SUPPORTING INFORMATION

For

Controlled radical polymerization of vinyl acetate mediated by a vanadium catalyst

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General Experimental Conditions

All experiments involving moisture and air sensitive compounds were performed under a nitrogen atmosphere using a Mbraun LABmaster sp glovebox system equipped with a -33°C freezer, a built in Siemens Simantic Touch Panel and $[H_2O]$ and $[O_2]$ analyzers.

Vinyl acetate (99% Adrich) and styrene (≥99% Aldrich) were dried over calcium hydride overnight, degassed by four freeze-thawing cycles after being distilled under reduced pressure and stored under nitrogen. Anhydrous THF, pentane and diethyl ether were obtained from an Innovative Technologies glove box with an inline Solvent Purification System, consisting of alumina and a copper catalyst. 2,6-diisopropylaniline (90%, Aldrich) was purchased at technical grade and was distilled under vacuum. 2,6-diacetylpyridine (99%, Aldrich), azobisisobutyronitrile (AIBN, 98%, Aldrich), propanethiol (99%, Aldrich), potassium hydroxide (KOH, Analar), vanadium(III) chloride (97% Aldrich), chloroform (HPLC grade, Fisher), methanol (MeOH, HPCL grade, Caledon) were used as received.

Characterization

Gel permeation chromatography (GPC) was carried out in THF (flow rate: 1 mL min^{-1}) at 50 °C with PL–GPC 50 Plus integrated GPC system includes three 300x7.5 mm Resipore columns. Polystyrene and/or poly(methyl methacrylate) standards were used for calibration. ^{1}H-NMR and 2-D spectra were recorded with a Bruker Avance Spectrometer (300 MHz) in CDCl$_3$ or D$_2$O. Elemental analyses were conducted by Guelph Analytical Laboratories. Polymer molecular weights were determined by two complementary methods: integration of initiator ^{1}H NMR signals from AIBN relative to the methine signal in poly(vinyl acetate) and those determined from GPC measurements corrected by Mark-Houwink parameters for low molecular weight (< 20kDa) vinyl acetate.[1] GPC molecular weights are reported in tables found in the paper and this Supporting Information, but molecular weights determined by NMR were consistently within 5% of these values.

[1] Gruendling, T.; Junkers, T.; Guilhaus, M.; Barner-Kowollik, C. *Macromol. Chem. Phys.* **2009**, *210*, ASAP. DOI: 10.1002/macp.200900323.

General Polymerization Procedure

[BIMPY]VCl$_3$ (3.130×10^{-4} mol), AIBN (1.879×10^{-4} mol) and vinyl acetate (0.031 mol) were placed into a 50 mL ampoule under an inert atmosphere. The ampoue was sealed and placed in a pre-heated oil bath for a defined period of time. At the end of the reaction, the ampoule was cooled to room temperature. Addition of 10 mL pentane induced the precipitation of the polymer that was collected by filtration. The polymer was then dissolved in 5 mL THF and precipitated with 10 mL pentane and then repeated. The deep red polymer sample was then dried under vacuum for 12h and weighed to gravimetrically determine % conversion, and characterized by GPC and NMR. For kinetic experiments, ampoules were loaded in parallel and removed at defined intervals to track polymerization progress over time.

Further Purification of the PVAc Polymer

A 10 cm silica gel column was used (100 – 200 mesh). 0.200 g of polymer was dissolved in THF and loaded onto the column using 50 mL of hexanes. After fully loaded onto the column, the column was eluted with 50 mL CHCl$_3$ to remove impurities. The remaining red fragment was eluted with 20 mL of THF. Solvent was evaporated under vacuum until approx. 5 mL and polymer precipitated by addition of 10 mL of pentane. The polymer was collected via filtration and dried under vacuum for 12h to isolate 0.122 g of purified PVAc.

General Procedure of Stop – Start Experiment

For this experiment three different ampoules were used. All three ampoules with same amount of AIBN-VCl$_3$BIMPY and VAc were heated and stirrred in oil-bath at 120°C for 3 hours. After 3 hours one of ampoule taken out and molecular weight was determined by GPC. Remaining two ampoule stored in the freezer (- 35 ^{o}C) for 24 hours. After 24 hours another one ampoule was taken out and it's molecular weight was determined by GPC. Last ampoule was putted into an oil bath at 120°C and heated for more 3 hours.

Preparation of Proton Terminated Poly(vinyl acetate)

0.200g (Run No: 5) PVAc polymer was added to a flask under an inert atmosphere in 10mL of degassed methanol. Then degassed 1-propanethiol was added with a syringe under an inert atmosphere. The mixture was heated to 50 ^{o}C for 24h. The polymer was precipitated in heptane before being dried under vacuum before analysis by GPC and NMR. Resulting polymer, M_n = 3077, color = off-white, weight = 0.122g. ^{1}H NMR (CDCl$_3$): 4.86 ppm (CH$_2$C*H*OCOCH$_3$, polymer chain); 3.87 (CH$_2$C*H$_2$*OCOCH$_3$, proton terminated polymer chain); 2.04 (CH$_2$CHOCOC*H$_3$*, polymer chain); 1.7-1.9 (C*H$_2$*CHOCOCH$_3$, polymer chain); 1.4-1.5 (AIBN, partially obscured).

Base-catalyzed Methanolysis to Produce Poly(vinyl alcohol)

0.200g VAc polymer (Run No: 6) was dissolved in 5 mL THF and 0.05g KOH was dissolved in 10 mL MeOH. The polymer solution was added slowly to KOH solution and this mixture stirred for 48h at room temperature. After removing all solvent under vacuum, the remaining residue was dissolved in 3mL distilled water and the polymer precipitated with 10mL of cold acetone. The product was collected by filtration and dried under vacuum before analysis by GPC and NMR. Resulting polymer,

color = white, weight = 0,097g. ^{1}H NMR (D$_2$O): 4.14 (CH$_2$CHOH, polymer chain); 3.45 (CH$_2$CH$_2$OH, end group); 1.5-1.8 (CH$_2$CHOH, polymer chain); AIBN end groups partially obscured.
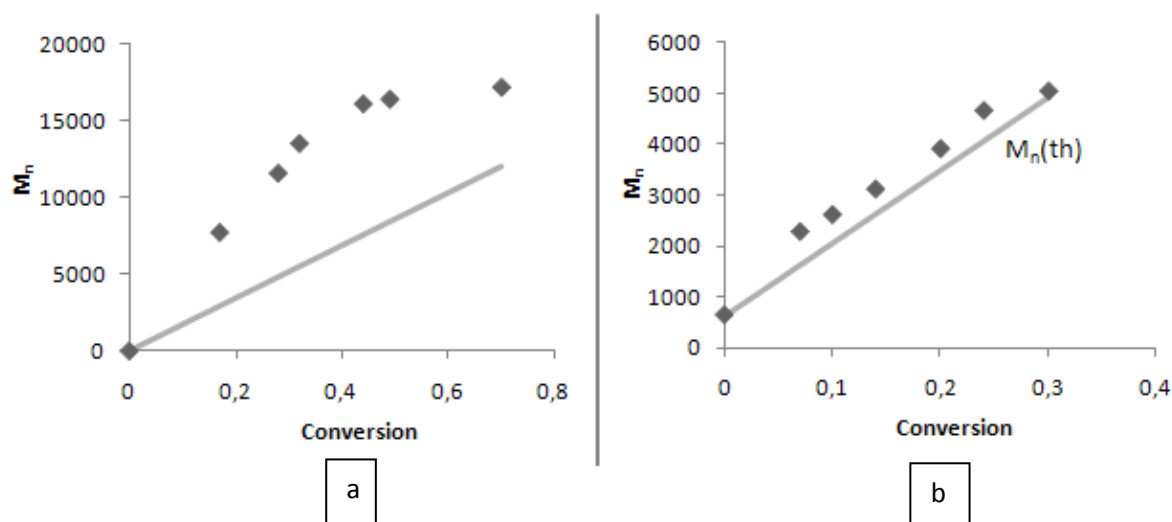
Figure 1S. Dependence of PVAc M_n on monomer conversion for the bulk polymerization of styrene (a) and vinyl acetate (b) at 120°C. [BIMPY]VCl$_3$:AIBN:VAc is 1:0.5:100.
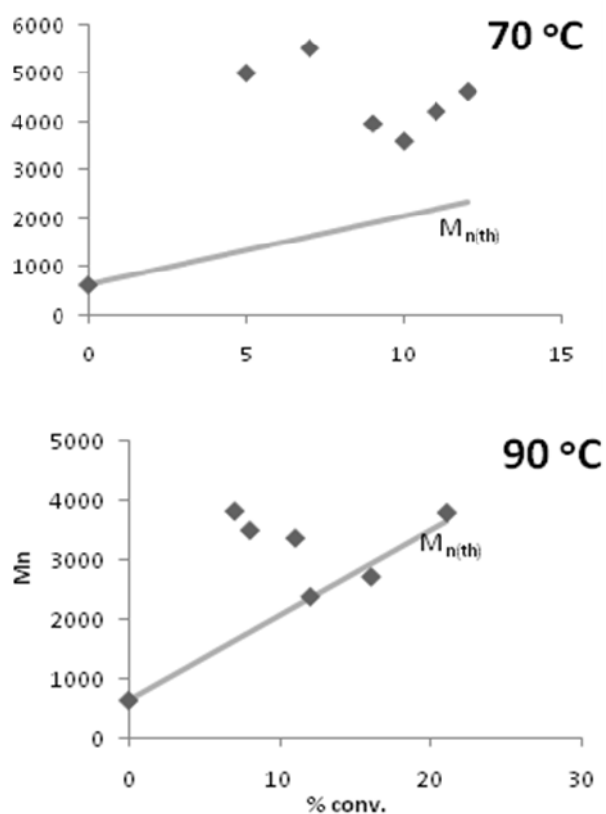
Figure 2S. Dependence of PVAc M_n on monomer conversion for the bulk polymerization of vinyl acetate at 70°C and 90°C. [BIMPY]VCl$_3$:AIBN:VAc is 1:0.6:100.
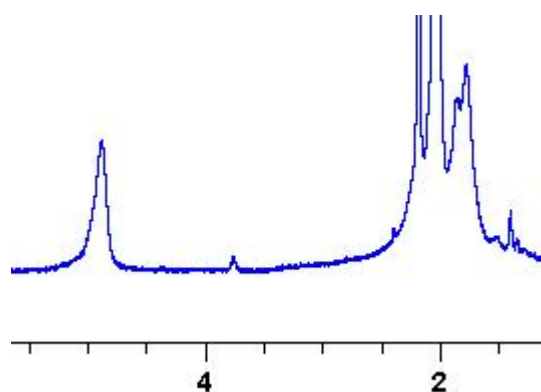
Figure 3S. ^{1}H NMR of proton terminated PVAc showing PVAc peaks at 1.8, 2.0 and 4.8 ppm, AIBN initiating groups at 1.5 ppm and terminal $–CH_2-O(C=O)CH_3$ groups at 3.8 ppm.

Table 1S: Kinetic Results

Run No.	Time (min)	Temp (°C)	Yield (g)	Conv. (%)	$M_{n(th)A}$	$M_{n(th)B}$	M_n	M_w	PDI
1	30	120	0.10	7	1140.92	1642.82	1640	2230	1.36
2	60	120	0.13	10	1356.02	2073.02	1975	2726	1.38
3	120	120	0.19	14	1642.82	2646.62	2480	3298	1.33
4	180	120	0.27	20	2073.02	3507.02	3277	4424	1.35
5	240	120	0.32	24	2359.82	4080.62	4031	5294	1.31
6	360	120	0.41	30	2790.02	4941.02	4412	5912	1.34
7	720	120	0.69	50	4224.02	7809.02	6440	8940	1.39
8	1080	120	0.98	72	5801.42	10963.82	9102	12834	1.41
9	30	90	0.09	7	1140.92	1642.82	3814	5492	1.44
10	60	90	0.11	8	1212.62	1786.22	3493	4961	1.42
11	120	90	0.15	11	1427.72	2216.42	3363	4810	1.43
12	180	90	0.17	12	1499.42	2359.82	2380	2594	1.09
13	240	90	0.21	16	1786.22	2933.42	2714	3935	1.45
14	360	90	0.28	21	2144.72	3650.42	3788	5796	1.53
15	30	70	0.02	5	997.52	1356.02	5020	6950	1.38
16	60	70	0.03	7	1140.92	1642.82	5332	6916	1.30
17	120	70	0.04	9	1284.32	1929.62	3970	5360	1.35
18	180	70	0.04	10	1356.02	2073.02	3610	5074	1.41
19	240	70	0.05	11	1427.72	2216.42	4220	5824	1.38
20	360	70	0.05	12	1499.42	2359.82	4640	5990	1.29

$M_{n(th)A}$ calculated where AIBN produces two active radicals; $M_{n(th)A}$ = [M]o/2[I] x (86.04g/mol) x %conv
$M_{n(th)B}$ calculated where AIBN produces one active radical; $M_{n(th)B}$ = [M]o/[I] x (86.04g/mol) x %conv