Supporting Information: A General Model for the Ideal Chain Length Distributions of Polymers Made with Reversible Deactivation

Madison M. Kearns[a,†], Colleen N. Morley[a, †], Kostas Parkatzidis,[b] Richard Whitfield,[b] Alvaro D. Sponza,[c] Progyateg Chakma,[a] Nethmi De Alwis Watuthanthrige[a], Melanie Chiu[c], Athina Anastasaki[b], and Dominik Konkolewicz[a,*]

a Department of Chemistry and Biochemistry, Miami University, 651 E High St, Oxford, OH, 45056.

b Laboratory for Polymeric Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland

c Stony Brook University, Department of Chemistry, Stony Brook, NY, 11794 USA

† Authors contributed Equally

* Correspondence: d.konkolewicz@miamiOH.edu

Experimental

Materials

All materials were purchased from commercial sources and used as received unless otherwise specified.

Synthesis of phenyl vinyl ketone (PVK) was adopted from a known method and used immediately to prevent degradation.[1] The synthesis of chain transfer agent 2-[[(dodecylthio)thioxomethyl]thio]-

2-methylpopanoic acid, or (isobutyric acid)yl dodecyl trithiocarbonate (iBADTC) was carried out using a known synthesis procedure in literature.[2]

Synthesis of PPVK-b-PBA block polymer

In a 25 mL round bottom flask equipped with a magnetic stirrer bar, azobisisobutyronitrile (AIBN) (2.49 $x10^{-3}$ g, 1.51 $x10^{-5}$ mol), iBADTC (5.51 $x10^{-2}$ g, 1.51 $x10^{-4}$ mol), PVK (1.00 g, 7.57 $x10^{-3}$ mol) and 1.06 g of dioxane were added. The reaction mixture was capped with a rubber septum and deoxygenated with nitrogen for 20 minutes and then stirred overnight at 65 °C. The monomer conversion (>98%) was confirmed by ^{1}H-NMR, giving the PPVK homopolymer.

To the previously prepared PPVK polymer mixture, azobisisobutyronitrile (AIBN) (2.49 $x10^{-3}$ g, 1.51 $x10^{-5}$ mol), BA (9.70 $x10^{-1}$ g, 7.57 $x10^{-3}$ mol) and 1.00 g of dioxane was added. The mixture was mixed, and deoxygenated with nitrogen for 20 minutes and then stirred overnight at 65 °C. The monomer conversion (>98%) was confirmed by ^{1}H-NMR.

NMR

^{1}H were obtained on a Bruker AV500 Ultra Shield (500 MHz) or Bruker Avance NEO 400i nanobay (400 MHz) spectrometer.

Size Exclusion Chromatography (SEC)

Size exclusion chromatography of the PPVK homopolymer and PPVK-PBA block copolymer was performed using an Agilent 1260 gel permeation chromatography system equipped with an isocratic pump, an autosampler, a guard and 2x PL Gel Mixed B columns, and a refractive index detector. The eluent was tetrahydrofuran running at 1mL/min at 30 °C. The system was calibrated with poly(methyl methacrylate) standards in the range of 617,000 to 1,010.

Supporting Data

Table S1. Degree of polymerization and dispersity for systems with k* = 0.1 and varied μ_{decap}. In all cases $[M]_0$ = 4 M, [P-X] = [D] = 0.04 M.

μ_{decap}	DP_n	Dispersity
1	15.881	2.2078
2	25.9576	1.611
3	33.8272	1.4163
5	46.3431	1.2628
10	67.8898	1.1399
20	88.8193	1.0808

Table S2. Degree of polymerization and dispersity for systems with μ_{decap} = 5 and varied k*. In all cases $[M]_0$ = 4 M, [P-X] = [D] = 0.04 M.

k*	DP_n	Dispersity
0.1	46.3431	1.2628
0.2	71.4329	1.2488
0.4	92.6084	1.3106
0.8	100.0926	1.6775
0.99	100.3238	1.9838

Table S3. Degree of polymerization and dispersity for systems with constant product of k* and μ_{decap}. In all cases $[M]_0$ = 4 M, [P-X] = [D] = 0.04 M.

k*	μ_{decap}	DP_n	Dispersity
0.1	10	67.8898	1.1399
0.2	5	71.4329	1.2488
0.33	3	74.4598	1.4067
0.5	2	75.8346	1.6649
0.99	1	64.1999	3.0826

Comparison of Models for Dispersity

The predictions of the developed model, labeled model below are compared to those developed by Goto et al.[3] using the equation below:

$$Đ = 1 + \frac{1}{DP_n} + \left(\frac{2 - conversion}{conversion}\right)\left(k^* \frac{[P - X]}{[D]}\right) \quad \text{(S1)}$$

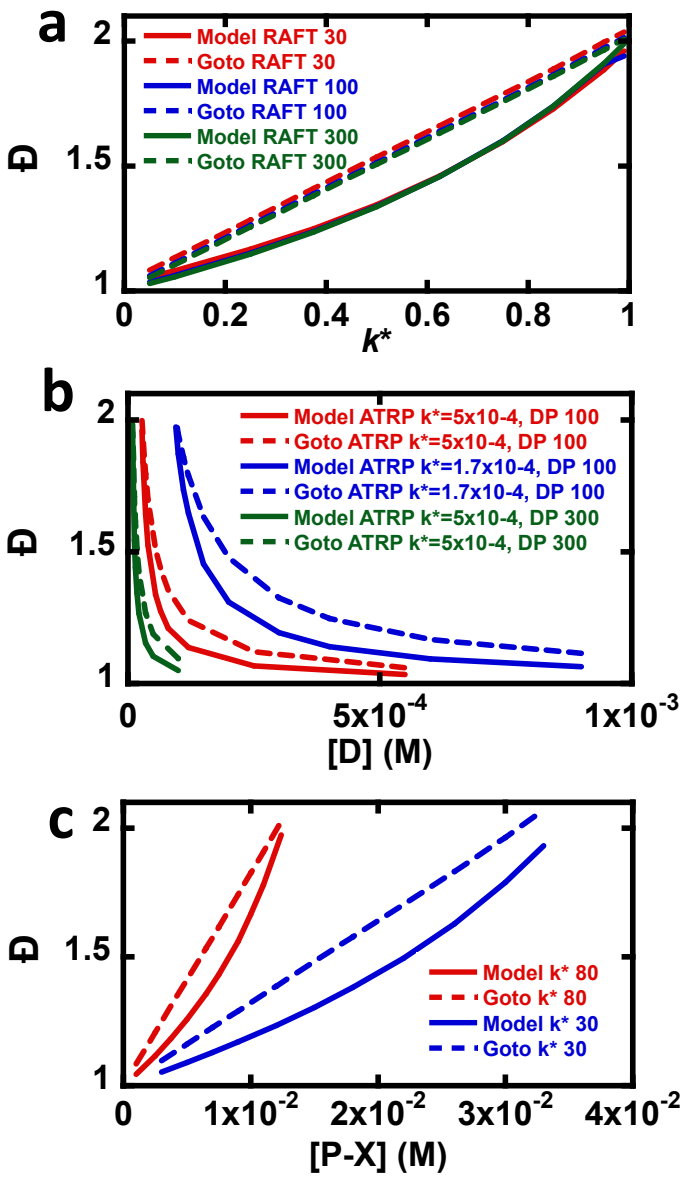

Figure S1: Comparison of dispersities (Đ) predicted by the developed model and the model outlined by Goto et al.[3] a) A RAFT system with $[M]_0$ = 5.5 M, [P-X]=[D] determined by the DP and the product of $k^* \times \mu_{decap}$ of 5. b) An ATRP system with $[M]_0$ = 5.5 M, k^* = 1.7×10^{-4} or 5×10^{-4}, [P-X] determined by the DP and the product of $k^* \mu_{decap}$ / [D] of ca. 100 for DP 100 systems and 300 for DP 300 systems. c) Cationic system with $[M]_0$ = 0.5 M, [D]=1 and [P-X] × μ_{decap} = 0.05 for k^* = 80 and [P-X] × μ_{decap} = 0.165 for k* = 30.

Convolution of two distributions

To predict the outcome of convolving two distributions, where a fraction of the chain length comes from a CTA that gives a narrow distribution and a fraction comes from a CTA that gives a broad distribution, the overall chain length is split by the fraction of CTA loading. For instance if a loading of *f* of a narrow distribution forming CTA is used with a 1-*f* fraction of the broad

distribution forming CTA was used, then the simulated traces would assume that of the total chain length, a fraction *f* of the final chain length came from the narrow distribution forming CTA and 1-*f* came from the broad distribution forming CTA. In this way the final distribution at chain length n can be found by the convolution below and also in eq 29 of the main text:

$$P_{con}\left(n \middle| \mu_{decap,1},\mu_{decap,2},k_1^*,k_2^*,[M]_{0,1},[M]_{0,2},[P-X]_1,[P-X]_2,[D]_1,[D]_2\right) =$$

$$\sum_{i=1}^{n} P_1(n-i+1|\mu_{decap,1},k_1^*,[M]_{0,1},[P-X]_1,[D]_1)P_2(i|\mu_{decap,2},k_2^*,[M]_{0,2},[P-X]_2,[D]_2) \quad \text{(S2)}$$

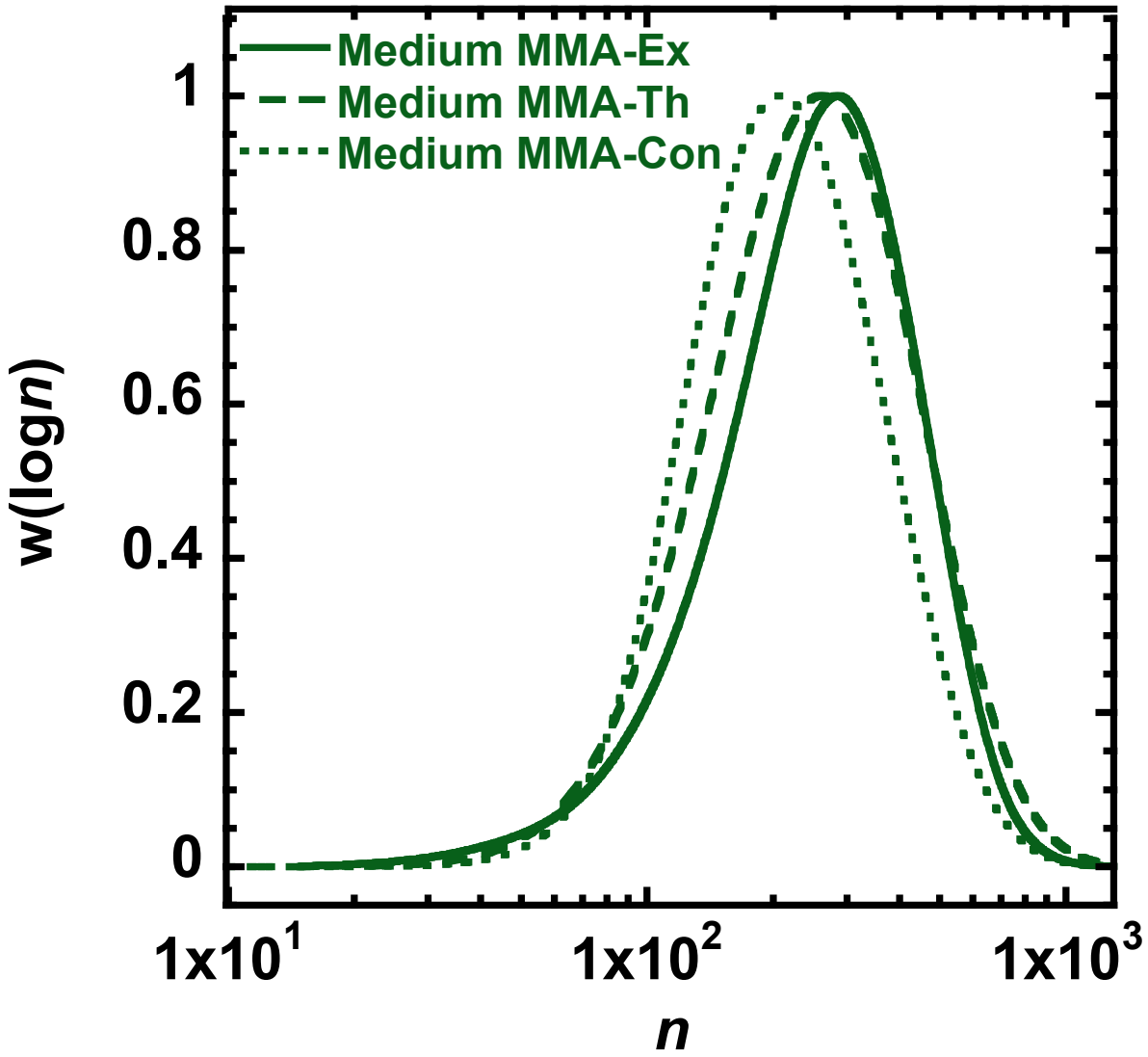

Figure S2: Comparison of experiment, fitted model and convolved polymers. In the convolution one was simulated with [M]:[P-X]:[D]= 1.4:0.02:0.02 using k*=0.128 & μ_{decap}= 14.7272 to match the fraction of 0.35 CTA giving a narrow distribution and the second polymer was

simulated as [M]:[P-X]:[D]= 2.6:0.02:0.02 using k*=0.726 & μ_{decap}= 3.2031 to match the fraction of 0.65 CTA giving a broad distribution.

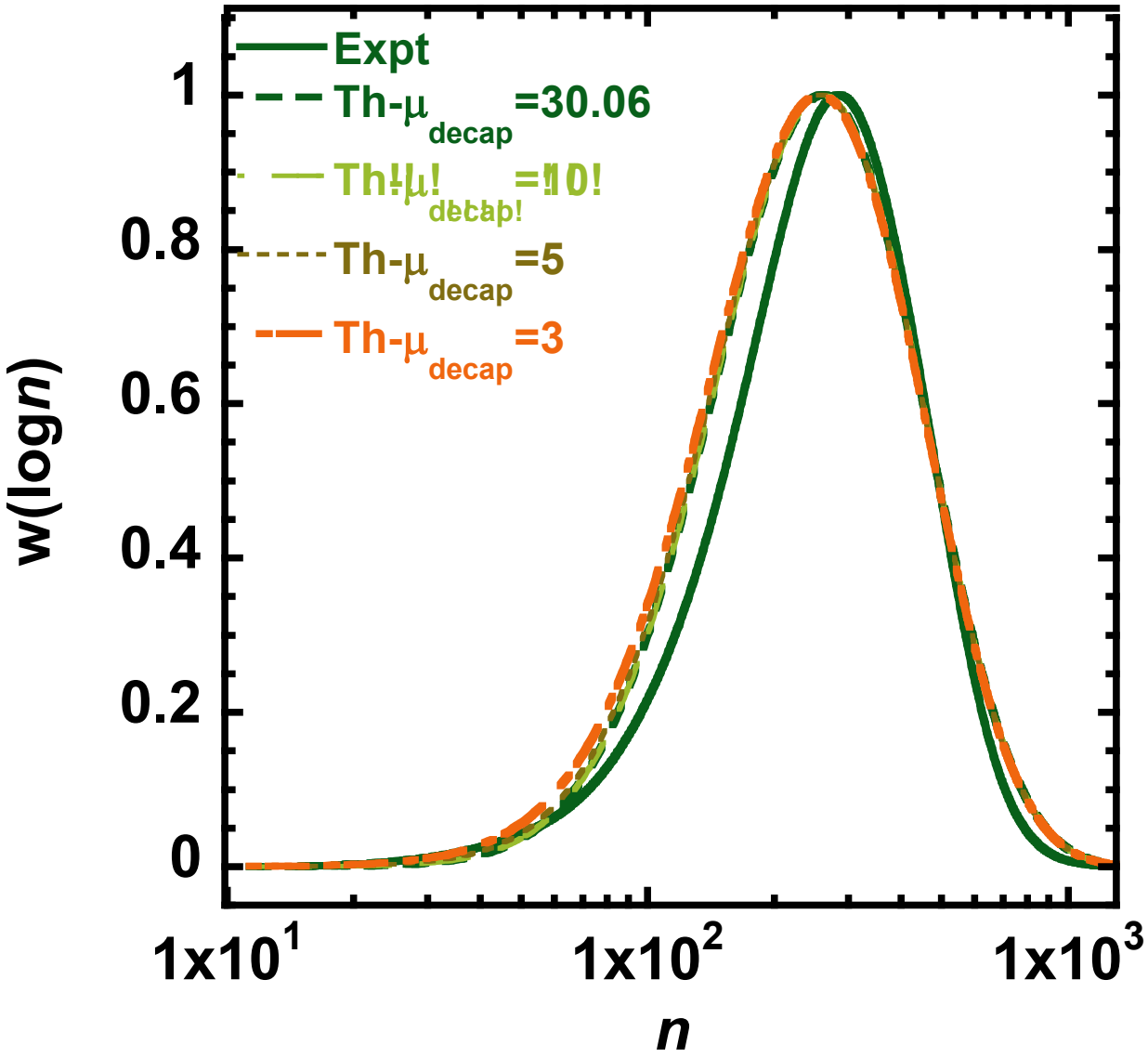

Figure S3: Effect of μ_{decap} on PMMA RAFT polymer of medium dispersity.

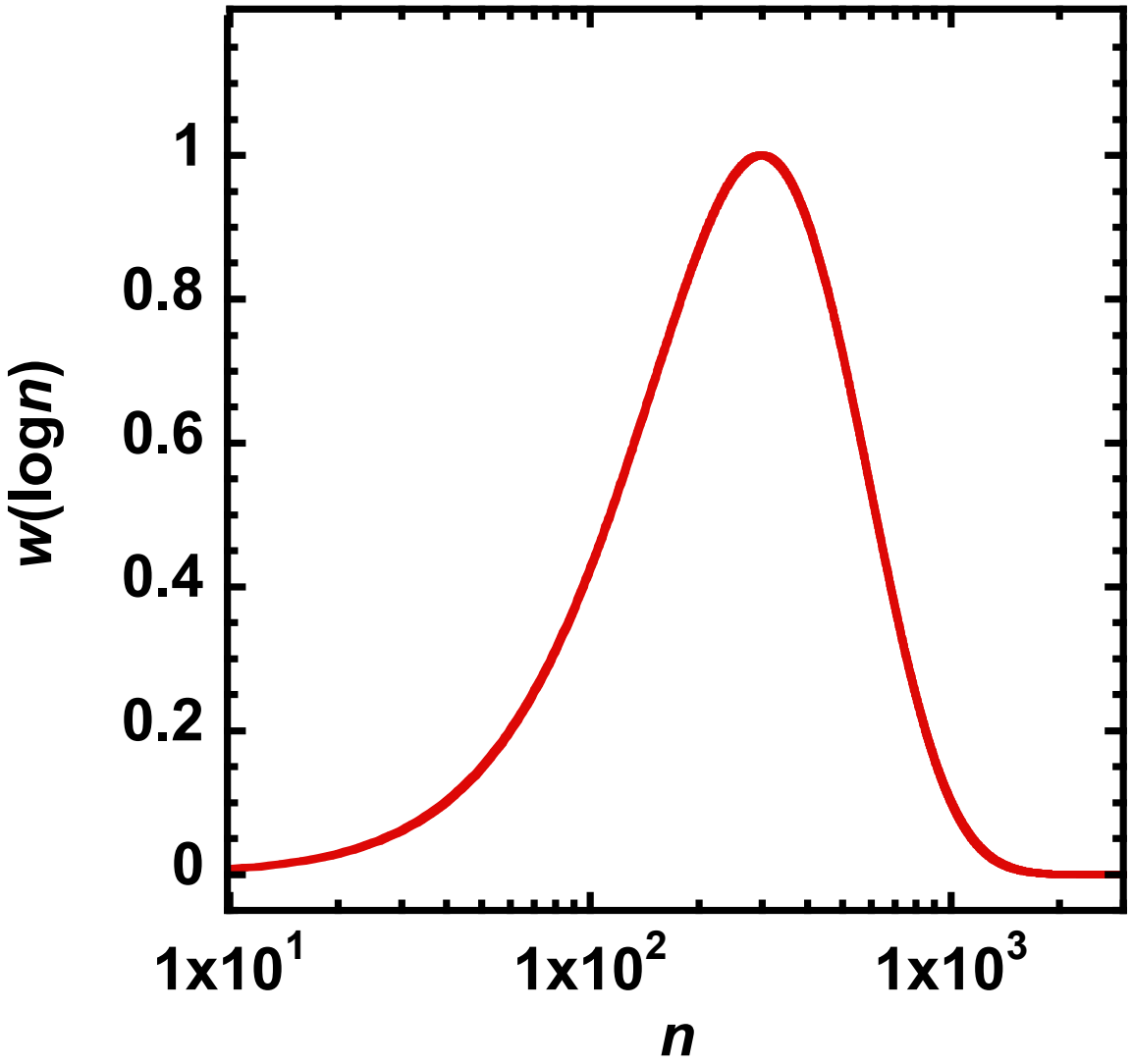

Figure S4. ATRP polymer simulated under: [M]: [P-X]:[D]=5.5: 3.667×10^{-2}:1.482×10^{-5}, with k*=0.0004 and μ_{decap}=3.6.

Table S4: Parameters used to model complex polymers such as blended or block copolymers.

System	Label	[M]:[P-X]:[D]	k*	μ_{decap}	$DP_{n\text{-}Ex}$	$Đ_{Ex}$	$DP_{n\text{-}Th}$	$Đ_{Th}$
ATRP Blended	Narrow	250:1:0.02	0.0015	13.7	175	1.09	171	1.10
	Broad	200:1:0.0005	0.00038	2.0	167	1.84	169	1.89
ATRP	PMMA Block	300:1:0.03	0.0011	21	150	1.10	162	1.07
PMMA-b-EA	PEA Block	300:1:0.03	0.0019	9	N/A[a]	N/A[a]	142	1.16
PhotoRAFT	PPVK block	50:1:1	0.22	9.9	45.6	1.16	42.9	1.17
PPVK-b-BA	PBA block	50:1:1	0.15	25	N/A[a]	N/A[a]	50	1.10
PET-RAFT	PMMA Block 1	100:1:1	0.44	10	103	1.37	100	1.29
PMMA-b-MMA	PMMA Block 2	400:1:1	0.5934	1.92	N/A[a]	N/A[a]	113	3.8

References:

1 S. Chanthamath, S. Takaki, K. Shibatomi, S. Iwasa, *Angew. Chem. Int. Ed.* 2013, **52**, 5818.

2 S. Harrisson, K. L. Wooley, *Chem. Commun.* 2005, 3259.

3 A. Goto, T. Fukuda, *Prog. Polym. Sci.* 2004, **29**, 329.