Supplementary Information for:

Organometallic mediated radical polymerization using bis(imino)pyridine vanadium trichloride complexes

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S1. X-ray crystallographic data

Table S1. Summary of X-ray experimental details for **12** and **14**

	12	**14**
Empirical Formula	C35 H47 Cl3 N3 V	C31 H23 Cl3 N3 V
Formula weight	708.10	635.87
Crystal size	0.50 × 0.40 × 0.05 mm^3	0.30 × 0.20 × 0.01 mm^3
Colour and habit	Black plate	Brown Plate
Crystal system	Triclinic	Orthorombic
Space group	P-1	Pbca
Unit cell dimensions	a = 17.658(9) Å α = 90° b = 13.195(6) Å β = 104.052(7)° c = 16.613(8) Å γ = 90°	a = 19.323(2) Å α = 90° b = 11.4292(14) Å β = 90° c = 27.637(3) Å γ = 90°
Volume	3755(3)$Å^3$	6103.4(13)$Å^3$
Z	4	8
Density (calculated)	1.253 Mg/m^3	1.384 Mg/m^3
Absorption coefficient	0.508 mm^{-1}	0.617 mm^{-1}
F(000)	1496	2608
Theta range for data collection	1.19 to 27.50°	1.47 to 27.49°
Completeness to theta = 25.00°	99.6%	100.0%
Reflections collected	15624	39589
Absorption correction	SADABS	SADABS
Hydrogen atoms	Calculated positions, riding model	Found, refined anisotropically
Max/min transmissions	0.9750 and 0.7853	0.9939 and 0.8365
Refinement method	Full-matric least-squares on F^2	Full-matric least-squares on F^2
Data / restraints / parameters	8380 / 0 / 0.1072	6941 / 0 / 371
Goodness-of-fit on F^2	0.945	1.161
Final indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.1072	R1 = 0.0651, wR2 = 0.1201
R indices (all data)	R1 = 0.1070, wR2 = 0.1210	R1 = 0.1619, wR2 = 0.1702

$$wR2 = (\sum[w(F_o^2-F_c^2)^2]/\sum[wF_o^4])^{1/2}$$

$$R1 = \sum \big| \, |F_o| - |F_c| \, \big| / \sum |F_o|$$

$$\text{Weight} = 1 / [\sigma^2(F_o^2) + (0.0577 * P)^2]$$

$$\text{where } P = (\max(F_o^2, 0) + 2 * F_c^2)/3$$

S2. Further polymerization data

Table S2. Effect of AIBN concentration on vinyl acetate polymerization using **1**.

AIBN equiv.	% conv.	M_n	PDI
0.6	21	2700	1.36
1.2	31	2640	1.31
6	46	1760	1.34

Reactions carried out in bulk, at 120°C for 6 h using AIBN. M_n corrected for VAc. Monomer:catalyst ratios of 100:1.

Table S3. Effect of temperature on vinyl acetate polymerization using **1**.

Temp. /°C	% conv.	$M_{n,th}$	M_n	PDI
120	25	4370	3380	1.29
110	23	4070	3870	1.37
100	26	4520	4300	1.37
90	29	4970	4490	1.50

Reactions carried out in bulk for 24 h using AIBN. Monomer:catalyst:initiator ratio of 100:1:0.6. M_n corrected for VAc. $M_{n,th}$ = [M]/[I]×MW(monomer)×conv.+ MW(cat)

Table S4. Effect of temperature on vinyl acetate polymerization using V-65 and **1**.

Temp. /°C	% conv.	$M_{n,th}$	M_n	PDI
110	27	4580	5650	1.35
100	25	4290	5830	1.40
90	24	4150	5630	1.43
80	29	4880	6400	1.49
70	33	5460	7410	1.57

Reactions carried out in bulk for 24 h. Monomer:catalyst:initiator ratio of 100:1:0.6. M_n corrected for VAc. $M_{n,th}$ = [M]/[I]×MW(monomer)×conv.+ MW(cat)

Table S5. Effect of temperature on vinyl propionate polymerization using **1**.

Temp. /°C	Time / h	% conv.	$M_{n,th}$	M_n	PDI
120	6	20	3990	3530	1.35
120	24	18	3660	3570	1.41
110	6	22	4330	3940	1.39
110	24	20	3990	3850	1.53
100	6	29	5500	4790	1.50
100	24	26	5000	5580	1.39
90	6	30	5670	5620	1.35
90	24	34	6340	5980	1.35

Reactions carried out in bulk using AIBN.
Monomer:catalyst:initiator ratio of 100:1:0.6. M_n corrected for VAc. $M_{n,th}$ = [M]/[I]×MW(monomer)×conv.+ MW(cat)

Table S6. Effect of temperature on vinyl pivalate polymerization using **1**.

Temp. /°C	Time / h	% conv.	$M_{n,th}$	M_n	PDI
120	6	36	8320	9340	1.36
120	24	30	7040	10550	1.43
110	6	32	7460	9770	1.36
110	24	36	8320	9920	1.39
100	6	49	11090	13570	1.42
100	24	32	7460	10010	1.36
90	6	53	11940	15010	1.37
90	24	50	11300	17880	1.42

Reactions carried out in bulk using AIBN.
Monomer:catalyst:initiator ratio of 100:1:0.6. M_n corrected for VAc. $M_{n,th}$ = [M]/[I]×MW(monomer)×conv.+ MW(cat)

Table S7. Effect of temperature on vinyl benzoate polymerization using **1**.

Temp. /°C	Time / h	% conv.	$M_{n,th}$	M_n	PDI
120	6	20	5620	3960	1.56
120	24	19	5370	3280	1.53
110	6	21	5860	3580	1.56
110	24	19	5370	3540	1.54
100	6	21	6110	3630	1.56
100	24	14	4120	4180	1.46
90	6	19	5370	3760	1.57
90	24	24	6610	3900	1.50

Reactions carried out in bulk using AIBN.
Monomer:catalyst:initiator ratio of 100:1:0.6. M_n corrected for VAc. $M_{n,th}$ = [M]/[I]×MW(monomer)×conv.+ MW(cat)

S3. GPC traces

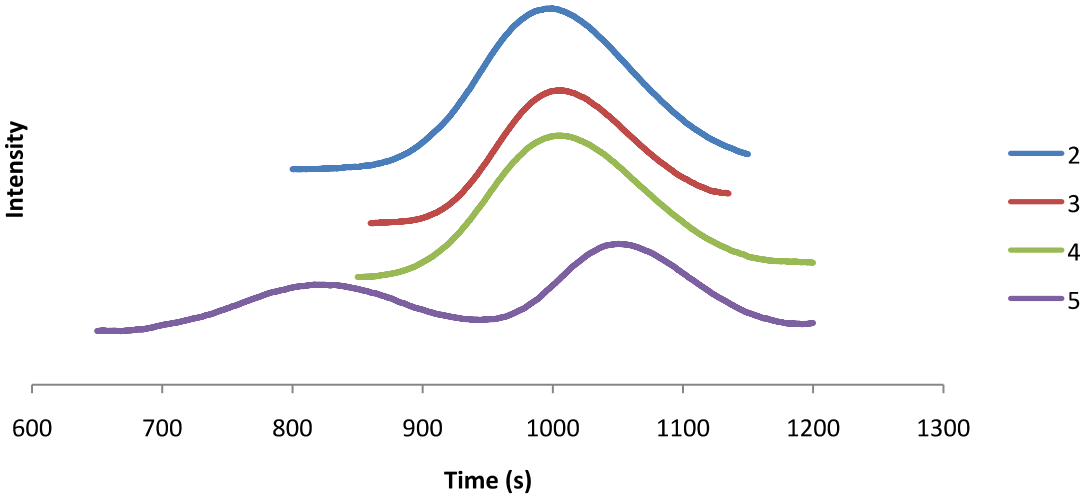

Fig. S1 GPC trace for complexes **2-5**. GPC conducted using a polymer concentration of 2 mg/mL.

S4. Kinetic data

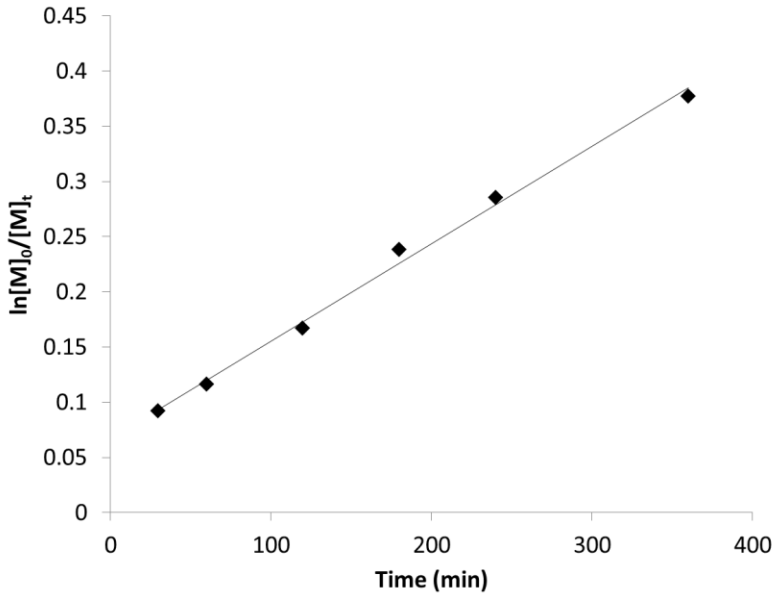

Fig. S2 Plot of $\ln[M]_0/[M]_t$ versus time for bulk vinyl acetate polymerization initiated by AIBN at 120°C using **1**, with monomer:catalyst:initiator ratio of 100:1:0.6.

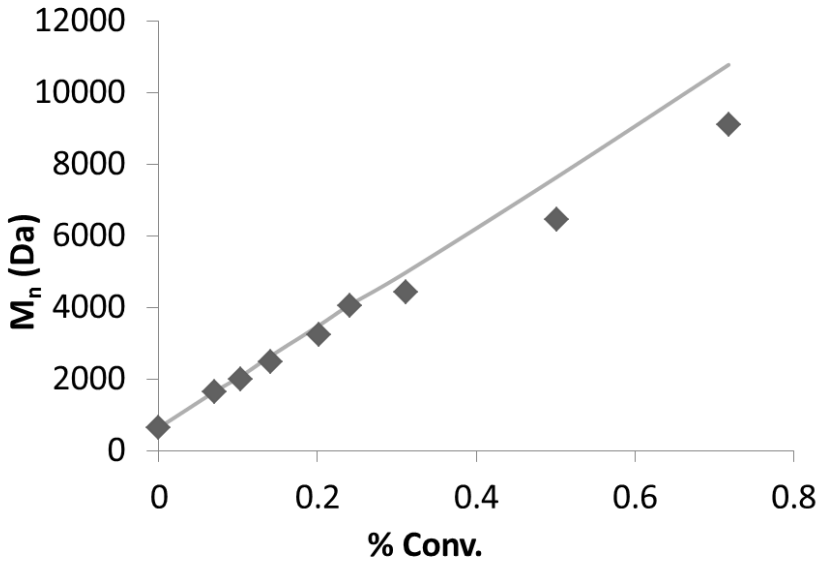

Fig. S3 Plot of M_n versus conversion for bulk vinyl acetate polymerization initiated by AIBN at 120°C using **1**, with monomer:catalyst:initiator ratio of 100:1:0.6.

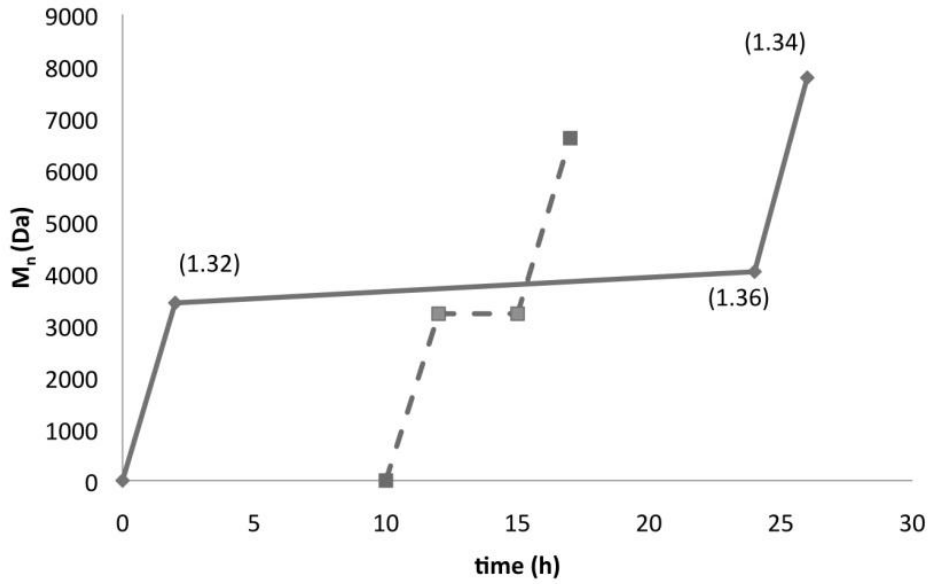

Fig. S4 Start-stop experiment for bulk vinyl acetate polymerization initiated by AIBN at 120°C using **1**, with monomer:catalyst:initiator ratio of 100:1:0.6. Experiment halted by freezing polymerization reaction for 22 h (solid line) and restarting by heating back to 120°C, or by isolating polymer and restarting polymerization with a new monomer aliquot (dashed line).