Electronic supporting information (ESI)

Complex coacervation and metal-ligand bonding as synergistic design element for aqueous viscoelastic materials

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Materials & Methods

Unless stated otherwise, chemicals were used as received. Acetonitrile (CH_3CN, anhydrous, 99.8%), KOH (powdered, for synthesis, $\geq$ 85.0%), 1,4-dibromobutane (99%), dimethylformamide (DMF, anhydrous, 99.8%), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, 99%), 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (4CDTPA, 97%), 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%), and, dimethylsulfoxide (DMSO, anhydrous, $\geq$99.9%) were obtained from Sigma-Aldrich, Germany. 4'-Chloro-2,2':6',2"-terpyridine ($>$98.0%), 3-amino-1-propanol ($>$98.0%) and, 2,6-bis(2-pyridyl)-4(1*H*)-pyridone ($>$98.0%) were obtained from TCI Europe. Dichloromethane (DCM, stabilized with ethanol, $\geq$ 99.9%), and, methanol (MeOH, HPLC, $\geq$ 99.9%) were procured from Biosolve. AIBN was recrystallized from methanol thrice. AMPS was crystallized from ethanol twice and freshly used. Dibromobutane was distilled at low pressure, and stored over molecular sieves (4Å). CH_3CN and DMSO were stored on molecular sieves (4Å).

Poly(N,N-dimethylethyl methacrylate)–35 kDa (pD^{222}, Đ=1.12) and poly(acrylic acid)–30 kDa (pA^{416}, Đ=1.12) were obtained from Polymer Source, Canada. Commercial pA was dried for several days on a Shlenk line, then dissolved in DMF and centrifuged at 2000g for 1h to remove insoluble impurities. Poly(N,N-dimethylethyl methacrylate)–161 kDa (pD^{1k}, Đ=1.43) and poly(acrylic acid)–30 kDa (pA^{250}, Đ=1.13) were synthesized using copper-catalyzed polymerizations as reported in the Experimental Section of the main text.

Methods

Synthesis of 3-aminopropoxyterpyridine The synthesis of 3-aminopropoxyterpyridine by Williamson ether synthesis was adapted from literature. [1] Under N_2 (g), 4'-chloro-2,2':6',2"-terpyridine (1.64 g, 6.36 mmol), powdered KOH (1.65 g, 29 mmol), and 3-amino-1-propanol (0.50 mL, 6.7 mmol) were added to 25 mL of dry DMSO in a round-bottomed flask. The mixture was stirred at 60 °C for 30 h, after which it was added to 300 mL saturated aqueous K_2CO_3 and extracted into DCM. The DCM solution was washed with 0.1 M NaOH and thrice with K_2CO_3, and dried over Na_2SO_4. After filtration and concentration *in vacuo*, 3-aminopropoxyterpyridine was obtained as a yellow solid. (1.04 g, 3.39 mmol, 53%).

^{1}H-NMR (400 MHz, $CDCl_3$: Figure S1. ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 167.07, 157.14, 156.10, 149.03, 136.78, 123.82, 121.34, 107.32, 67.09, 33.26, 29.35, 27.65. MS (ESI): $[M+K]^+$ found at 345.1109, expected 345.1111, $[M+Na]^+$ at 329.1369, expected 329.1369.

Synthesis of 4-bromobutoxyterpyridine The synthesis of 4-bromobutoxyterpyridine was adapted from literature. [2] 2,6-bis(2-pyridyl)-4(1H)-pyridone (0.867 g, 3.48 mmol) was added to 50 mL of dry CH_3CN in a round-bottomed flask. Dibromobutane (4.1, 34 mmol) and K_2CO_3 (1.0 g, 7.0 mmol) were introduced into the white suspension, which was left to reflux overnight. The caramel-coloured crude was left to cool down, was filtrated and then con-

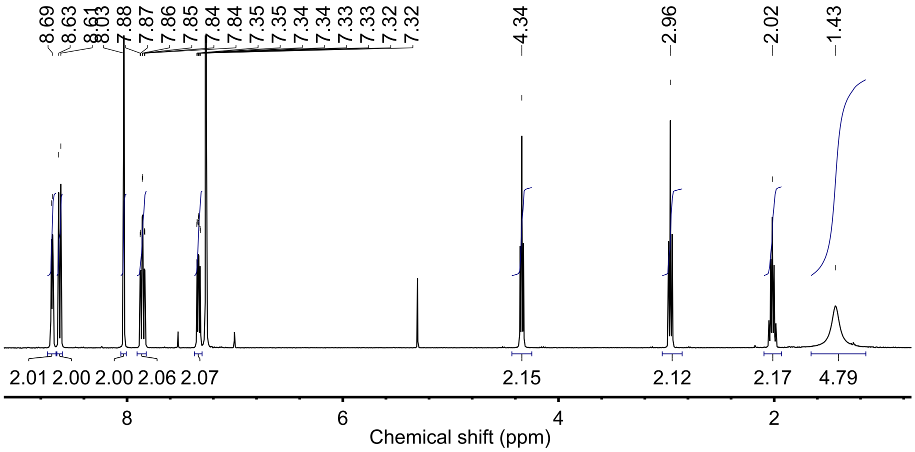

Figure S1: ^{1}H-NMR (400 MHz, $CDCl_3$ of 3-aminopropoxyterpyridine.)

centrated *in vacuo*. The brown oil was chromatographed over SiO_2 and eluted with 5% MeOH in DCM, yielding 4-bromobutoxyterpyridine (0.78 g, 2.0 mmol, 59%).

^{1}H-NMR (400 MHz, $CDCl_3$: Figure S2. ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 167.07, 157.14, 156.10, 149.03, 136.78, 123.82, 121.34, 107.32, 67.09, 33.26, 29.35, 27.65. MS (ESI): $[M+K]^+$ found at 422.0261 and 424.0241, expected 422.0261 and 424.0241.

Synthesis of poly(2-acrylamide-2-methylsulfonic acid) Poly(2-acrylamide-2-methylsulfonic acid) was obtained through RAFT synthesis. To a round-bottomed flask was added 5.0 g of AMPS (24.2 mmol, 500 eq), 19.5 mg (0.048 mmol, 1 eq) of 4CDTPA, and 1.6 mg of AIBN (0.2 eq). To this was added 10 mL of DMF, and a septum was fitted into the neck of the flask. The mixture was bubbled for 30 min. with N_2, after which the flask was submerged into a pre-heated oil bath at 70 ° C. After 4 h, polymerization was stopped by admitting oxygen and placing the flask on ice. The residue was purified by reprecipitation, thrice in acetone.

SEC-MALLS (HFIP, 0.02 M KTFA): M_n=165 kDa, M_w=186 kDa, = 1.13.

Synthesis of homopolymer polyelectrolytes

The nature of this work required access to larger quantaties of relatively monodisperse polyelectrolytes at low price. Therefore, we based our synthetic practice on copper-based polymerization techniques from the recent literature, [3, 4] albeit with minor optimizations towards the reactivity of *tert*-butyl acrylate and N,N-dimethyl ethyl methacrylate. We believe these modifications to be of some merit to the polymer chemist, and report them in detail here.

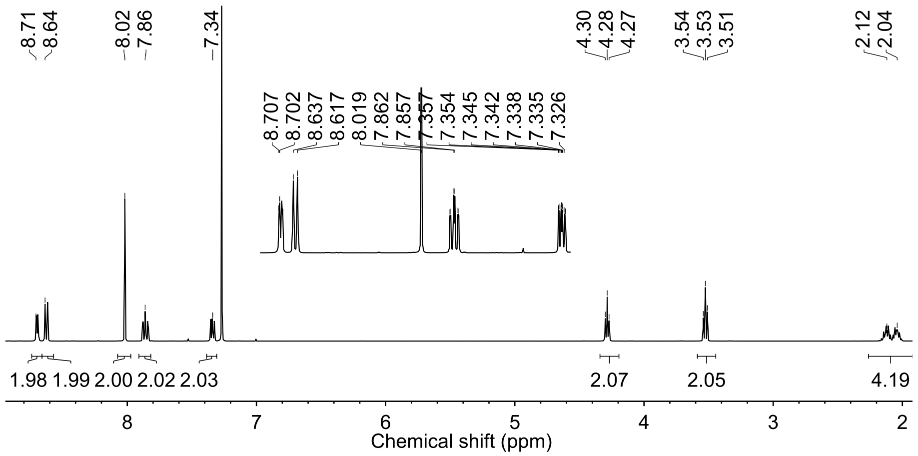

Figure S2: ^{1}H-NMR (400 MHz, CDCl$_3$ of 4-bromobutoxyterpyridine.

Synthesis of poly(acrylic acid)

Poly(acrylic acid) was obtained through de-*tert*-butylation of poly(*tert*-butyl acrylate). The latter was made using Cu(0)-catalyzed polymerization, following Haddleton et al. with substitution of *n*-butyl acrylate for *tert*-butyl acrylate. [4] In this procedure, initiating radicals derived from a halide are generated by a complex of Cu(0) and a strongly ligating tertiary amine, whereas the corresponding Cu^{II} complex catalyzes formation of halogen caps from radical chain ends, forming Cu^{I} simultaneously. The latter then proceeds to generate radicals from halogenated polymers or unused initiator. For appropriate combinations of monomers, ligand, and initiator, a uniform rate of propagation is thus achieved.

The ligand used was Me$_6$TREN, the initiator ethyl α-bromoisobutyrate. The reaction is elementary to set up, yet rivals anionic methods in terms of dispersity ($Đ$=1.13 without any optimization). We used the condition 50% $^{v}/_{v}$ *tert*-butyl acrylate in DMF with [M]:[I]:[L]:[Cu^{II}Br$_2$] being 250:1:0.12:0.02. Kinetics did not follow the pseudo-first order rate law (Figure S3), but HFIP-SEC showed excellent agreement to nominal molecular weight and narrow dispersities. The slow-down in the effective addition rate constant is likely due to termination at the rather high conversions employed, and can easily be avoided by an earlier termination of the polymerization.

Synthesis of poly(N,N-dimethyl ethyl methacrylate)

Poly(N,N-dimethyl ethyl methacrylate) (pD) was synthesized using copper-based photocatalysed polymerization. To this end, we extended the work of Haddleton et al. [3], in which poly(acrylates) are conveniently synthesized by photocatalysis of a Cu(II)-Me$_6$TREN complex, towards methacrylates. However, we found that the suggested conditions do not allow photocatalyzed polymerization of DMAEMA, since the polymerizations terminate at low conver-

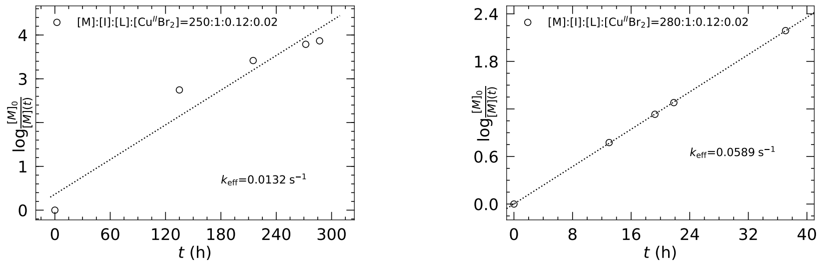

Figure S3: Pseudo-first order kinetics of (left) *tert*-butyl acrylate and (right) *N,N*-dimethylethyl methacrylate

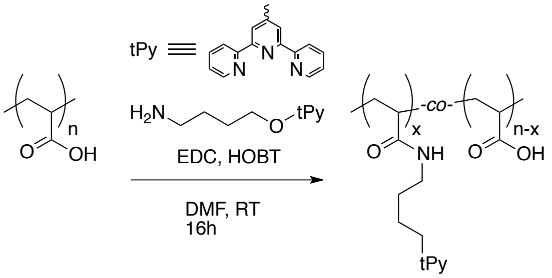

Figure S4: Synthesis of terpyridylated pAA copolymers by carbodiimde-driven peptide formation of pAA and an aminoalkyl terpyridine.

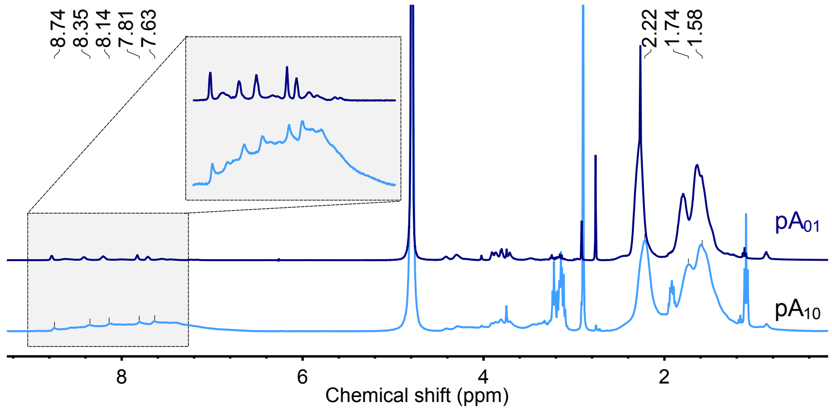

Figure S5: Proton NMR spectra (400 MHz, D_2O) of solutions of 1% and 10% terpyridylated pAA, pA$_{01}$ and pA$_{10}$. The inset shows a magnification of the aromatic (terpyridine) region.

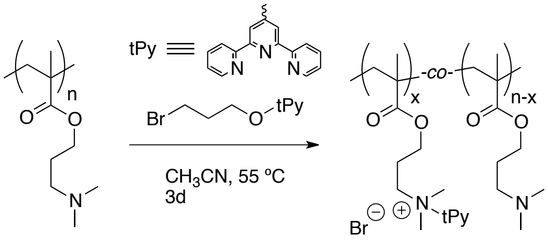

Figure S6: Synthesis of terpyridylated pDMAEMA copolymers by Menschutkin reaction of a terpyridyl alkylbromide with pDMAEMA.

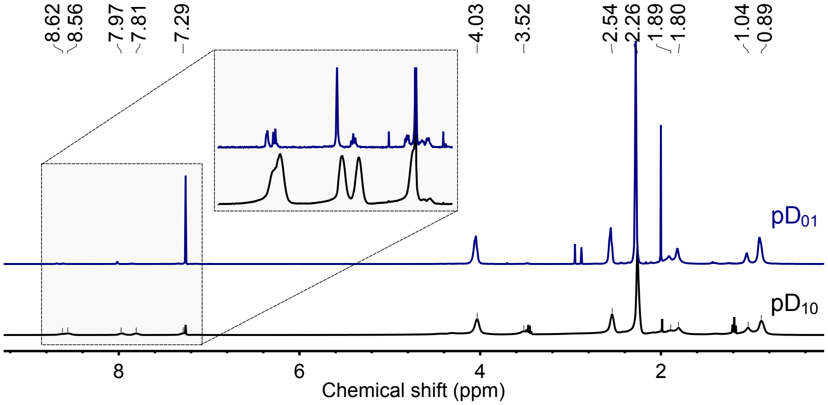

Figure S7: Proton NMR spectra (400 MHz, CDCl$_3$) of solutions of 1% and 10% terpyridylated pDMAEMA, pD$_{01}$ and pD$_{10}$. The inset shows a magnification of the aromatic (terpyridine) region.

sions. We also note a brown discoloration of the reaction medium. Following another work by Haddleton et al. [4], we swapped the initiator for methyl α-bromo phenylacetate (MBPA).

Copper(II)-Me$_6$TREN-catalyzed photopolymerization of DMAEMA yielded the polymer straightforwardly, at a convenient (50 g) scale. The kinetics adhered to the pseudo-first order rate law strictly (Figure S3), eliminating concerns over end of chain-end reactivity due to Menschutkin coupling with polymeric or monomeric DMAEMA. SEC-MALLS in HFIP (see main text) revealed a rather high dispersity (Đ=1.43) and a five-fold deviation from the conversion-based molecular weight (DP=216, M_{nominal} = 34 kDa). However, since we did not seek to compare relaxation times between complexes of polyelectrolytes of various molecular weights as has already been done, [5] but rather between complexes with different *added* transient bonds, we deemed the molecular weight to be sufficiently defined.

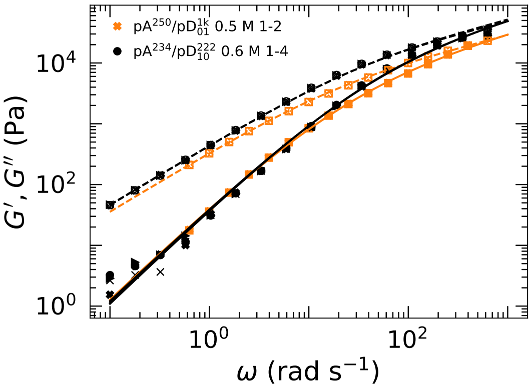

Figure S8: Storage (filled symbols) and loss (empty symbols) moduli G', G'' as function of ω, the frequency of oscillation for two complex coacervate pairs. The symbols are measured data, whereas the lines are fits to the fractional Maxwell model (Equation 3 of the main text).

"Native" viscoelasticity of coacervate complexes used in this work

To alleviate concerns about the presence of entanglements, we compare the viscoelasticity of two "native" coacervate complexes (i.e., no additional transient crosslinks): one made from commercial polymers (see Table 1 of the main text), and the other from polymer synthesized as described here (*vide supra*). Figure S8 shows frequency sweeps for the two coacervate pairs at similar salt concentrations. It can be readily seen that both samples have a strikingly similar viscoelasticity: most of the points lie in the terminal (viscous) regime, where $G' \propto \omega^2$ and $G'' \propto \omega^1$. The frequencies of crossover also appear similar, excluding serious slow-down in the dynamics as required by the presence of entanglements.

We estimate the crossover frequency using a fit to the fractional Maxwell model (see main text). The corresponding crossover times (here defined as $2\pi\tau_R = \omega_c^{-1}$) are 0.8 ms for pA^{234}/pD^{222} at 0.6 M NaCl and 1.2 ms for pA^{250}/pD^{1k} at 0.5 M NaCl, the superscripts denoting the degrees of polymerization. We can account for the difference in salt concentration c_s by noting that τ_R scales with $\exp -\sqrt{c_s}$ and carrying out an interpolation. [5,6] This estimates τ_R at 1.3 ms for pA^{234}/pD^{222} at 0.5 M NaCl, versus a measured τ_R of 1.2 ms for pA^{250}/pD^{1k} at the same c_s. In short, the relaxation times of the two complexes are essentially indistinguishable, despite the difference in M_n reported by SEC. Thus, we do not find evidence for the presence of entanglements, which would result in a severe increase of τ_R.

For unentangled monodisperse polyelectrolytes, $\tau_R \propto N^2$, which does not support the finding of similar relaxation times for chains with a four-fold difference in M_n. We reconcile the discrepancy by noting the increased polydispersity of pD^{1k}, and speculate that the lower molecular weight fraction of the residue acts to plasticize the coacervates. Alternatively, noting that the conversion-based degrees of polymerization of both poly(cations) are essentially identical (216 and 222), M_n or M_w could have been overestimated by SEC due to absorption of pD on the column. Again, we do not directly compare relaxation times between complexes derived from the two distinct pA/pD pairs, and thus the residue is defined enough in terms of molecular mass. Instead, we focus on the very strong effect of added transient bonds in unentangled coacervate complexes.

References

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