Supporting Information: Exploring High Molecular Weight Vinyl Ester Polymers made by PET-RAFT

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Methods

Characterization

Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H NMR spectra were obtained on a Bruker 400 MHz spectrometer. Monomer conversions were determined via proton (^{1}H) NMR spectroscopy. Data is reported in ppm using $CDCl_3$ as solvent unless otherwise specified.

Size exclusion Chromatography (SEC)

All size exclusion chromatography (SEC) was performed using an Agilent SEC system equipped with an autosampler, an Agilent 1260 isocratic pump, 1 × Agilent MixedB-guard and 2 × AgilentMixed-B analytical columns and an Agilent 1260 refractive index (RI) detector. The eluent Tetrahydrofuran (THF) at 30 °C with a flow rate of 1 mL/min. The system was calibrated with poly(methyl methacrylate) standards with molecular weights the range of 617500 to 1010. All sample were filtered through a 200 nm PTFE filter prior to injection. Experimental molecular weights for VA and VPiv monomers were corrected using Mark-Houwink parametrs[1] while experimental molecular weights for VPro monomer were reported without any correction. Theoretical molecular weights were calculated. [1]

Materials

All materials were purchased from commercial sources and used as received unless otherwise specified. The chain transfer agent 2-(ethoxycarbonothioyl) sulfanyl propanoic acid (EtPAX) was prepared from known literature procedure.[2]

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[1] $M_{n,Theory} = M_{Monomer} \times ([Monomer]_o / [CTA]_o) \times Monomer\ Conversion$

where $M_{Monomer}$ is the molecular weight of vinyl ester monomer, $[Monomer]_o$ is the initial concentration of vinyl ester monomer, $[CTA]_o$ is the initial concentration of the CTA.

Synthesis

Synthesis of 2-(ethoxycarbonothioyl) sulfanyl propanoic acid (EtPAX)
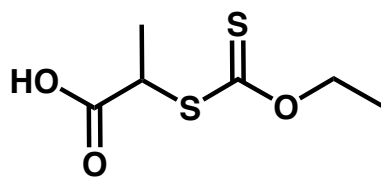

Chart S1- Structure of EtPAX

1) Synthesis of Potassium ethyl xanthogenate

KOH (6.5 g, 0.11 mol) was dissolved in ethanol (63 mL) and cooled to 0 °C. Carbon disulfide (7.3 mL, 0.12 mol) was added dropwise until a yellow precipitate formed. The excess solvent was then removed under reduced pressure.

2) Synthesis of EtPAX

2-bromopropanoic acid (5.27 g, 0.0374 mol) was dropwise added to a solution of potassium ethyl xanthogenate (6 g, 0.0374 mol) and acetone (25 mL) and allowed to stir at room temperature for 3 h. The residual solvent was removed under reduced pressure. The solid was dissolved in saturated sodium carbonate and washed with diethyl ether. The aqueous layer was acidified using HCl and the product was extracted with diethyl ether. The organic layer was then washed with distilled water, brine, and dried with anhydrous sodium sulfate. Residual solvents removed under reduced pressure. ^{1}H NMR (500 MHz, CDCl3) δ 4.68 (q, J = 7.1 Hz, 2H), 4.45 (q, J = 7.4 Hz, 1H), 1.64 (d, J = 7.4 Hz, 3H), 1.45 (t, J = 7.1 Hz, 3H) in agreement with the literature.[3]

Preparation of Ir(ppy)₃ (1000 ppm) solution

Ir(ppy)$_3$ (10.00 mg) was dissolved in DMF (10.00 mL) and sonicated for 10 mins.

Preparation of Ir(ppy)₃ (5000 ppm) solution

Ir(ppy)$_3$ (50.00 mg) was dissolved in DMF (10.00 mL) and sonicated for 10 mins.

General procedure for polymerization of vinyl ester monomers

A 10 mL Schlenk flask was equipped with a Teflon stir bar, EtPAX, Ir(ppy)$_3$ (1000 ppm), vinyl ester monomer (VPro, VA, and VPiv) were measured based on the DP value. The reaction mixture was deoxygenated using freeze thaw method. The polymerization reaction was carried out in blue LED light photoreactor (Cylindrical photo reactor with diameter = 15 cm and height = 14 cm, Intensity = 7.9±0.4 mW/cm^2, λ_{max} = 450 ± 10 nm). Aliquots were taken at time intervals (For VA and VPro- 1, 5, 7, 15 and 24 h and for VPiv- 1, 2.5, 4, 7, and 15 h) using a long needle, syringe, and N$_2$ line to insure an inert atmosphere. Samples were subsequently analyzed using ^{1}H NMR and GPC (THF).

Table S1: Mole ratios, moles, and masses/volumes of monomer, EtPAX and Ir(ppy)$_3$ used when targeting chain lengths of 200 units.

Monomer	Mole Ratio EtPAX:Monomer:Ir(ppy)$_3$	Moles of Monomer (mmol)	Mass of Monomer (g)	Moles of EtPAX (mol)	Mass of EtPAX (mg)	Moles of Ir(ppy)$_3$ (mol)	Volume of Ir(ppy)$_3$ (1000 ppm) (µL)
VPro	1 : 200 : 0.002	9.99	1.00	4.9994 X 10^{-5}	9.70	0.99 X 10^{-7}	65.41
VA	1 : 200 : 0.002	11.6	1.00	5.8079 X 10^{-5}	11.30	1.16 X 10^{-7}	76.07
VPiv	1 : 200 : 0.002	7.80	1.00	3.9011 X 10^{-5}	7.57	0.78 X 10^{-7}	51.09

Light ON-OFF experiment

Light ON-OFF experiment was performed to demonstrate the effect of the blue light for the polymerization. VPiv monomer (DP 200) polymerization was studied for total 7 h period, with light on and off periods. Samples were collected before and after light off, and during light on periods as in the general polymerization procedure. All samples were analyzed using ^{1}H NMR and GPC (THF).

VPiv polymerization using 5000 ppm Ir(ppy)$_3$ solution

A 10 mL Schlenk flask was equipped with a Teflon stir bar, EtPAX, Ir(ppy)$_3$ (5000 ppm), VPiv monomer were measured based on the DP value. The reaction mixture was deoxygenated using freeze thaw method. The polymerization reaction was carried out for 15 h in blue light photoreactor. Samples were subsequently analyzed using ^{1}H NMR and GPC (THF).

Chain extension experiment

1) Chain extension for DP 200 system

First polymerization reaction was carried out for VPiv monomer using the mole ratio of VPiv: EtPAX:Ir(ppy)$_3$ = 200:1:0.002. The polymerization was performed as in the general polymerization procedure for 4 h. After the first polymerization reaction and checking the monomer conversion, the chain extension reaction was performed by adding an appropriate amount of monomer under deoxygenated condition to maintain macro-CTA:VPiv monomer = 1:400. The chain extension was carried under blue light irradiation for 15 h. The chain extension and monomer conversion were determined using GPC (THF) and ^{1}H NMR.

2) Chain extension for DP 1500 system

The same procedure was followed for DP 1500 system using the mole ratio of VPiv: EtPAX:Ir(ppy)$_3$ = 1500:1:0.015 for the synthesis of macro-CTA and the ratio of macro-CTA:VPiv monomer = 1:400 for the extension.

Supporting Data

Determination of optimal photocatalyst concentration

Polymerization kinetics of VPiv monomer (DP 1500) were carried out as general polymerization procedure in the presence of varied concentrations of Ir(ppy)$_3$ (3, 10, 30 ppm relative to monomer).
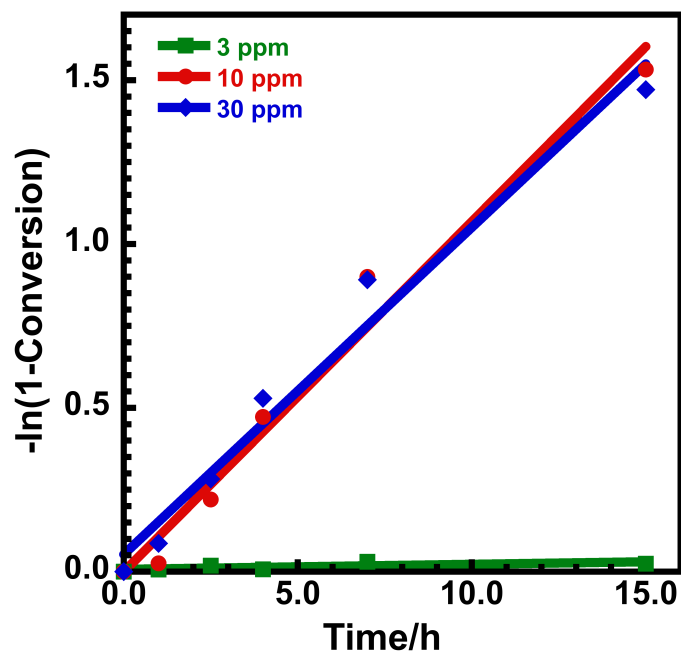

Figure S1: Semilogarithmic kinetic plots for PVPiv. Polymerization reactions were performed at room temperature and under blue light irradiation, using a 3, 10 and 30 ppm of Ir(ppy)$_3$ relative to monomer and [VPiv]:[EtPAX] = 1500: 1.

Table S2: Molecular weight distributions for VPiv system (DP 1500) with 10 and 30 ppm of Ir(ppy)$_3$

Time/h	10 ppm		30 ppm	
	M_n	M_w/M_n	M_n	M_w/M_n
0				
1				
2.5	45426	1.29	35444	1.38
4	72313	1.29	50850	1.38
7	105298	1.39	58284	1.51
15	107311	1.54	59415	1.68

Table S3: Conversions for VPiv system (DP 1500-12000) with 1% DMF.

DP	Conversion %
1500	73
3000	80
6000	78
12000	71

Table S4: M_n, M_w/M_n, and conversion at each time point of VPro system (DP 200-6000).

Time/h	VPro 200			VPro 400			VPro 800		
	Conversion %	M_n	M_w/M_n	Conversion %	M_n	M_w/M_n	Conversion %	M_n	M_w/M_n
5	23	5400	1.29	14	6800	1.39	20	15800	1.41
7	34	9200	1.23	23	11100	1.39	29	19500	1.59
15	64	13200	1.53	55	23400	1.53	46	39900	1.53
24	82	21800	1.86	70	26400	1.83	66	50300	1.93

Time/h	VPro 1500			VPro 3000			VPro 6000		
	Conversion %	M_n	M_w/M_n	Conversion %	M_n	M_w/M_n	Conversion %	M_n	M_w/M_n
5	26	22100	1.43	12	25200	1.57	9	43600	1.49
7	28	27700	1.59	16	30700	1.54	15	49300	1.43
15	59	49700	1.79	55	49200	2.04	44	64300	1.62
24	78	60900	2.18	73	66800	2.29	67	88700	2.00

Table S5: M_n, M_w/M_n, and conversion at each time point of VA system (DP 200-12000).

Time/h	VA 200			VA 400		
	Conversion %	M_n	M_w/M_n	Conversion %	M_n	M_w/M_n
5	29	5200	1.23	39	13000	1.21
7	49	7900	1.27	49	16800	1.27
15	77	15700	1.31	76	35600	1.29
24	89	18600	1.34	85	36700	1.29

Time/h	VA 800			VA 1500		
	Conversion %	M_n	M_w/M_n	Conversion %	M_n	M_w/M_n
5	30	23400	1.24	36	38400	1.27
7	49	27600	1.30	55	46100	1.32
15	62	44800	1.26	73	51400	1.36
24	87	46500	1.46	84	58600	1.58

Time/h	VA 3000			VA 6000			VA 12000		
	Conversion %	M_n	M_w/M_n	Conversion %	M_n	M_w/M_n	Conversion %	M_n	M_w/M_n
5	24	49300	1.37	28	53700	1.40	14	83400	1.44
7	32	65300	1.44	29	69500	1.39	15	93900	1.55
15	68	74800	1.60	58	68800	1.66	50	110100	1.87
24	75	81200	1.84	75	103900	1.82	74	115500	1.92

Table S6: M_n, M_w/M_n, and conversion at each time point of VPiv system (DP 200-12000).

Time/h	VPiv 200			VPiv 400		
	Conversion %	M_n	M_w/M_n	Conversion %	M_n	M_w/M_n
2.30	19	4300	1.34	28	15400	1.91
4	41	15700	1.11	43	26300	1.16
7	67	23600	1.24	57	35600	1.21
15	83	26800	1.30	80	40500	1.33

Time/h	VPiv 800			VPiv 1500		
	Conversion %	M_n	M_w/M_n	Conversion %	M_n	M_w/M_n
2.30	31	33300	1.27	20	45500	1.29
4	50	49200	1.29	38	72400	1.29
7	66	59000	1.39	59	105300	1.39
15	80	83600	1.48	78	107400	1.54

Time/h	VPiv 3000			VPiv 6000			VPiv 12000		
	Conversion %	M_n	M_w/M_n	Conversion %	M_n	M_w/M_n	Conversion %	M_n	M_w/M_n
2.30	11	37900	1.36	10	53300	1.54	4	53000	1.53
4	18	62200	1.50	26	113400	1.42	10	97900	1.50
7	39	107600	1.31	54	139600	1.59	28	171900	1.58
15	76	136900	1.65	72	163800	1.73	63	173600	1.80

Table S7: Selected high M_n and low M_w/M_n of PVPiv, PVA and PVPro polymers made by PET-RAFT polymerization. Conditions: Polymerization reactions were performed at room temperature and under blue light irradiation (Intensity = 7.9±0.4 mW/cm^2, λ_{max} = 450 ± 10 nm) and deoxygenated conditions using a molar ratio of [Ir(ppy)$_3$]/[M] = 10 ppm and [M]:[EtPAX] = X:1 (X = The value of DP, e.g., for DP 200, X = 200).

DP	[Ir]/[M] ppm	Monomer	Time/h	Conversion %	M_n	M_w/M_n
1500	10	VPiv	7	59	105300	1.39
3000	10	VPiv	7	39	107600	1.31
6000	10	VPiv	4	26	113400	1.42
1500	10	VA	15	73	51400	1.36
3000	10	VA	7	32	65300	1.44
6000	10	VA	7	29	69500	1.39
12000	10	VA	5	14	83400	1.44
6000	10	VPro	7	15	49300	1.43
6000	10	VPro	15	44	64300	1.62

Table S8: M_n, M_w/M_n, and conversion of VPiv system in the presence of 5% DMF and 5% DMSO. Conditions: Polymerization reactions were performed at room temperature and under blue light irradiation (Intensity = 7.9±0.4 mW/cm^2, λ_{max} = 450 ± 10 nm) and deoxygenated conditions using a molar ratio of [Ir(ppy)$_3$]/[M] = 10 ppm and [M]:[EtPAX] = 1500:1.

DP	Monomer	Photocatalyst	Solvent	Time/h	Conversion %	M_n	M_w/M_n
1500	VPiv	Ir(ppy)$_3$	5% DMF	15	78	107300	1.54
1500	VPiv	Ir(ppy)$_3$	5% DMSO	24	89	172800	1.73
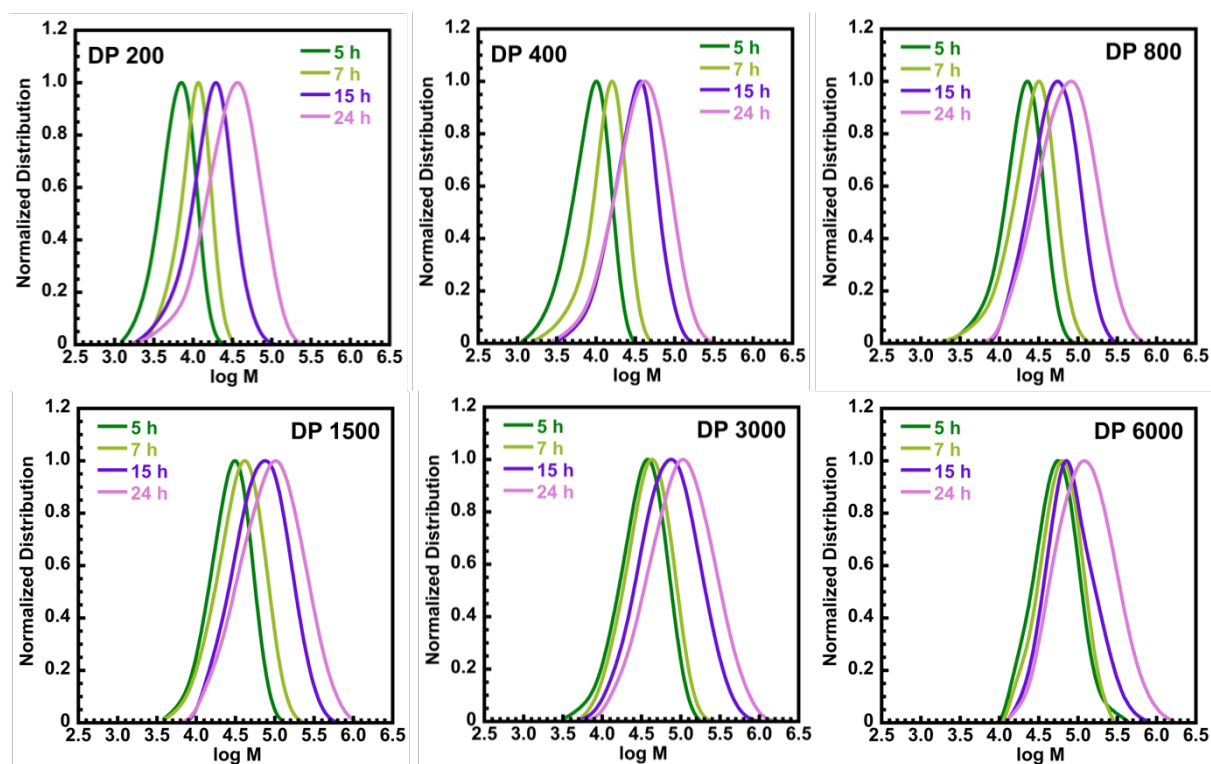
Figure S2: Normalized molecular weight distribution at each time point showing molecular weight evolution for VPro system (DP 200-6000).
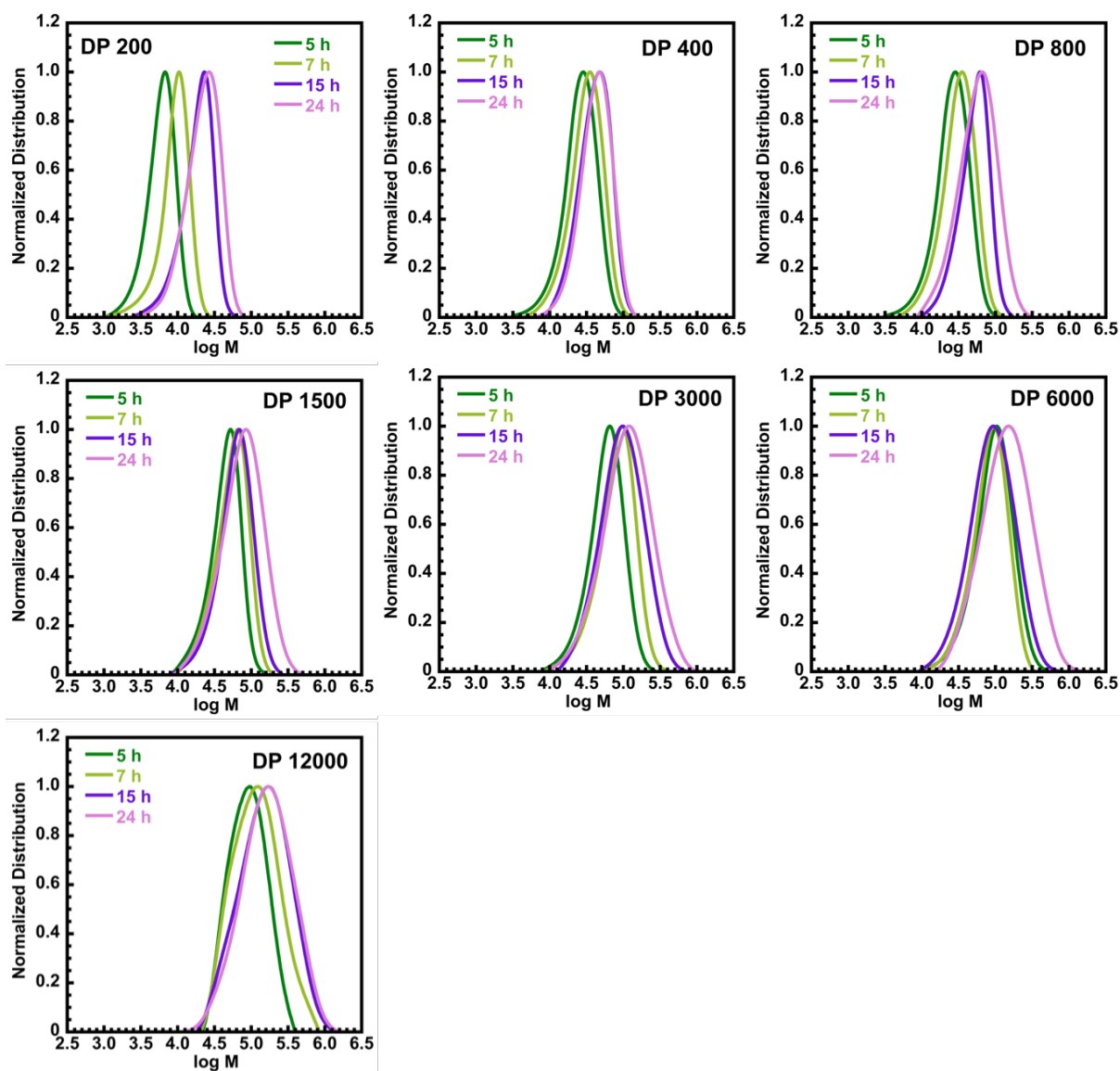
Figure S3: Normalized molecular weight distribution at each time point showing molecular weight evolution for VA system (DP 200-12000).
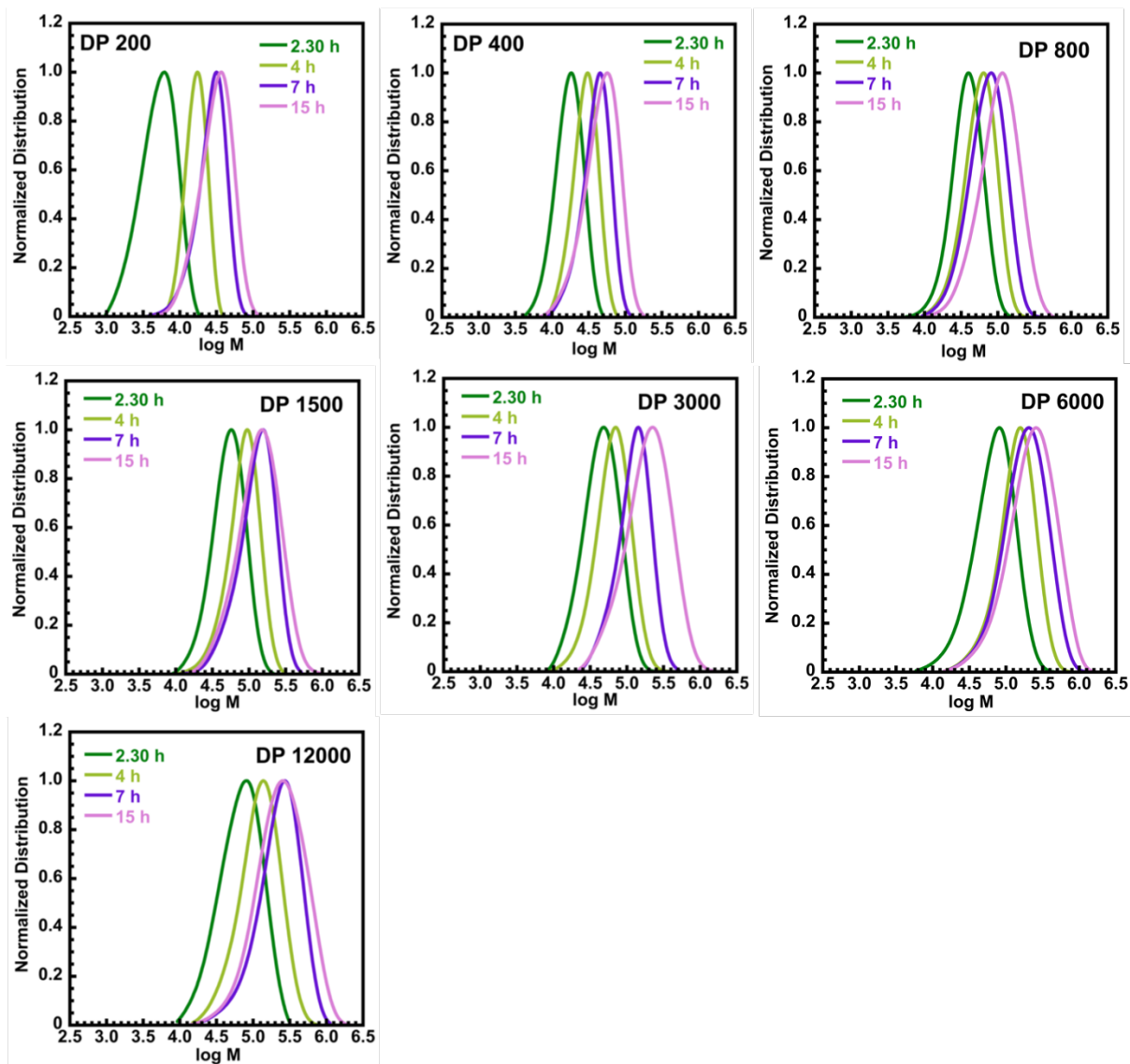
Figure S4: Normalized molecular weight distribution at each time point showing molecular weight evolution for VPiv system (DP 200-12000).
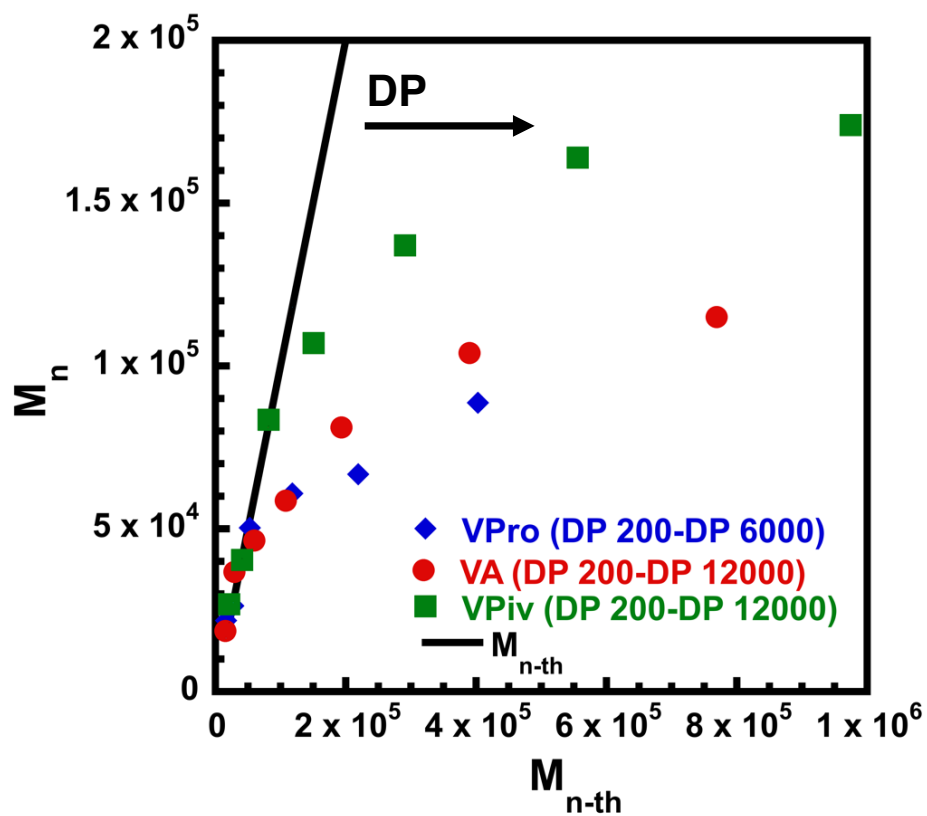
Figure S5: $M_{n\text{-GPC}}$ vs $M_{n\text{-th}}$ graphs for VPro, VA and VPiv polymers. Polymerization reactions were performed at room temperature and under blue light irradiation (Intensity = 7.9±0.4 mW/cm², λ_{max} = 450 ± 10 nm) and deoxygenated conditions using a molar ratio of [Ir(ppy)₃]/ [M] = 10 ppm and [M]:[EtPAX] = X:1 (X = The value of DP, e.g., for DP 200, X = 200).

Considering the M_n as the ratio of consumed monomer to polymer end groups as follows gives:

$$M_n = M_{monomer} \frac{[M]_0 conv}{[CTA] + k_{tr}[S][P^\bullet]t} \tag{S1}$$

Assuming fast initiation, where M_n is the number averaged molecular weight, $M_{monomer}$ is the molecular weight of the monomer, $[M]_0$ is the initial monomer concentration, conv is conversion, [CTA] is the concentration of CTA, k_{tr} is the transfer rate coefficient to solvent, [S] is the solvent concentration and $[P^\bullet]$ is the radical concentration with t being the time. This can be rewritten as follows:

$$1/M_n = 1/M_{n-theory} + 1/M_{monomer} \left(\frac{k_{tr-S}[S][P^\bullet]t}{[M]_0 conv} \right) \tag{S2}$$

With conversion being given by, assuming pseudo first order kinetics:

$$conv = 1 - Exp[-k_p[P^\bullet]t] \tag{S3}$$

This can be approximated as (at least for lower conversions):

$$conv = k_p[P^\bullet]t \tag{S4}$$

Hence

$$1/M_n = 1/M_{n-theory} + 1/M_{monomer} \left(\frac{k_{tr-S}[S][P^\bullet]t}{k_p[P^\bullet][M]_0 t} \right) \tag{S5}$$

Which gives:

$$1/M_n = 1/M_{n-theory} + 1/M_{monomer} \left(\frac{k_{tr-S}[S]}{k_p[M]_0} \right) = 1/M_{n-th} + 1/M_{monomer} C_S \left(\frac{[S]}{[M]_0} \right) \tag{S6}$$

This is equivalent to the Mayo equation with $C_S = \frac{k_{tr-S}}{k_p}$.[4,5] Hence the intercept is proportional to the ratio of solvent to monomer, the reciprocal of the monomer molecular weight and the solvent transfer constant. Therefore, at a fixed solvent to monomer ratio such as 5% C_s can be estimated. This is given in Table S9.

Table S9: Estimates of Cs for VPro, VA, VPiv with $[S]/[M]_0 = 0.05$

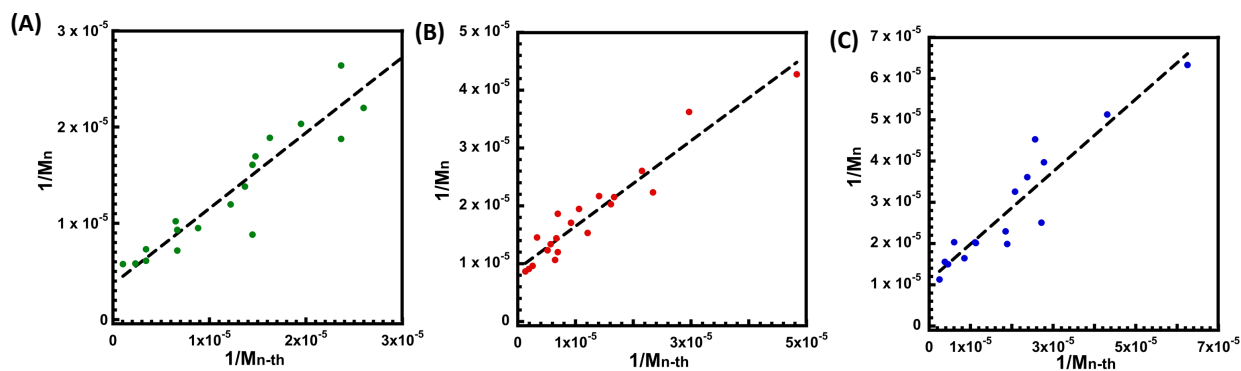| Monomer	Intercept $1/M_n$ vs $1/M_{n-th}$	$M_{monomer}$	C_s
VPro	1.1×10^{-5}	100.118	0.022
VA	9×10^{-6}	86.09	0.015
VPiv	4×10^{-6}	128.17	0.01

Figure S6: $1/M_n$ vs $1/M_{n\text{-}th}$ graphs of (A)Vpiv (DP 800-DP 12000) (B)VA (DP 800-DP 12000) (C)VPro (DP 800-DP 6000).

References

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