

## Orthogonal Control of Dissociation Dynamics Relative to Thermodynamics in a Main-Chain Reversible Polymer

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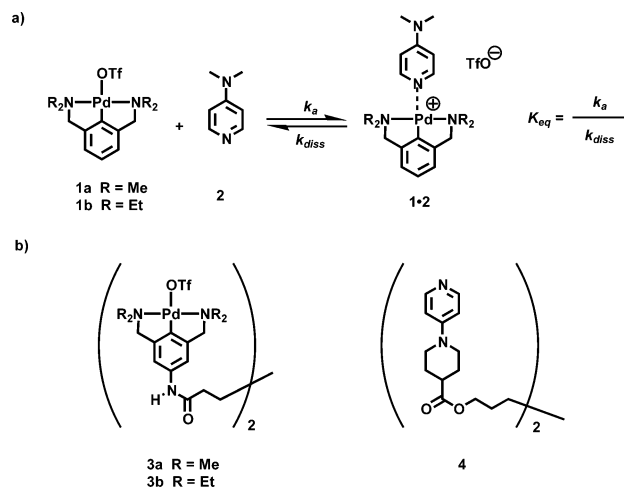
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We report here two homologous reversible polymers in which the equilibrium structures are nearly identical but the dissociation dynamics along the main chain differ by ca. 2 orders of magnitude. This work is motivated by the increasing use of self-assembly as a route to complex, supramolecular structures and materials.<sup>1</sup> As the number of accessible supramolecular structures grows, relating the properties of an assembly to those of its molecular constituents becomes an increasingly desirable objective. As reviewed by Raymond,<sup>2</sup> the dynamics of supramolecular assemblies are a particularly rich means by which chemists might engineer properties such as catalysis,<sup>3</sup> templation effects,<sup>4</sup> interconversion of assemblies,<sup>5</sup> and kinetic compartmentalization.<sup>6</sup>

Our specific interest currently involves main-chain reversible polymers (RPs).<sup>7</sup> RP monomers comprise two or more molecular recognition end groups that are covalently linked. Reversible association of the end groups defines a linear, polymeric assembly. Under nonequilibrium conditions such as those imposed by mechanical stress or concentration gradients, association/dissociation dynamics along the main chain might contribute to the bulk properties of RPs. To exert dynamic control at the molecular level, however, the effects of dynamics ( $k_{\text{diss}}$ , Figure 1) must be delineated from the contributions of thermodynamics ( $K_{\text{eq}}$ ). This delineation is problematic with most reversibly assembled systems, for example, those based on hydrogen bonding, because association typically occurs at or near the diffusion rate, and  $K_{\text{eq}}$  and  $k_{\text{diss}}$  are therefore strongly anticorrelated. For RPs, the inverse correlation of  $k_{\text{diss}}$  and  $K_{\text{eq}}$  subtly but intrinsically frustrates efforts to determine their relative importance. High  $K_{\text{eq}}$  values lead to higher RP molecular weights and slower equilibrium polymeric dynamics, while lower  $k_{\text{diss}}$  values lead to slower reversible dynamics along the main chain. Dynamic properties, whether controlled by equilibrium structure or main-chain reversibility, are slowed by both mechanisms!

Orthogonal control of dissociation rates relative to thermodynamics is therefore critical, and pincer metal–ligand coordination motifs such as **1**·**2** (Figure 1a) seem well-suited to this goal. Following Rehahn, numerous metal–ligand systems have been applied to soluble RPs.<sup>8</sup> Pincer compound **1** and analogues have been synthesized and studied extensively by van Koten.<sup>9</sup> With other organometal motifs,<sup>10</sup> they have found use in supramolecular chemistry by Reinhoudt, van Koten, and others.<sup>11</sup> The dynamics of interest now correspond to ligand exchange, which occurs through a sterically congested associative mechanism. Bulk in the *N*-alkyl substituents R should slow the exchange, while exerting a lesser effect on the ligand association thermodynamics. These expectations are qualitatively confirmed in room-temperature NMR spectra of the R = Me and Et complexes. At identical concentrations (DMSO-*d*<sub>6</sub>; 1 mM in **1a/b**, 3 mM in **2**), nearly indistinguishable ratios of free and bound **2** are observed; the measured association constants are 1.6 and 1.3 × 10<sup>3</sup> M<sup>-1</sup>, respectively, for **1a** and **1b** (Table 1). While the spectrum of **1b**·**2** is sharp, that of **1a**·**2** shows broad peaks that are indicative of exchange near the NMR time



**Figure 1.** (a) Reversible organopalladium–pyridine coordination. Added steric bulk in **1b** relative to **1a** slows  $k_a$  and  $k_{\text{diss}}$  without affecting  $K_{\text{eq}}$ . (b) Components of main-chain reversible polymers based on association shown in (a).

**Table 1.** Ligand Association Constants (25 °C) and Dissociation Rates for Organopalladium Complexes (Figure 1) in DMSO-*d*<sub>6</sub>

complex	$k_{\text{diss}}$ (s <sup>-1</sup> )	$K_{\text{eq}}$ (M <sup>-1</sup> )
<b>1a</b> · <b>2</b>	100 ± 30, <sup>a</sup> > 70 <sup>b</sup>	1.6 (0.4) × 10 <sup>3</sup>
<b>1b</b> · <b>2</b>	1.0 ± 0.1 <sup>b</sup>	1.3 (0.4) × 10 <sup>3</sup>

<sup>a</sup> Measured by <sup>1</sup>H NMR coalescence at 30 °C. <sup>b</sup> Measured by <sup>1</sup>H NMR spin magnetization transfer (EXSY) at 25 °C.

scale. Heating the NMR sample to only 30 °C leads to coalescence of the peaks and corresponds to an exchange rate of 100 s<sup>-1</sup> at that temperature. In contrast, the same peaks in **1b**·**2** remain separated until 90 °C, above which the reduced concentration of bound ligand makes coalescence impossible to identify clearly.

The slower dynamics in **1b**·**2** are quantified by EXSY spin exchange experiments. The rate of chemical exchange between bound and unbound **2**, measured at 25 °C for five different mixing times, is 1.0 ± 0.1 s<sup>-1</sup>, nearly 2 orders of magnitude slower than that in **1a**·**2**. The difference in exchange dynamics deters the use of one technique to measure kinetics in both systems; exchange in **1a**·**2** is essentially complete in 25 ms at 25 °C. The lower limit of ~70 s<sup>-1</sup> for  $k_{\text{diss}}$  at 25 °C is consistent with the coalescence data at 30 °C.

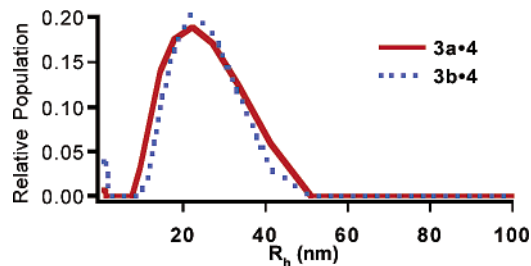
The **1**·**2** motif was incorporated into RPs (**3**·**4**, Figure 1b). Previous work suggests that thermodynamic and kinetic properties of **3**·**4** should be very similar to those observed in **1**·**2**.<sup>12</sup> Consistent with those expectations,  $K_{\text{eq}}$  is indistinguishable from that of the **1**·**2** analogues, and the coalescence behavior is similarly unchanged (insufficient peak resolution in **3**·**4** precludes EXSY).

A 1:1<sup>13</sup> mixture of **3a**:**4** (4.6 wt %) forms polymers in DMSO, as evidenced by an increased viscosity relative to solutions of the individual components (Table 2). The viscosity increases with

**Table 2.** Viscosities of Reversible Polymer Solutions **3a·4** and Monomer Controls in DMSO (4.6 wt %, Cannon–Ubbelohde Viscometer, 23 °C)<sup>a</sup>

solute	$\eta$ (cSt)	$\eta_{re}$
<b>3a·4</b>	4.31	2.2
<b>3b·4</b>	4.22	2.2
<b>3a</b>	2.22	1.2
<b>3b</b>	2.37	1.2
<b>4</b>	2.47	1.3
<b>3a·4</b> + 20 mol % <b>2</b>	3.22	1.7
none	1.94	1.0

<sup>a</sup> Uncertainties are  $\pm 0.05$  cSt.



**Figure 2.** Distribution of hydrodynamic radii for **3a·4** and **3b·4**, as measured by quasi-elastic light scattering (Wyatt QELS) at 2.8 wt %.

[**3a·4**]<sup>1,3</sup>, consistent with RPs in dilute concentrations. The viscosity is immediately reduced by the addition of 20 mol % **2**, which terminates the RP chain. This result confirms reversibility and rules out unspecific aggregation and ionic effects, which should not change with added **2**. A similar solution of **3b·4** exhibits the same viscosity, indicating that the equilibrium structures are nearly identical, as expected.

Quasi-elastic light scattering provides corroborating evidence. The hydrodynamic radii  $R_h$  values of RPs **3a·4** and **3b·4** (2.8 wt %) are shown in Figure 2. The two structures are indistinguishable, with an average effective  $R_h$  value of 26 nm. At 4.6 wt %,  $R_h$  values of both RPs increase identically to 36 nm (not shown), reflecting a reasonable concentration dependence of the RP size. The coalescence studies and model EXSY studies cited above, however, reveal that the main-chain equilibration dynamics of the two RPs differ by a factor of 50–100.

The thermodynamics and kinetics in **3·4** can be studied simultaneously using NMR, and they are therefore well-suited for these model studies. The strategy, however, is general and can be applied to higher molecular weight RPs based on larger or branched RP monomers. Ligands with higher affinity for the pincer complexes could also be used, thus permitting studies of dynamic contributions across a range of  $K_{eq}$  and RP molecular weights. Phthalimide salts are one example of ligands with high association constants ( $> 10^6$  M<sup>-1</sup>) and similar affinities for R = Me versus Et (4:1 by NMR). Finally, the pincer systems have the additional general advantage that the association is robust to varied solvent conditions: for **1·2**,  $K_{eq} = 2 \times 10^3$ ,  $1.3 \times 10^3$ , and  $1 \times 10^3$  M<sup>-1</sup> in CDCl<sub>3</sub>, MeOD, and 1:1 D<sub>2</sub>O/DMSO-*d*<sub>6</sub>, respectively. A range of RP systems can therefore be studied in varied solvent conditions.

In conclusion, steric effects in a ligand exchange process provide a simple but effective mechanism for probing the dynamic

properties of reversible polymers and supramolecular systems. The polymers thus formed permit a direct view, heretofore occluded, of the contribution of main-chain dissociation dynamics to the properties of reversibly polymerized materials. These contributions are central to dynamic mechanical behavior not observed in conventional covalent polymers, including self-repair.<sup>14</sup> The potential utility of RPs as a materials platform has been established in seminal work by Meijer.<sup>7b</sup> A challenge for chemists is to relate behavior at the level of polymer physics to molecular behavior over which chemists can exercise control through synthesis. Orthogonal control of main-chain dynamics represents a useful strategy for assessing these contributions.

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**Supporting Information Available:** Experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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