Rate Retardation Trends in RAFT - An Emerging Monomer Classification Tool?

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Experimental

1.Materials

All materials were purchased from commercial sources and used as received unless otherwise specified. Phenyl vinyl ketone was (PVK) was synthesized from known methods¹ and used immediately. The chain transfer agents, 2-(ethoxycarbonothioyl) sulfanyl propanoic acid (Etpax)², 2-cyano-2-propyl ethyl trithiocarbonate (CPETC)³, *S*-2-cyano-2-propyl-*O*-ethyl xanthate or cyano isopropyl ethyl xanthate (CiPEX) were prepared from known methods.⁴

2. Characterization

NMR

¹H nuclear magnetic resonance (NMR) spectra were recorded at 400 or 500 MHz, calibrated using residual undeuterated solvent as an internal reference calibrated using residual undeuterated solvent as an internal reference (CHCl₃, δ 7.27 ppm), reported in parts per million relative to trimethylsilane (TMS, d 0.00 ppm), and presented as follows: chemical shift (d ppm), multiplicity

(s = singlet, br s = broad singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, t = triplet, m = multiplet), coupling constants (J, Hz).

Size Exclusion Chromatography (SEC)

All size exclusion chromatography (SEC) of MA, MMA, Sty, PVK, and VA 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 was tetrahydrofuran (THF) at 30 °C with a flow rate of 1 mL min⁻¹. The system was calibrated with poly (methyl methacrylate) standards with molecular weights the range of 617500 to 1010. All samples were filtered through a 200 nm PTFE filter prior to injection.

All size exclusion chromatography (SEC) of DMAm and NVP was performed using an Agilent SEC system equipped with an autosampler, an Agilent 1260 isocratic pump, 1× Agilent Polargel-M Guard and 2× Agilent Polargel-M analytical columns and an Agilent 1260 refractive index (RI) detector. The eluent was N,N-dimethylformadide (DMF) with 0.1 wt% LiBr at 50 °C with a flow rate of 1 mL min⁻¹. The system was calibrated with poly (methyl methacrylate) standards with molecular weights the range of 617500 to 1010. All samples were filtered through a 200 nm PTFE filter prior to injection.

Theoretical molecular weights were calculated as $M_{n, \text{Theory}} = M_{\text{monomer}} \times [\text{Monomer}]_0/([\text{CTA}]_0) \times \text{Conversion}$, where M_{monomer} is the molecular weight of monomer, [monomer]_0 is the initial monomer concentration, [CTA]_0 is the initial CTA concentration.

3. Chain Transfer Agent Synthesis Procedures

Synthesis of 2-cyano-2-propyl ethyl trithiocarbonate (CPETC)



Ethanethiol (10.5 mL, 0.839 g/mL, 140.0 mmol) was added dropwise to a stirred solution of sodium hydroxide (6.14 g, 153.0 mmol) in 50 mL water at 0 °C. After 1 h, CS₂ (10 mL, 12.66 g,

166.0 mmol) was added dropwise to the reaction at 0 °C, and a yellow color was formed. The reaction was allowed to stir overnight. The reaction was washed with diethyl ether ($3 \times 80 \text{ mL}$) getting rid of the unreacted CS₂. To the aqueous layer, a solution of potassium ferricyanide in water was added until a yellow oil was formed. The yellow oily product was extracted with diethyl ether ($3 \times 80 \text{ mL}$) and concentrated under reduced pressure before being redissolved in ethyl acetate. AIBN (11.0 g, 66.9 mmol) was added to the resulting solution which was refluxed overnight at 70 °C. After 20 h, the reaction was cooled to room temperature and concentrated under reduced pressure. The residue was purified via flash chromatography ($15 \times 5.0 \text{ cm}$; 1:9 ethyl acetate/hexane) to afford CPETC as orange liquid (15.1 g, 52%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 1.35 (t, J = 7.4 Hz, 3H, CH₃CH₂); 1.82 (s, 6H, (CH₃)₂CCN); 3.33 (q, J = 7.4 Hz, 2H, CH₃CH₂S) in agreement with the literature.⁵

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



KOH (6.5 g, 0.11 mol) was dissolved in ethanol (63 mL) and cooled 0 °C. Carbon disulfide (7.3 mL, 0.12 mol) was added dropwise until yellow precipitate was formed. The excess solvent was then removed under reduced pressure to yield potassium ethyl xanthogenate. To the solution of potassium ethyl xanthogenate (6 g, 0.0374 mol) in acetone (25 mL), 2-bromopropanoic acid (5.27 g, 0.0374 mol) was added dropwise and allowed to stir at room temperature for 3 h. Afterwards the residual solvent was removed under reduced pressure. The solid was dissolved in saturated sodium carbonate and washed with diethyl ether, subsequently, the organic layer was washed with distilled water, and brine and dried with anhydrous sodium sulfate. Residual solvents were removed under reduced pressure. ¹H NMR (500 MHz, CDCl₃) δ ppm: 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) as reported in the literature⁶

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



The synthesis of CiPEX, was adopted from the procedure reported in the literature.¹ Anhydrous ethanol (18.9 mL) was carefully added to a flask containing potassium hydroxide (19.5 g, 0.34 mol) and immersed in an ice bath. The mixture was stirred, and when the potassium hydroxide had dissolved, the ice bath was removed and carbon disulfide (3.0 mL, 0.050 mol) was added dropwise over a 10 min time at room temperature, maintaining vigorous stirring. The solvent was subsequently removed under reduced pressure and the crude mixture was purified by recrystallization of EtOH. The crude yellow solid of potassium O-ethyl carbonodithioate was dissolved in water (50.0 mL). To this solution, iodine (3.3 g, 0.013 mol) and potassium iodide (1.76g, 0.011mol) in water (50.0 mL) were added dropwise in small portions with vigorous stirring. The resulting slurry was stirred at room temperature for 48 h under nitrogen atmosphere. The solution was extracted with diethyl ether $(3 \times 25 \text{ mL})$, washed with an aqueous solution of (10 % w/v) sodium thiosulfate $(2 \times 25 \text{ mL})$ and brine $(1 \times 25 \text{ mL})$ and excess solvent was removed under reduced pressure. Under nitrogen atmosphere, the crude bis-O-ethyl xanthate (6.76g, 27.8 mmol) intermediate, AIBN (9 g, 54.8 mmol) and dioxane (40 mL) were added to a two necked round bottom flask equipped with a reflux condenser. The reaction was stirred and heated to 100 °C for 16 h, under nitrogen atmosphere. Then, the mixture was allowed to cool at room temperature and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel using a gradient of hexane and ethyl acetate as eluents. S-2-cyano-2-propyl-O-ethyl xanthate was obtained as a viscous yellow liquid (4.15 g, 44% overall yield). ¹H NMR (400 MHz, CDCl₃) δ ppm: 4.76 (q, *J*=7.1 Hz, 2H), 1.77 (s, 6H), 1.54 (t, *J*=7.1 Hz, 3H).

4. Polymerizations

Polymerization of Vinyl Acetate (VA)

In a 10 mL Schlenk flask equipped with a Teflon stir bar was added EtPax, AIBN (0.163 mmol, 0.005 equiv), 3.0 mL of VA and 3.0 mL of DMSO. The reaction flask was purged with Ar for 10 min before being placed in an oil bath at 55 °C. Sample aliquots were taken at intervals between 0 min and 150 min, using a long needle, syringe, and Ar line to maintain an inert atmosphere. Sample aliquots were subsequently analyzed using the NMR and GPC (THF).

EtPax amounts 52 mg (0.33 mmol, M:CTA = 100:1) 17 mg (0.11 mmol, M:CTA = 100:0.33) 5.8 mg (0.0036 mmol, M:CTA = 100:0.11) 1.9 mg (0.0012 mmol, M:CTA = 100:0.037)

Polymerization of Methyl Acrylate (MA)

In a 10 mL Schlenk flask equipped with a Teflon stir bar was added CIPEX, AIBN (0.163mmol, 0.002equiv), 3.0 mL of MA and 3.0 mL of DMSO. Concurrently another Schlenk flask containing stir bar was charged with CPETC, AIBN (0.0067 mmol, 0.002 equiv.), 3.0 mL MA and 3.0 mL of DMSO. The reaction flasks were purged with Ar for 10 min before being place in an oil bath at 60 °C. Sample aliquots were taken at intervals between 0 min and 240 min, using a long needle, syringe, and Ar line to maintain an inert atmosphere. Sample aliquots were subsequently analyzed using the NMR and GPC (THF).

CIPEX amounts 191 mg (1.00 mmol, M:CTA = 100:3) 63 mg (0.33 mmol, M:CTA = 100:1) 19 mg (0.010 mmol, M:CTA = 100:0.3)

CPETC amounts 68mg (0.33 mmol, M:CTA = 100:1) 23mg (0.11 mmol, M:CTA = 100:0.3) 7.5mg (0.0037 mmol, M:CTA = 100:0.11)

2.5mg (0.012 mmol, M:CTA = 100:0.037)

Polymerization of Methyl Methacrylate (MMA)

In a 10 mL Schlenk flask equipped with a Teflon stir bar was added CPETC, AIBN (0.0057 mmol, 0.002 equiv.), 3.0 mL of MMA and 3.0 mL of DMSO. The reaction flask was purged with Ar for 10 min before being place in an oil bath at 70 °C. Sample aliquots were taken at intervals between 0min and 420 min, using a long needle, syringe, and Ar line to maintain an inert atmosphere. Sample aliquots were subsequently analyzed using the NMR and GPC (THF).

CPETC amounts 58 mg (0.28 mmol, M:CTA = 100:1)

19 mg (0.093 mmol, M:CTA = 100:0.3) 6 mg (0.0031 mmol, M:CTA = 100:0.11) 2 mg (0.010 mmol, M:CTA = 100:0.037)

Polymerization of Styrene (STY)

In a 10 mL Schlenk flask equipped with a Teflon stir bar was added CPETC, AIBN (0.0052 mmol, 0.002 equiv.), and 3.0 mL STY. The reaction flask was purged with Ar for 10 min before being place in an oil bath at 65 °C. Sample aliquots were taken at intervals between 0 h and 7 h, using a long needle, syringe, and Ar line to maintain an inert atmosphere. Sample aliquots were subsequently analyzed using the NMR and GPC (THF)

CPETC amounts 54 mg (0.26 mmol, M:CTA = 100:1) 18 mg (0.087 mmol, M:CTA = 100:0.3) 6 mg (0.0029 mmol, M:CTA = 100:0.11)

Polymerization of Phenyl Vinyl Ketone (PVK)

In a 10 mL Schlenk flask equipped with a Teflon stir bar was added CPETC, AIBN (0.005 mmol, 0.001 equiv.), 1.0 mL PVK and 2.0 mL of Dioxane. The reaction flask was purged with Ar for 10

min before being place in an oil bath at 60 °C. Sample aliquots were taken at intervals between 0 min and 240 min, using a long needle, syringe, and Ar line to maintain an inert atmosphere. Sample aliquots were subsequently analyzed using the NMR and GPC (THF).

CPETC amounts 155 mg (0.76 mmol, M:CTA = 100:10) 47 mg (0.23 mmol, M:CTA = 100:3) 16 mg (0.0076 mmol, M:CTA = 100:1) 5 mg (0.0025 mmol, M:CTA = 100:0.3)

Polymerization of Dimethyl Acrylamide (DMAm)

In a 10 mL Schlenk flask equipped with a Teflon stir bar was added CPETC, AIBN (0.005 mmol, 0.001 equiv.), with the DMA: DMSO in a 1:1 ratio. Reactions at targeted chain lengths of 100, 300 and 900 used 1 g (0.0101 mol) of DMAm. Reactions at targeted chain lengths of 2700 and 9000 used 3.0 g (0.0303 mol) of DMAm. The reaction flask was purged with Ar for 10 min before being place in an oil bath at 60 °C. Sample aliquots were taken at intervals between 0 min and 150 min, using a long needle, syringe, and Ar line to maintain an inert atmosphere. Sample aliquots were subsequently analyzed using the NMR and GPC (DMF).

CPETC amounts

20.7 mg (0.1 mmol, M:CTA = 100:1, Using 1 g DMAm) 6.9 mg (0.034 mmol, M:CTA = 100:0.3, Using 1 g DMAm) 2.3 mg (0.012 mmol, M:CTA = 100:0.11, Using 1 g DMAm) 2.1 mg (0.0011 mmol, M:CTA = 100:0.037, Using 3 g DMAm) 0.65 mg (0.0003 mmol, M:CTA = 100:0.011, Using 3 g DMAm)

Polymerization of N-vinyl Pyrrolidone (NVP)

In a 10 mL Schlenk flask equipped with a Teflon stir bar was added EtPax, AIBN (0.05 mmol, 0.002 equiv.), 1.0 mL NVP and 1.5 mL of DMSO. The reaction flask was purged with Ar for 10

min before being place in an oil bath at 60 °C. Sample aliquots were taken at intervals between 0 min and 990 min, using a long needle, syringe, and Ar line to maintain an inert atmosphere. Sample aliquots were subsequently analyzed using the NMR and GPC (DMF).

> EtPax amounts 48 mg (0.3 mmol, M:CTA = 100:3.3)16 mg (0.1 mmol, M:CTA = 100:1.1)5 mg (0.03 mmol, M:CTA = 100:0.33)2 mg (0.0011 mmol, M:CTA = 100:0.12)

Slow Fragmentation Model Radical Concentrations and Kinetics

Using the equation for radical concentration in RAFT under the SFM compared to that of a polymerization under ideal free radical polymerization conditions gives.⁶

$$\frac{[P^{\cdot}]}{[P^{\cdot}]_{0}} = tanh\left(\frac{[P^{\cdot}]_{0}k_{t}t}{K_{RAFT}[CTA]}\right)$$
(S1)

Where $[P^{\cdot}]$ is the radical concentration in the RAFT polymerization, $[P^{\cdot}]_0$ is the radical concentration under ideal free radical polymerization, k_t is the termination rate coefficient, K_{RAFT} is the RAFT equilibrium constant and [CTA] is the CTA concentration. Combining the radical concentration with standard monomer consumption kinetics below gives:6

$$\frac{d[M]}{dt} = -k_p \left[M\right]\left[P'\right] = -k_p \left[M\right]\left[P'\right]_0 tanh\left(\frac{\left[P'\right]_0 k_t t}{K_{RAFT}[CTA]}\right)$$
(S2)

Where [M] is the monomer concentration and k_p is the propagation rate coefficient. Eq S2 can be solved to give the following form⁶:

$$ln\left(\frac{[M]_{0}}{[M]_{t}}\right) = k_{p}\frac{K_{RAFT}[CTA]}{k_{tc}}ln\left(cosh\left(\frac{[P']_{0}k_{t}t}{K_{RAFT}[CTA]}\right)\right)$$
(S3)

Eq S3 can be fitted to a series of kinetic data to extract K_{RAFT} with other parameters already fixed.

e a predicted
$$\frac{[P^{\cdot}]}{[P^{\cdot}]_0}$$
 for each timepoi

This in turn can give int.

Intermediate Radical Termination and Slow Fragmentation Model Approaches to Fitting RAFT equilibrium and kinetics

For the IRT model, the K_{RAFT} and k_t values were fit to experimental data taking advantage of the fact that the slope of the semilogarithmic kinetic plot is proportional to the radical concentration. Where possible literature known k_p values were used as highlighted in Table S1. Therefore a χ^2 value was possible for the IRT model as shown below:

$$\chi_{IRT}^{2}(K_{RAFT}, [P^{\cdot}]_{0}) = \sum_{[CTA]} ([P^{\cdot}]_{Expt} - [P^{\cdot}]_{Th})^{2}$$
(S4)

Where $[P']_{Expt}$ is determined from the experimental data using the slope of the semilogarithmic plot as below:

$$[P^{\cdot}]_{Expt} = \frac{Slope \ Semilog}{k_p} \tag{S5}$$

 $[P^{\cdot}]_{Th}$ is estimated by rearranging the functional form for the IRT retardation equation⁶:

$$[P^{\cdot}]_{Th} = \frac{[P^{\cdot}]_{0}}{\left(1 + K_{RAFT}[CTA]\right)^{1/2}}$$
(S6)

In the SFM, the K_{RAFT} is estimated by fitting the experimental $ln\left(\frac{[M]_0}{[M]_t}\right)$ to the one predicted by the model in Eq S3. Keeping the same k_t as in the IRT allows optimization of the function below:

$$\chi_{SFM}^{2}(K_{RAFT}) = \sum_{[CTA]} \sum_{t} \left(ln \left(\frac{[M]_{0}}{[M]_{t}} \right)^{Expt} - ln \left(\frac{[M]_{0}}{[M]_{t}} \right)^{Th} \right)^{2}$$
(S7)

These kitting protocols yielded the following results in Table S1. In general the estimated parameters agreed well with anticipated results. Values for k_t generally lay in the range of 10⁷-10⁸ M⁻¹ s⁻¹, typical for radical polymerization⁷. Where earlier estimates of K_{RAFT} were measured, the values estimated in this work agreed broadly, and were typically within the same order of magnitude⁶.

Supplementary Figures and Data

Table S1. Kinetic and RAFT equilibrium constant data used to fit the retardation kinetic

 experiments in both SFM and IRT models.

a. No known k_p values available form PLP-SEC to the authors' knowledge, however, k_p was estimated from $[P^{-}]_{0}$ using a fixed k_t of $10^8 \text{ M}^{-1} \text{ s}^{-1}$. b. Estimated using solvent dependent k_p values for DMAm using 60% monomer. c. Estimated for 100% NVP due to low polarity of dioxane solvent. d. Estimated by fitting Eq S4. e. Estimated by fitting Eq S7.

Monomer	RAFT	Temp	k _p	$k_{ m t}$	$[P^{\cdot}]_{0}(M)$	K _{RAFT-IRT}	K _{RAFT-}
	Agent	(°C)	$(M^{-1}s^{-1})$	$(M^{-1}s^{-1})^a$	()	$(M^{-1})^{d}$	SFM
							$(M^{-1})^{e}$
MMA	CPETC	70	10508	1.7×10^{7}	1.6×10 ⁻⁷	1.8×10^{1}	5.4×10 ⁵
STY	CPETC	65	406 ⁹	7.0×10^{7}	7.4×10^{-8}	7.7×10^{0}	2.0×10^{6}
PVK	CPETC	60	13000 a	1.0×10^{8}	1.3×10^{-8}	1.0×10^{0}	2.3×10^{4}
DMAm	CPETC	65	43000^{10} b	7.8×10^{7}	3.7×10 ⁻⁸	5.3×10^{2}	2.0×10^{6}
MA	CPETC	60	3310011	2.1×10^{8}	2.4×10^{-8}	1.9×10^{2}	2.0×10^{6}
MA	CIPEX	60	3310011	2.1×10^{8}	2.4×10 ⁻⁸	8.0×10^{1}	9.1×10 ⁵
VA	EtPAX	55	922012	2.2×10^{7}	4.9×10 ⁻⁸	1.1×10^{2}	9.9×10 ⁵
NVP	EtPAX	60	2300 ¹³ c	3.6×10 ⁷	7.7×10 ⁻⁸	1.9×10^{2}	4.1×10 ⁶



Figure S1: Evolution of M_n and M_w/M_n for DMAm polymerization with different CPETC concentrations at 60 °C with [DMAm]:[AIBN] = 100:0.2 and DMAm:CPETC ratios given in the captions at 50% monomer in DMSO. Solid points represent M_n and hollow points represent M_w/M_n .



Figure S2: Evolution of M_n and M_w/M_n for MMA polymerization with different CPETC concentrations at 70 °C with [MMA]:[AIBN] = 100:0.2 and MMA:CPETC ratios given in the captions at 50% monomer in DMSO. Solid points represent M_n and hollow points represent M_w/M_n .



Figure S3: Evolution of M_n and M_w/M_n for Sty polymerization with different CPETC concentrations at 65 °C with [Sty]:[AIBN] = 100:0.2 and Sty:CPETC ratios given in the captions in bulk styrene. Solid points represent M_n and hollow points represent M_w/M_n .



Figure S4: Evolution of M_n and M_w/M_n for PVK polymerization with different CPETC concentrations at 60 °C with [PVK]:[AIBN] = 100:0.067 and PVK:CPETC ratios given in the captions at 33% monomer in DMSO. Solid points represent M_n and hollow points represent M_w/M_n .



Figure S5: Evolution of M_n and M_w/M_n for NVP polymerization with different EtPAX concentrations at 60 °C with [NVP]:[AIBN] = 100:0.56 and NVP:EtPAX ratios given in the captions at 40% monomer in DMSO. Solid points represent M_n and hollow points represent M_w/M_n .



Figure S6: Evolution of M_n and M_w/M_n for VA polymerization with different EtPAX concentrations at 55 °C with [VA]:[AIBN] = 100:0.5 and VA:EtPAX ratios given in the captions at 50% monomer in DMSO. Solid points represent M_n and hollow points represent M_w/M_n .



Figure S7: Fits of IRT and SFM models to MA polymerization using CPETC as the CTA. Reactions were run at 60 °C with [monomer]:[AIBN] = 100:0.2 in the captions at 50% monomer in DMSO. Experiment A [monomer]:[CTA] = 100:0.037, Experiment B [monomer]:[CTA] = 100:0.11, Experiment C [monomer]:[CTA] = 100:0.3, Experiment D [monomer]:[CTA] = 100:1.



Figure S8: Fits of IRT and SFM models to MA polymerization using CIPEX as the CTA. Reactions were run at 60 °C with [monomer]:[AIBN] = 100:0.2 at 50% monomer in DMSO. Experiment A [monomer]:[CTA] = 100:0.3, Experiment B [monomer]:[CTA] = 100:1, Experiment C [monomer]:[CTA] = 100:3.



Figure S9: Fits of IRT and SFM models to MMA polymerization using CPETC as the CTA. Reactions were run at 70 °C with [monomer]:[AIBN] = 100:0.2 at 50% monomer in DMSO. Experiment A [monomer]:[CTA] = 100:0.037, Experiment B [monomer]:[CTA] = 100:0.11, Experiment C [monomer]:[CTA] = 100:0.3, Experiment D [monomer]:[CTA] = 100:1.



Figure S10: Fits of IRT and SFM models to DMAm polymerization using CPETC as the CTA. Reactions were run at 60 °C with [monomer]:[AIBN] = 100:0.2 at 50% monomer in DMSO. Experiment A [monomer]:[CTA] = 100:0.011, Experiment B [monomer]:[CTA] = 100:0.037, Experiment C [monomer]:[CTA] = 100:0.11, Experiment D [monomer]:[CTA] = 100:0.3, Experiment E [monomer]:[CTA] = 100:1.



Figure S11: Fits of IRT and SFM models to PVK polymerization using CPETC as the CTA. Reactions were run at 60 °C with [monomer]:[AIBN] = 100:0.067 at 33% monomer in DMSO. Experiment A [monomer]:[CTA] = 100:0.037, Experiment B [monomer]:[CTA] = 100:0.11, Experiment C [monomer]:[CTA] = 100:0.3, Experiment D [monomer]:[CTA] = 100:1.



Figure S12: Fits of IRT and SFM models to Sty polymerization using CPETC as the CTA. Reactions were run at 65 °C with [monomer]:[AIBN] = 100:0.2 in bulk monomer. Experiment A [monomer]:[CTA] = 100:0.11, Experiment B [monomer]:[CTA] = 100:0.3, Experiment C [monomer]:[CTA] = 100:1.



Figure S13: Fits of IRT and SFM models to NVP polymerization using EtPAX as the CTA. Reactions were run at 60 °C with [monomer]:[AIBN] = 100:0.56 in 40% monomer in DMSO. Experiment A [monomer]:[CTA] = 100:0.12, Experiment B [monomer]:[CTA] = 100:0.3, Experiment C [monomer]:[CTA] = 100:1.1, Experiment D [monomer]:[CTA] = 100:3.3.



Figure S14: Fits of IRT and SFM models to VA polymerization using EtPAX as the CTA. Reactions were run at 55 °C with [monomer]:[AIBN] = 100:0.5 in 50% monomer in DMSO. Experiment A [monomer]:[CTA] = 100:0.037, Experiment B [monomer]:[CTA] = 100:0.11, Experiment C [monomer]:[CTA] = 100:0.3, Experiment D [monomer]:[CTA] = 100:1.

[MA]:[CPETC]	Time (min)	conv	M _n	M _{n-th}	M _w /M _n
100:1	0	0			
100:1	15	0			
100:1	30	0			
100:1	45	0.01		120	
100:1	60	0.26	4100	2200	1.19
100:1	90	0.64	11000	5500	1.15
100:1	120	0.80	14000	6900	1.11
100:0.33	0	0			
100:0.33	15	0.002		57	
100:0.33	30	0.23	9100	6018	
100:0.33	45	0.58	24000	15003	1.16
100:0.33	60	0.77	31000	19777	1.10
100:0.33	90	0.86	35000	22310	1.09
100:0.33	120	0.91	38000	23614	1.10
100:0.11	0	0			
100:0.11	10	-0.01			
100:0.11	20	0.39	4600	29873	1.13
100:0.11	30	0.68	76000	52672	1.11
100:0.11	40	0.79	79000	61255	1.18
100:0.11	60	0.88	99000	67874	1.14
100:0.037	0	0			
100:0.037	5	0.01			
100:0.037	15	0.53	110000	122100	1.16
100:0.037	30	0.79	190000	183403	1.07
100:0.037	60	0.91	170000	212245	1.29

 Table S2: Kinetic time points for MA polymerization under the conditions [MA]:[AIBN]=100:0.2

 at 60 °C using CPETC.

[MA]:[CiPEX]	Time (min)	conv	M _n	M _{n-th}	M _w /M _n
100:3	0	0			
100:3	30	0.03			
100:3	62	0.09			
100:3	123	0.29		809	
100:3	140	0.37	1700	1057	1.73
100:3	160	0.58	2400	1649	1.74
100:3	180	0.72	2900	2047	1.69
100:1	0	0			
100:1	30	0.06			
100:1	60	0.31	4700	2707	1.86
100:1	75	0.60	7100	5190	1.82
100:1	90	0.76	8300	6583	1.72
100:0.3	0	0			
100:0.3	10	0.11			
100:0.3	20	0.29	15000	7527	1.88
100:0.3	30	0.59	24000	15231	1.82
100:0.3	40	0.76	34000	19734	1.52
100:0.3	50	0.82	42000	21050	1.41

Table S3: Kinetic time points for MA polymerization under the conditions [MA]:[AIBN]=100:0.2 at 60 °C using CiPEX.

Table S4: Kinetic time points for DMAm polymerization under the conditions[DMAm]:[AIBN]=100:0.2 at 60 °C using CPETC.

[DMAm]:[CPETC]	Time (min)	conv	M _n	M _{n-th}	M _w /M _n
100:1	0	0			
100:1	20	-0.001			
100:1	40	0.000		86	
100:1	70	0.24		2361	
100:1	90	0.47	3300	4611	1.08
100:1	120	0.68	5100	6760	1.07
100:1	150	0.78	6000	7745	1.06
100:0.33	0	0			
100:0.33	15	0.11		3173	
100:0.33	32	0.40	10000	11919	1.12
100:0.33	47	0.66	21000	19637	1.09
100:0.33	62	0.78	27000	23171	1.10
100:0.33	92	0.92	34000	27471	1.10
100:0.11	0	0			
100:0.11	2	0.006		529	
100:0.11	4	0.008		693	
100:0.11	6	0.007		583	
100:0.11	10	0.15		13055	
100:0.11	15	0.29		26092	
100:0.11	30	0.58	57000	51704	1.15

100:0.11	60	0.87	85000	77645	1.24
100:0.037	0	0			
100:0.037	2	0.07			
100:0.037	4	0.24	120000	63630	1.37
100:0.037	6	0.32	150000	84549	1.39
100:0.037	8	0.50	190000	134216	1.59
100:0.037	10	0.57	250000	152910	1.59
100:0.011	0	0			
100:0.011	2	0.007			
100:0.011	4	0.17	170000	149119	1.69
100:0.011	6	0.39	200000	346626	2.7
100:0.011	10	0.50	160000	447632	3.4
100:0.011	15	0.64	110000	569441	5.0

Table S5	S: Kinetic	time points	for Sty pol	ymerization	under the	e conditions	[Sty]:[AIBN]=100:0.2
at 65 °C	using CP	ETC.						

[Sty]:[CPETC]	Time (h)	conv	M _n	M _{n-th}	M _w /M _n
100:1	0	0			
100:1	4	0.17393891			
100:1	6	0.25966878	5900	2704	1.17
100:1	8	0.34413458	6100	3584	1.22
100:1	11	0.4606307	8000	4797	1.20
100:1	14	0.58587862	12000	6101	1.09
100:1	17	0.69506148	12000	7239	1.15
100:0.33	0	0			
100:0.33	4	0.22	7000	6843	1.24
100:0.33	6	0.32	12000	9960	1.26
100:0.33	8	0.45	11000	14215	1.13
100:0.33	11	0.60	19000	18863	1.06
100:0.33	14	0.75	24000	23282	1.06
100:0.11	0	0			
100:0.11	4	0.22059626	30601	20677.5904	1.36
100:0.11	6	0.31013443	48069	29070.4509	1.22
100:0.11	8	0.4040875	58645	37877.1422	1.21
100:0.11	11	0.55488864	71670	52012.4862	1.21
100:0.11	14	0.70896374	71884	66454.716	1.31

Table	S6:	Kinetic	time	points	for	MMA	polymerization	under	the	conditions
[MMA]]:[AIB	N]=100:0	.2 at 70	°C using	g CPE	ETC.				

[MMA]:[CPETC]	Time (min)	conv	M _n	M _{n-th}	M _w /M _n
100:1	0	0			
100:1	15	0.04			
100:1	30	0.11			
100:1	45	0.18	6000	1802	1.59
100:1	60	0.22	8400	2245	1.38

100:1	90	0.33	9600	3338	1.38
100:1	120	0.43	11000	4331	1.32
100:1	180	0.59	17000	5946	1.11
100:1	300	0.84	16000	8411	1.34
100:1	420	0.95	19000	9475	1.26
100:0.33	0	0			
100:0.33	15	0.06			
100:0.33	30	0.16	22000	4876	1.37
100:0.33	45	0.25	26000	7404	1.28
100:0.33	60	0.32	26000	9652	1.34
100:0.33	90	0.48	31000	14302	1.27
100:0.33	120	0.59	36000	17757	1.23
100:0.33	180	0.83	37000	25052	1.29
100:0.11	0	0			
100:0.11	5	0.03			
100:0.11	10	0.05			
100:0.11	20	0.10			
100:0.11	30	0.16	70000	14709	1.27
100:0.11	45	0.24	67000	21255	1.29
100:0.11	60	0.31	67000	27793	1.34
100:0.11	90	0.44	73000	39557	1.34
100:0.11	120	0.58	82000	52668	1.27
100:0.11	180	0.79	86000	70955	1.36
100:0.037	0	0			
100:0.037	5	0.03			
100:0.037	10	0.07			
100:0.037	15	0.11			
100:0.037	20	0.15			
100:0.037	30	0.21	130000	56612	1.61
100:0.037	60	0.40	130000	107229	1.65
100:0.037	90	0.54	140000	147221	1.65
100:0.037	120	0.71	140000	190796	1.61

Table	S7:	Kinetic	time	points	for	PVK	polymerization	under	the	conditions
[PVK]:	[AIBN	J]=100:0.0	67 at 6	0 °C usir	ig CP	ETC.				

[PVK]:[CPETC]	Time (min)	conv	M _n	M _{n-th}	M _w /M _n
100:10	0	0			
100:10	30	0.09		120	
100:10	60	0.18		232	
100:10	120	0.66	600	875	1.25
100:10	180	0.83	850	1091	1.12
100:3	0	0			
100:3	30	0		22	
100:3	63	0.14		631	
100:3	120	0.50	1800	2199	1.17

100:3	150	0.65	2100	2840	1.27
100:3	214	0.81	2600	3579	1.18
100:1	0	0			
100:1	5	0.04			
100:1	15	0.081		1070	
100:1	30	0.19		2448	
100:1	45	0.31		4081	
100:1	60	0.44	4000	5786	1.23
100:1	90	0.58	5600	7640	1.21
100:1	150	0.75	7300	9879	1.18
100:1	210	0.85	8200	11242	1.18
100:0.33	0	0			
100:0.33	15	0.08087787			
100:0.33	30	0.25482625		10102	
100:0.33	55	0.43228002	14000	17137	1.25
100:0.33	65	0.50066043	16000	19848	1.25
100:0.33	90	0.62375533	20000	24728	1.18
100:0.33	150	0.78083723	24000	30956	1.18

Table S8:Kinetic time points for NVP polymerization under the conditions[NVP]:[AIBN]=100:0.56 at 60 °C using EtPAX.

[NVP]:[EtPAX]	Time (min)	conv	M _n	M _{n-th}	M _w /M _n
100:3.3	0	0		0	
100:3.3	60	0.22		740	
100:3.3	180	0.28	550	947	1.12
100:3.3	335	0.43	700	1441	1.16
100:3.3	510	0.57	810	1901	1.23
100:3.3	750	0.66	920	2196	1.29
100:3.3	990	0.72	960	2416	1.33
100:1.1	0	0		0	
100:1.1	30	0		0	
100:1.1	60	0.098		978	
100:1.1	120	0.17		1749	
100:1.1	180	0.28	2000	2759	1.31
100:1.1	300	0.47	3100	4713	1.40
100:1.1	420	0.65	4400	6457	1.36
100:0.33	0	0			
100:0.33	10	-0.1377726			
100:0.33	20	-0.066962			
100:0.33	60	0.11964894		3989	
100:0.33	120	0.34535549	5600	11514	1.765
100:0.33	180	0.51664585	6100	17226	2.269
100:0.33	240	0.67107843	17000	22375	1.234
100:0.33	300	0.77753728	21000	25924	1.173
100:0.33	360	0.85924917	21000	28649	1.253

100:0.12	0	0			
100:0.12	15	-0.04			
100:0.12	65	0.32		32192	
100:0.12	90	0.43	6400	43031	3.2
100:0.12	155	0.69	24000	69439	1.45
100:0.12	220	0.82	24000	81924	1.58

 Table S9: Kinetic time points for VA polymerization under the conditions [VA]:[AIBN]=100:0.5

 at 55 °C using EtPAX.

[VA]:[EtPAX]	Time (min)	conv	M _n	M _{n-th}	M _w /M _n		
100:1	0	0					
100:1	15	0.17		1463			
100:1	30	0.36	2100	3064	1.24		
100:1	60	0.63	4500	5437	1.28		
100:1	90	0.76	6500	6527	1.33		
100:1	150	0.88	9500	7600	1.36		
100:0.33	0	0		0			
100:0.33	15	0.35		8928			
100:0.33	30	0.52	13000	13503	1.24		
100:0.33	60	0.73	23000	18814	1.24		
100:0.33	90	0.83	27000	21504	1.34		
100:0.33	150	0.92	34000	23730	1.35		
100:0.11	0	0					
100:0.11	5	0.07		5378			
100:0.11	20	0.22		17366			
100:0.11	30	0.38	51000	29622	1.29		
100:0.11	40	0.48	61000	37178	1.30		
100:0.11	65	0.81	91000	62729	1.35		
100:0.037	0	0					
100:0.037	2	0.17		39417			
100:0.037	5	0.19		44698			
100:0.037	10	0.25		58094			
100:0.037	15	0.32		74231			
100:0.037	20	0.43		100170			
100:0.037	30	0.56	160000	129784	1.18		
100:0.037	45	0.72	170000	168044	1.76		
100:0.037	60	0.86	170000	198949	1.47		



Figure S15: SEC traces for end points of MA polymerization under the conditions [MA]:[AIBN]=100:0.2 at 60 °C using CPETC.



Figure S16: SEC traces for end points of MA polymerization under the conditions [MA]:[AIBN]=100:0.2 at 60 °C using CiPEX.



Figure S17: SEC traces for end points of DMAm polymerization under the conditions [DMAm]:[AIBN]=100:0.2 at 60 °C using CPETC.



Figure S18: SEC traces for end points of Sty polymerization under the conditions [Sty]:[AIBN]=100:0.2 at 65 °C using CPETC.



Figure S19: SEC traces for end points of MMA polymerization under the conditions [MMA]:[AIBN]=100:0.2 at 70 °C using CPETC.



Figure S20: SEC traces for end points of PVK polymerization under the conditions [PVK]:[AIBN]=100:0.067 at 60 °C using CPETC.



Figure S21: SEC traces for end points of VA polymerization under the conditions [VA]:[AIBN]=100:0.5 at 55 °C using EtPAX.



Figure S22: SEC traces for end points of NVP polymerization under the conditions [NVP]:[AIBN]=100:0.56 at 60 °C using EtPAX.

References

- Nwoko, T.; Watuthanthrige, N. D. A.; Parnitzke, B.; Yehl, K.; Konkolewicz, D. Tuning the Molecular Weight Distributions of Vinylketone-Based Polymers Using RAFT Photopolymerization and UV Photodegradation. *Polym Chem.* 2021, *12* (46), 6761–6770.
- (2) Hakobyan, K.; Gegenhuber, T.; McErlean, C. S. P.; Müllner, M. Visible-light-driven MADIX Polymerisation via a Reusable, Low-cost, and Non-toxic Bismuth Oxide Photocatalyst. *Angewandte Chemie International Edition.* 2019, *58* (6), 1828–1832.
- Haven, J. J.; De Neve, J. A.; Junkers, T. Versatile Approach for the Synthesis of Sequence-Defined Monodisperse 18-and 20-Mer Oligoacrylates. *ACS Macro Lett.* 2017, 6 (7), 743–747.
- (4) 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. *Macromol Chem Phys.* 2020, 221 (13), 2000053.
- Bradford, K. G. E.; Gilbert, R. D.; Weerasinghe, M. A. S. N.; Harrisson, S.; Konkolewicz,
 D. Spontaneous Gradients by ATRP and RAFT: Interchangeable Polymerization Methods? *Macromolecules*. 2023,
- (6) Bradford, K. G. E.; Petit, L. M.; Whitfield, R.; Anastasaki, A.; Barner-Kowollik, C.; Konkolewicz, D. Ubiquitous Nature of Rate Retardation in Reversible Addition– Fragmentation Chain Transfer Polymerization. J Am Chem Soc. 2021, 143 (42), 17769– 17777.
- Johnston-Hall, G.; Monteiro, M. J. Bimolecular Radical Termination: New Perspectives and Insights. *Journal of Polymer Science Part A: Polymer Chemistry*. Wiley Online Library 2008, 10, 3155–3173.
- (8) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Olaj, O. F.; Russell, G. T.; Schweer, J.; Van Herk, A. M. Critically Evaluated Rate Coefficients for Free-radical Polymerization, 2. Propagation Rate Coefficients for Methyl Methacrylate. *Macromol Chem Phys.* 1997, 198 (5), 1545–1560.
- Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. Critically Evaluated Rate Coefficients for Free-radical Polymerization, 1. Propagation Rate Coefficient for Styrene. *Macromol Chem Phys.* 1995, *196* (10), 3267–3280.

- (10) Schrooten, J.; Lacík, I.; Stach, M.; Hesse, P.; Buback, M. Propagation Kinetics of the Radical Polymerization of Methylated Acrylamides in Aqueous Solution. *Macromol Chem Phys.* 2013, 214 (20), 2283–2294.
- (11) Buback, M.; Kurz, C. H.; Schmaltz, C. Pressure Dependence of Propagation Rate Coefficients in Free-radical Homopolymerizations of Methyl Acrylate and Dodecyl Acrylate. *Macromol Chem Phys.* **1998**, *199* (8), 1721–1727.
- (12) Junkers, T.; Voll, D.; Barner-Kowollik, C. Determination of Vinyl Acetate Propagation Rate Coefficients via High Frequency Pulsed Laser Polymerization. *E-Polymers*. 2009, 9 (1), 076.
- (13) Stach, M.; Lacik, I.; Chorvat Jr, D.; Buback, M.; Hesse, P.; Hutchinson, R. A.; Tang, L. Propagation Rate Coefficient for Radical Polymerization of N-Vinyl Pyrrolidone in Aqueous Solution Obtained by PLP- SEC. *Macromolecules*. **2008**, *41* (14), 5174–5185.