Tuning Molecular Weight Distributions of Vinylketone Based Polymers using RAFT Photopolymerization and UV Photodegradation

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Experimental

Characterization

<u>NMR</u>

All Nuclear magnetic resonance (NMR) was performed on a Bruker 400 MHz spectrometer unless otherwise specified to be on a Bruker 500 or 300 MHz spectrometer.

UV-Visible spectroscopy

UV-Visible spectra of the reaction components were measured on a Perkin-Elmer Lambda spectrometer.

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× Agilent Mixed-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 200nm PTFE filter prior to injection. Theoretical molecular weights were calculated as $M_{n, Theory} = M_{PVK} \times [PVK]_o/([iBADTC]_o + [Cipex]_o) \times Monomer Conversion,$ $where <math>M_{PVK}$ is the molecular weight of PVK monomer, $[PVK]_o$ is the initial concentration of PVK monomers, $[Cipex]_o$ is the initial concentration of Cipex and $[iBADTC]_o$ is the initial concentration of iBADTC RAFT agent.

Photoreactor characterization

Photoreactor intensity determined using a Thorlabs PM100A light power meter. The blue LED photoreactor emission spectrum was evaluated using a HORIBA Fluorolog-3 luminescence spectrometer. Peak wavelengths for the UV photoreactor has been previously reported.¹

Materials

All materials were purchased from commercial sources and used as received unless otherwise specified. Phenyl vinyl ketone (PVK) was synthesized from known methods and used immediately.¹ The Chain transfer agents 2-[[(dodecylthio)thioxomethyl]thiio]-2-methylpropanoic acid, or (isobutyric acid)yl dodecyl trithiocarbonate (iBADTC) and CIPEX were prepared from known methods.^{2,3}

Synthesis

Synthesis of (isobutricacid)yldodecyl trithiocarbonate (iBADTC)

iBADTC was synthesized in accordance with the procedure reported in the literature.²

Dodecanethiol (5.0 ml, 21 mmol, 14 eq) was dissolved in a suspension of K₃PO₄ (3.5 g, 16.5 mmol, 1.1 eq) in acetone (60ml at ambient temperature) (4 ml water + 56 ml acetone) After stirring for 20 minutes at ambient temperature, carbon Sulfide was added (2.72 ml, 45 mmol, 3.0 eq) The reaction mixture was stirred additional 20 minutes at ambient temperature. 2 Bromo-2-methylpropionic acid (2.505 g, 15 mmol, 1.0 eq) was added and the reaction was stirred overnight at ambient temperature. 1M HCl (200 mL) was added, and the mixture was extracted with DCM (2× 150 mL). The combined organic phases were washed with deionized water (75 mL), saturated aqueous brine solution (75 mL) and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure. The crude product was purified by recrystallization from hexane to afford dodecylthiocarbonylthio-2-methylpropanoic acid (5.2g 14.3 mmol, 95% recovery) as pale yellow crystals. ¹H NMR (400 MHz, CDCl₃, δ) 3.28 (t, J = 7.6 Hz, 2H), 1.72 (s, 6H), 1.67 (t, J=7.1 Hz, 2H); 1.38 (m, 2H), 1.25 (br, 16H), 0.88 (t, J= 6.7 Hz, 3H)

Synthesis of S-2-cyano-2-propyl-O-ethyl xanthate or cyanoisopropylethyl xanthate (CiPEX).

The synthesis of CiPEX, was adopted from the procedure reported in the literature.⁴ Anhydrous ethanol (18.9ml mL) was carefully added to a flask containing potassium hydroxide (19. g, 0.34 mol) and immersed in an ice bath. The mixture was stirred, and when all the potassium hydroxide had dissovled, the ice bath was removed and carbon disulfide (3 mL, 0.05 mol) was added, dropwise, over a 10-minute time, maintaining vigorous stirring.

The resulting slurry was stirred at room temperature for 48 h under nitrogen atmosphere. The solvent was then removed under reduced pressure and the crude mixture was purified by recrystallization of EtOH to give the crude potassium O-ethyl carbonodithioate (88%) as a yellow solid. To a solution of potassium O-ethyl carbonodithioate (3 g, 0.02 mol) in ethanol (37 mL), iodine (3.3 g, 0.01 mol) was added in small portions with vigorous stirring. The mixture was stirred for 15 min and an aqueous solution of potassium iodide (1.76 g, 0.01 mol/1.5 mL water) was added. The resulting slurry was stirred at room temperature for one week. The solvent was then removed under reduced pressure and 20 mL of water were added to the crude; the solution was extracted with diethyl ether (3x25 mL), washed with an aqueous solution of (10 % w/v) sodium thiosulfate (2x25 mL) and brine (1x25 mL). The combined organic extracts were dried over anhydrous sodium sulfate and filtered; the solvent was removed under reduced pressure and the crude mixture was purified by column chromatography on silica gel using a gradient of hexane and ethyl acetate as eluent, to give bis-O-ethyl xanthate as a viscous yellow liquid

Under nitrogen atmosphere, bis-O-ethyl xanthate (2 g, 8.25 mmol) was refluxed in toluene (20 mL) and AIBN (1.63 g, 9.9 mmol) was added in five portions during 1h; the reaction was stirred and heated to 70-72 °C for 8 h, under nitrogen atmosphere. Then, the mixture was allowed to cool at room temperature and the solvent was removed under reduced pressure to dryness. The crude residue was purified by column chromatography on silica gel using a gradient of hexane and ethyl acetate as eluent. S-2-cyano-2-propyl-O-ethyl xanthate was obtained as a viscous yellow liquid. ¹H NMR (200 MHz, CDCl₃) δ ppm: 4.76 (q, *J*= 7.1 Hz, 2H), 1.77 (s, 6H), 1.54 (t, *J*= 7.1 Hz, 3H).

Synthesis of PVK

PVK was synthesized adapting a procedure reported in the literature.¹

2 g (1 equivalent, 15.2 mmol) of 3-chloropropiophenone was dissolved in 100 ml of chloroform and brought to 0 °C. Once cooled, 4 ml (1.9 equivalents 28.6 mmol) of triethylamine was added

slowly. The reaction was stirred for 18h followed by washing with 0.2 M HCl (2×50 ml), saturated NaHCO₃ solution (2×50 ml) and brine solution (2×50 ml). the residue was dried over MgSO₄ and concentrated in vacuo. This yeilded PVK with no further purification needed as confirmed by ¹H NMR. ¹H NMR (400MHz, CDCL3, δ ppm): 7.91 (d, *J*=7.8Hz, 2H) 7.51 (t, *J*=7.2Hz, 1H), 7.42 (t, *J*=7.6Hz, 2H), 7.12 (dd, *J*=17.2Hz, *J*=10.8Hz, 1H), 6.41 (d, *J*=16.8 Hz, 1H), 5.91(d, *J*=10.5Hz, 1H).

General Procedure for Photopolymerization of PVK

All polymerizations were performed at room temperature in 10ml Schlenk flasks equipped with a Teflon stir bar. PVK (300 mg, 2.27 mmol) was added to the Schlenk flask. The appropriate amount of iBADTC and CIPEX were then added following the amounts and ratios given in Table S1 for chain lengths of 100 or Table S2 for chain lengths of 50 units. All were dissolved in 0.6 ml of 1,4-dioxane. The flask was then deoxygenated by 4 freeze-pump-thaw-cycles and put in blue light for two hours. Time samples were taken using a long needle and a syringe and a nitrogen line to preclude any oxygen from entering the system. Monomer/CTA 100/1 and 50/1 were run for 120 minutes. Conversion was determined by NMR and molecular weight distributions were evaluated by SEC. The conversion of small molecule CTA to macroCTA was monitored by the CH₂ ethoxy protons of CiPEX at 4.76 ppm, or the CH₃ signals from the R group at 1.7 ppm for iBADTC.

Entry	Mole Ratio	Mass of	Moles of	Mass of	Moles of
	iBADTC: CIPEX	iBADTC (mg)	iBADTC (mmol)	CIPEX (mg)	CIPEX (mmol)
1	1:0	8.28	2.27×10 ⁻²	0	0
2	0.75: 0.25	6.21	1.70×10 ⁻²	1.07	5.67×10 ⁻³
3	0.5: 0.5	4.13	1.13×10 ⁻²	2.14	1.13×10 ⁻²
4	0.25: 0.75	2.1	5.76×10 ⁻³	3.20	1.69×10 ⁻²
5	0: 1	0	0	4.30	2.27×10 ⁻²

Table S1: CTA Ratios and masses used when targeting chain lengths of 100 units.

Mole Ratio	Mass of	Moles of	Mass of	Moles of
iBADTC: CIPEX	iBADTC (mg)	iBADTC (mmol)	CIPEX (mg)	CIPEX (mmol)
1:0	16.6	4.54×10 ⁻²	0	0
0.75: 0.25	12.4	3.41×10 ⁻²	2.15	1.14×10 ⁻²
0.5: 0.5	8.28	2.27×10 ⁻²	4.30	2.27×10 ⁻²
0.25: 0.75	4.14	1.14×10 ⁻²	6.45	3.41×10 ⁻²
0:1	0	0	8.59	4.54×10 ⁻²
	Mole Ratio iBADTC: CIPEX 1: 0 0.75: 0.25 0.5: 0.5 0.25: 0.75 0: 1	Mole RatioMass ofiBADTC: CIPEXiBADTC (mg)1: 016.60.75: 0.2512.40.5: 0.58.280.25: 0.754.140: 10	Mole RatioMass ofMoles ofiBADTC: CIPEXiBADTC (mg)iBADTC (mmol)1: 016.64.54×10 ⁻² 0.75: 0.2512.43.41×10 ⁻² 0.5: 0.58.282.27×10 ⁻² 0.25: 0.754.141.14×10 ⁻² 0: 100	Mole RatioMass ofMoles ofMass ofiBADTC: CIPEXiBADTC (mg)iBADTC (mmol)CIPEX (mg)1: 016.6 4.54×10^{-2} 00.75: 0.2512.4 3.41×10^{-2} 2.150.5: 0.58.28 2.27×10^{-2} 4.300.25: 0.754.14 1.14×10^{-2} 6.450: 1008.59

Table S2: CTA Ratios and masses used when targeting chain lengths of 50 units.

General Procedure for Photopolymerization of MVK

All polymerizations were performed at room temperature in 10 ml Schlenk flasks equipped with a Teflon stir bar. MVK (250 mg, 3.57 mmol) was added to the Schlenk flask. The appropriate amount of iBADTC and CIPEX were then added. All were dissolved in 0.5 ml of 1,4-dioxane. The flask was then deoxygenated by 4 freeze-pump-thaw-cycles and put in blue light for two hours. Time samples were taken using a long needle and a syringe and a nitrogen line to preclude any oxygen from entering the system. Conversion was determined by NMR and molecular weight distributions were evaluated by SEC.

General Procedure for Block polymerization of PVK and EA

All polymerizations were performed at room temperature in 10ml Schlenk flasks equipped with a Teflon stir bar. PVK (300 mg, 2.27 mmol) was added to the Schlenk flask. The appropriate amount of iBADTC and CIPEX were then added, following the amounts listed in Table S2 for a targeted chain length of 50 units with a targeted ratio of iBADTC:CiPEX. All were dissolved in 0.6 ml of 1,4-dioxane. The flask was then deoxygenated by 4 freeze-pump-thaw-cycles and put in blue light for three hours to ensure maximum conversion of the monomers. Using a long needle, a syringe and a Nitrogen line, EA (230 mg 2.3 mmol) was added to the Schenck flask content. Nitrogen gas was allowed to flow through the schlenck flask content for 15 minutes to deoxygenate possibly trapped air. The flask was put in blue light and allowed to stay for twenty-four hours. Conversion was determined by NMR and molecular weight distributions were evaluated by SEC.

General Procedure for Gradient polymerization of PVK and EA

All polymerizations were performed at room temperature in 10ml Schlenk flasks equipped with a Teflon stir bar. PVK (300 mg, 2.27 mmol) and EA (230 mg, 2.27 mmol) was added to the Schlenk flask. The appropriate amount of iBADTC and CIPEX were then added following the amounts for a targeted chain length of 100 total units given in Table S1. All were dissolved in 0.6 ml of 1,4-dioxane. The flask was then deoxygenated by 4 freeze-pump-thaw-cycles and put in blue light for twenty-four hours. Time samples were taken using a long needle and a syringe and a nitrogen line to preclude any oxygen from entering the system. Conversion was determined by NMR and molecular weight distributions were evaluated by SEC. The conversion of small molecule CTA to macroCTA was monitored by the CH₂ ethoxy protons of CiPEX at 4.76 ppm.

Typical Degradation study

All reactions were performed at room temperature in 40 ml vial equipped with a Teflon stir bar. Poly Phenyl vinyl ketone (PPVK) was synthesized according to the previously reported procedures in a schlenck flask. To the synthesized PPVK, 0.5 ml of dioxane was added and the Schlenk flask content transferred to a 40 ml vial and exposed to appropriate irradiation for two and five hours. Time samples were taken and analyzed by SEC.

Supplemental Data

irradiation by blue light (450 \pm 10 lim, 7.9 \pm 0.4 m w/cm ²) under conditions [MVK]:				
[CTA]=100:1 with 33 vol% monomer. Different ratios of iBADTC:CiPEX CTAs were used.				
iBADTC:CiPEX	Conversion (%)	M _{n-th}	M_n	M_w/M_n
1:0	78	5467	5900	1.24
0.75:0.25	73	5117	6700	1.30
0.5:0.5	84	5888	6000	1.48
0.25:0.75	87	6098	6400	1.70
0:1	77	5397	5400	1.81

Table S3: Kinetic and molecular weight data for the polymerization of MVK after 24 h of irradiation by blue light $(450 \pm 10 \text{ nm}, 7.9 \pm 0.4 \text{ mW/cm}^2)$ under conditions [MVK]: [CTA]=100:1 with 33 vol% monomer. Different ratios of iBADTC:CiPEX CTAs were used.

Table S4: Kinetic and molecular weight data for the polymerization of PVK and EA copolymerization after 24 h of irradiation by blue light $(450 \pm 10 \text{ nm}, 7.9 \pm 0.4 \text{ mW/cm}^2)$ under conditions [PVK]:[EA]:[CTA]=50:50:1 with 33 vol% monomer. Different ratios of iBADTC:CiPEX CTAs were used

iBADTC:CiPEX	Conversion PVK	Conversion EA	M _{n-th}	M _n	M_w/M_n
	(%)	(%)			
1:0	>95%	84%	11251	13000	1.14
0.75:0.25	>95%	87%	10520	12000	1.29
0.5:0.5	>95%	84%	10806	12000	1.37
0.25:0.75	>95%	78%	10917	12000	1.50
0:1	>95%	91%	11523	12000	1.57



Figure S1: Emission Spectrum of Blue LED system.



Figure S2: Photopolymerization kinetics of PVK under blue light $(450 \pm 10 \text{ nm}, 7.9 \pm 0.4 \text{ mW/cm}^2)$ under conditions [PVK]:[CTA]=50:1 or 100 or no CTA, with 33 vol% monomer. Both iBADTC and CiPEX CTAs were used.



Figure S3: Conversion of small molecule CTA to macroCTA for the photopolymerization of PVK under blue light $(450 \pm 10 \text{ nm}, 7.9 \pm 0.4 \text{ mW/cm}^2)$ under conditions of either [PVK]:[iBADTC]=50:1 or [PVK]:[CiPEX]=50:1, with 33vol% monomer.



Figure S4: Photopolymerization of PVK under blue light $(450 \pm 10 \text{ nm}, 7.9 \pm 0.4 \text{ mW/cm}^2)$ under conditions [PVK]:[CTA]=100:1, with 33vol% monomer. Ratios of iBADTC:CiPEX CTAs were varied between 1:0 and 0:1 in 0.25 increments. a) semilogarithmic kinetic plot for each ratio of iBADTC:CiPEX, b) Evolution of M_n and M_w/M_n with conversion for each ratio of iBADTC:CiPEX, c) M_w/M_n at the 2h time point compared for each ratio of iBADTC:CiPEX as well as with no CTA.

Table S5: Apparent propagation rate coefficients, calculated as the slope of the semilogarithmic plot for PVK photopolymerization under blue light ($450 \pm 10 \text{ nm}$, $7.9 \pm 0.4 \text{ mW/cm}^2$) under conditions [PVK]:[CTA]=100:1 or 50:1 with different ratios of CiPEX and iBADTC.

iBADTC:CiPEX	k _p ^{app} [PVK]:[CTA]= 50:1 (min ⁻¹)	k _p ^{app} [PVK]:[CTA]= 100:1 (min ⁻¹)
1:0	0.027	0.024
0.75:0.25	0.026	0.018
0.5:0.5	0.030	0.019
0.25:0.75	0.023	0.014
0:1	0.025	0.021



Figure S5: SEC derived molecular weight distributions for the polymerization of PVK after 2 h of irradiation by blue light $(450 \pm 10 \text{ nm}, 7.9 \pm 0.4 \text{ mW/cm}^2)$ under conditions [PVK]:[CTA]=100:1 with 33 vol% monomer. Different ratios of iBADTC:CiPEX CTAs were used.



Figure S6: SEC derived molecular weight distributions for the polymerization of MVK after 24 h of irradiation by blue light $(450 \pm 10 \text{ nm}, 7.9 \pm 0.4 \text{ mW/cm}^2)$ under conditions [MVK]:[CTA]=100:1 with 33 vol% monomer. Different ratios of iBADTC:CiPEX CTAs were used.



Figure S7: SEC derived molecular weight distributions for the polymerization of PVK after 3 h of irradiation by blue light $(450 \pm 10 \text{ nm}, 7.9 \pm 0.4 \text{ mW/cm}^2)$ under conditions [PVK]:[CTA]=50:1 with 33 vol% monomer. Different ratios of iBADTC:CiPEX CTAs were used.



Figure S8: SEC derived molecular weight distributions for the polymerization of EA after 24 h of irradiation by blue light $(450 \pm 10 \text{ nm}, 7.9 \pm 0.4 \text{ mW/cm}^2)$ under conditions [EA]: [PPVK-CTA] =50:1 with 47 vol% monomer. Different ratios of iBADTC:CiPEX CTAs were used.



Figure S9: Conversion of PVK, EA and small molecule CiPEX to macroCTA for the photopolymerization of PVK under blue light $(450 \pm 10 \text{ nm}, 7.9 \pm 0.4 \text{ mW/cm}^2)$ under conditions of either [PVK]:[EA]:[CiPEX]=50:1, with 33vol% monomer.

References:

- (1) Reeves, J. A.; de Alwis Watuthanthrige, N.; Boyer, C.; Konkolewicz, D. Intrinsic and Catalyzed Photochemistry of Phenylvinylketone for Wavelength-Sensitive Controlled Polymerization. *ChemPhotoChem* **2019**, *3* (11), 1171–1179.
- (2) Plucinski, A.; Willersinn, J.; Lira, R. B.; Dimova, R.; Schmidt, B. V. K. J. Aggregation and Crosslinking of Poly (N, N-dimethylacrylamide)-b-pullulan Double Hydrophilic Block Copolymers. *Macromolecular Chemistry and Physics* **2020**, *221* (13), 2000053.
- (3) Reeves, J. A.; Allegrezza, M. L.; Konkolewicz, D. Rise and Fall: Poly (Phenyl Vinyl Ketone) Photopolymerization and Photodegradation under Visible and UV Radiation. *Macromolecular rapid communications* **2017**, *38* (13), 1600623.
- (4) Segura, T.; Menes-Arzate, M.; León, F.; Ortega, A.; Burillo, G.; Peralta, R. D. Synthesis of Narrow Molecular Weight Distribution Polyvinyl Acetate by Gamma–Rays Initiated RAFT/MADIX Miniemulsion Polymerization. *Polymer* 2016, *102*, 183–191.