20	55.0	-1.45
10	57.7	-1.46
5	65.6	-1.87
0	66.7	-1.86
-5	70.0	-2.01

Supplementary Table 2. Percentage conversion of monomer **5** to polymer **7** and free energy change (ΔG) as a function of temperature ($t = 24$ h) in sample **7_c** (initial monomer concentration = 0.44 M). Free energy change was calculated using the equation $\Delta G = \Delta G^0 + RT \ln[M]_c$ ($[M]_c$ = equilibrium monomer concentration).

$1/T$ (K ⁻¹)	[M _c] (M)	ln[M _c]
0.003003003	0.308689517	-1.175419306
0.00304878	0.29713991	-1.213552175
0.003095975	0.286423388	-1.250284185
0.003144654	0.272146833	-1.301413531
0.003194888	0.264724647	-1.329065062
0.003246753	0.244019926	-1.410505394
0.00330033	0.220603872	-1.511386619
0.003412969	0.196754805	-1.62579697
0.003533569	0.184691614	-1.689067796
0.003597122	0.150101604	-1.896442856
0.003663004	0.145598556	-1.926902063
0.003731343	0.13116987	-2.031262078

Supplementary Table 3. Reciprocal temperature ($1/T$), molar equilibrium monomer concentration ([M_c]) and ln[M_c] of the equilibrium between monomer **5** and polymer **7** at temperatures between -5 °C and 60 °C. The plot of ln[M]_c vs. reciprocal temperature (Shown in Figure 5a) is characterised by a linear equation: $y = -1186.4x + 2.4219$.

	Angle (°)	Energy (kJ mol ⁻¹)
NiCp₂	0.0	0
	1.4	1
	7.1	3
	12.7	10
	17.9	19
	21.8	33
	27.2	50
	31.3	72
	34.1	99
	36.7	132
	40.2	170
FeCp₂	0	0
	5	8
	10	15
	15	27
	20	44
	25	68
	30	108
	35	160
	40	232

Supplementary Table 4. Total energy (kJ mol⁻¹) vs. tilt angle (°) for nickelocene and ferrocene.

Sample	[M] ₀ (molar conc.)	T _c (°C)
bulk 5	6.61	1090
7_a	1.31	278
7_b	0.79	173
7_c	0.44	92
7_d	0.22	28
7_e	0.11	−17
7_f	0.04	−63

Supplementary Table 5. Calculated ceiling temperatures for polymerisations of monomer **5** in pyridine carried out at concentrations ranging from 0.04 and 1.31 M. The equilibrium concentration is assumed equal to the initial monomer concentration, [M]₀.

Concentration (M)	value of ω at $G' = G''$ (rad/s)	ν (s ^{−1})	τ (s)
0.98	32.1	5.10	0.20
0.87	34.9	5.55	0.18
0.79	58.8	9.36	0.11
0.71	195.4	31.1	0.03
0.66	300.0	47.7	0.021
0.60	355.5	56.6	0.018
0.56	471.4	75.0	0.013

Supplementary Table 6. Rheological data obtained from DLS microrheology of solutions of polymer **7** in pyridine between 0.56 and 0.98 M.

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