Supporting Information

Universal Scaling Behavior During Network Formation in Controlled Radical Polymerizations

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Contents

1 Effective Molarity Analysis

1.1 Overlap Concentration (c^*) Calculation

$$c^* = \frac{\frac{V_m}{N_a}}{R_g^3} = \frac{M * DP}{d * N_a * (\frac{b*(2*DP)^{0.6}}{2.45})^3} \tag{S1}$$

Table S1: Overlap Concentrations for DMA at varying DPs

	DP 25	DP 50	DP 100
wt %	20.7	11.9	6.8
Molarity	2.1	1.2	.7

1.2 Derivation and Fitted Data

Crosslink efficiency (XLE) is defined as the propensity of a crosslink over a loop. An XLE of 1 indicates no loop formation while an XLE of 0.5 indicates equal formation of crosslinks and loops. Therefore we treat XLE in equation S2.

$$XLE = \frac{rate_{crosslink}}{rate_{crosslink} + rate_{loop}} \tag{S2}$$

Crosslinking is a bimolecular reaction while loop formation is unimolecular. We then transform this equation into S3.

$$XLE = \frac{k_{xl}[p^*][x-linker]}{k_{xl}[p^*][x-linker] + k_l[EM]} \tag{S3}$$

Effective Molarity (EM) is defined as the the rate of loop formation over crosslink formation, and simultaneously used as a molarity for a unimolecular reaction. Higher effective molarities lead to lower XLE.

$$EM = \frac{k_l}{k_{xl}} \tag{S4}$$

And therefore* :

$$XLE = \frac{1}{1 + \frac{[EM]^2}{[p^*][x-linker]}} \tag{S5}$$

F-S Ideality implies macroscopic gelation when.

$$\frac{[MVM]_{GP}}{[CTA]} = \frac{1}{2} \tag{S6}$$

However this ignored the formation of intramolecular loops. We can rearrange the equation to solve for the XLE

$$XLE = \frac{1}{2} * \frac{[CTA]}{[MVM]_{GP}} \tag{S7}$$

We approximate [p*] to be [Radical Initiator]. We experimentally measure $[\mathrm{MVM}]_{\mathrm{GP}}$ values as a function of [DMA]. This affords us the ability to solve for [EM] as a function of $\frac{[\mathrm{MVM}]_{\mathrm{GP}}}{[\mathrm{CTA}]}$ for each DP. The experimentally measured $[\mathrm{MVM}]_{\mathrm{GP}}$ are listed below in SI Table 2. We plot [EM] as a function of $\frac{[\mathrm{MVM}]_{\mathrm{GP}}}{[\mathrm{CTA}]}$ in SI Figure 1, which were fit linearly.

* We approximate [p]* as the concentration of radical initiators due to the difficulty in calculating this value.

Table S2: Experimentally measured $[\mathrm{MVM}]_{\mathrm{GP}}$ and derived [EM] for DMA at DP 25, 50, 100 at [DMA] = 1, 1.75, 2.5, 3.5, and 5M when utilizing MBAM as the MVM

	$[\mathrm{MVM}]_{\mathrm{GP}}/[\mathrm{CTA}]$			[EM]		
[DMA]	DP 25	DP 50	DP 100	DP 25	DP 50	DP 100
1	4.5	5.5	5.5	107	66	33
1.75	2.6	2.8	3.0	103	56	30
2.5	2.5	2.5	2.5	97	48	24
3.5	1.4	1.4	1.4	99	50	25
5	1.1	1.1	1.1	102	51	26

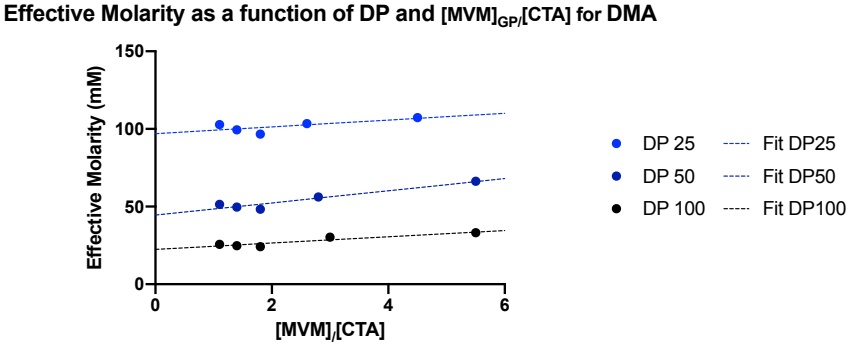

Figure S1: Effective Molarities plotted as a function of $\frac{[\mathrm{MVM}]}{[\mathrm{CTA}]}$ for polymerizations of DMA and MBAM at DP 25, 50, and 100 with a linear fit plotted over the data.

This analysis allows us to solve $[\mathrm{MVM}]_{\mathrm{GP}}$ as a function of [DMA] for each DP by solving equation S8, which is used in Figure 2A

$$XLE(DP,[DMA],\frac{[MVM]_{GP}}{[CTA]})*\frac{[MVM]_{GP}}{[CTA]}=\frac{1}{2} \tag{S8}$$

2 Polymerization Characterization

2.1 Polymerization Kinetics (Linear)

Polymerization rate constants were determined for the RAFT polymerization of MORPH, DMA, NIPAM, and MPAM in DMF at 60°C targeting a DP of 100 at [VM] = 3.5M. A typical polymerization is as follows. DMA (1.39 g, 100 eq, 14 mmol, filtered through basic alumina), 2-CPDT(48.4 mg , 1eq, 0.14 mmol), and AIBN (4.6 mg, 0.2 eq, 0.028 mmol) with trioxane as an internal standard were combined and diluted until 4mL in DMF. The reaction was distributed evenly into multiple 8 ml scintillation vials fitted with PTFE septa. Each separate vial was purged with nitrogen gas for 15 minutes polymerized at 60°C for different reaction times (60, 90, 150, 240, 360 min). When the timepoint was reached the vial was exposed to air, chilled in an ice bath, and subjected to ^{1}H NMR spectroscopy in $CDCl_3$. The pre and post polymerization ratios of $\frac{[\text{trioxane}]}{[\text{DMA}]}$ ((trioxane, δ = 5.08, s) and the VMs were used to determine the degree of conversion.

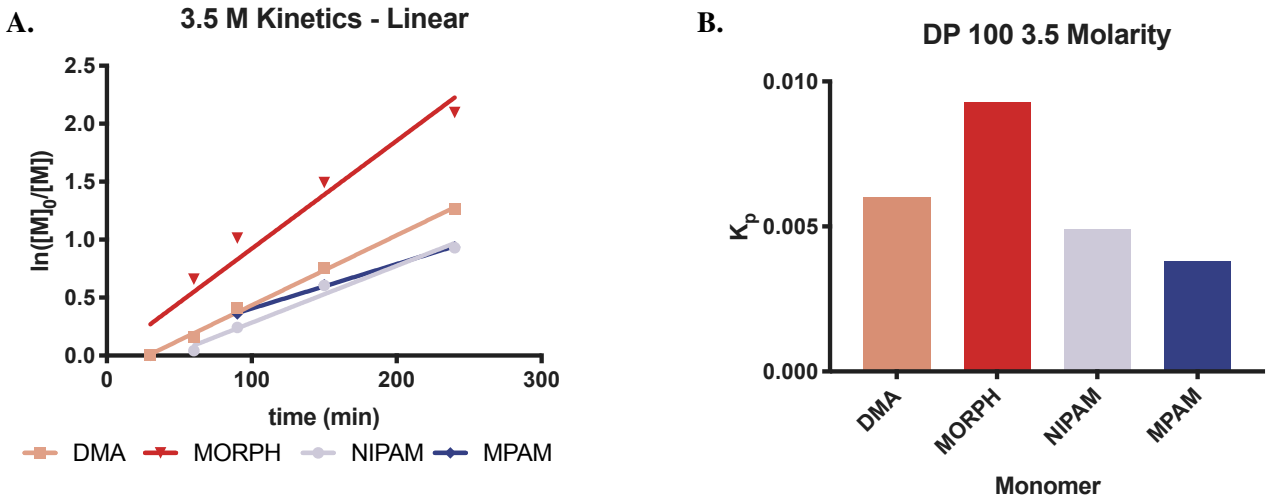

Figure S2: A. Monomer Consumption for the RAFT polymerization of MORPH, DMA, NIPAM, and MPAM in DMF at 60°C targeting a DP of 100 at [VM] = 3.5M. **B.** Slopes of the lines from A. to show the difference in polymerization kinetics for the different acrylamide derivative vinyl monomers.

2.2 Polymerization Kinetics (Branched)

The controlled growth of primary chains was confirmed for the RAFT copolymerization of NIPAM, and MBAM in DMF at 60°C targeting a DP of 50 at [VM] = 3M. A typical polymerization is as follows. NIPAM (1.750, 50 eq, 15.4 mmol), 2-CPDT(106.5 mg, 1 eq, 0.31 mmol), and AIBN (10.2 mg, 0.2 eq, 0.062 mmol) were combined and diluted until 5mL in DMF and transferred into a 20 mL scintillation vials fitted with a PTFE septa. The vial was purged with nitrogen gas for 15 minutes and polymerized at 60°C. Aliquots were removed at different reaction times under positive nitrogen pressure and subjected to ^{1}H NMR spectroscopy in $CDCl_3$ and Size Exclusion Chromatography (SEC) in DMF using PEG standards. NIPAM conversion was determined by the disappearance of NIPAM vinyl peaks (δ = 5.57, d) compared to DMF (δ = 7.97, s) as an internal standard.

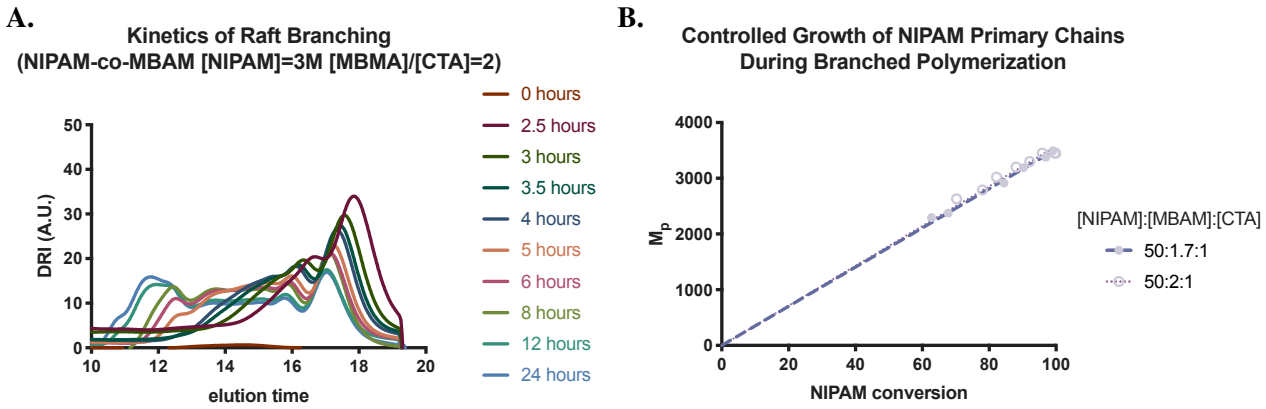

Figure S3: Kinetic experiment exploring the controlled nature of chain growth during the following polymerizations. **A.** Size Exclusion Chromatograms of the RAFT copolymerization of NIPAM and MBAM at [NIPAM] = 3M at 60°C at a $\frac{[MBAM]}{[CTA]}$ ratio of 2:1. The SEC RI traces are normalized to have equal AUCs. **B.** M_p values of the primary chain (right-most peak in part A) determined by DMF SEC with the use of PEG standards as a function of NIPAM conversion indicating controlled primary chain growth during branching.

2.3 Polymerization Reactivity Ratios

Polymerization reactivity ratios were determined for NIPAM and DMA, and DMA and MORPH through RAFT polymerization in DMF at 60°C [VM] = 3.5M. A brief experimental design to determine reactivity ratios for NIPAM and DMA is as follows. Three copolymerization ratios (75% DMA and 25% NIPAM, 50% DMA and 50% NIPAM, 25% DMA and 50% NIPAM) are prepared separately. Each copolymerization is split up into 4 separate reaction vials and polymerized to different global conversions. We measure the monomer conversion via ^{1}H NMR spectroscopy in $CDCl_3$ of DMA and NIPAM as a function of global monomer conversion and solve for the reactivity ratios through nonlinear regression of the Meyer Lowry method. A typical reaction procedure is as follows. DMA (521 mg, 50 eq, 5.25 mmol, filtered through basic alumina), NIPAM (594 mg, 50 eq, 5.25 mmol), 2-CPDT(36.3 mg , 1eq, 0.105 mmol), and AIBN (3.5 mg, 0.2 eq, 0.021 mmol) were combined and diluted until 3mL in DMF. The reaction was distributed evenly into three 8 ml scintillation vials fitted with PTFE septa. Each separate vial was purged with nitrogen gas for 15 minutes polymerized at 60°C for either 60, 120, or 180 minutes. The disappearance of vinyl peaks of DMA (δ = 5.56, d) and NIPAM (δ = 5.535, d) compared to DMF (δ = 7.97, s) as an internal standard were used to determine monomer conversion via ^{1}H NMR spectroscopy in $CDCl_3$.

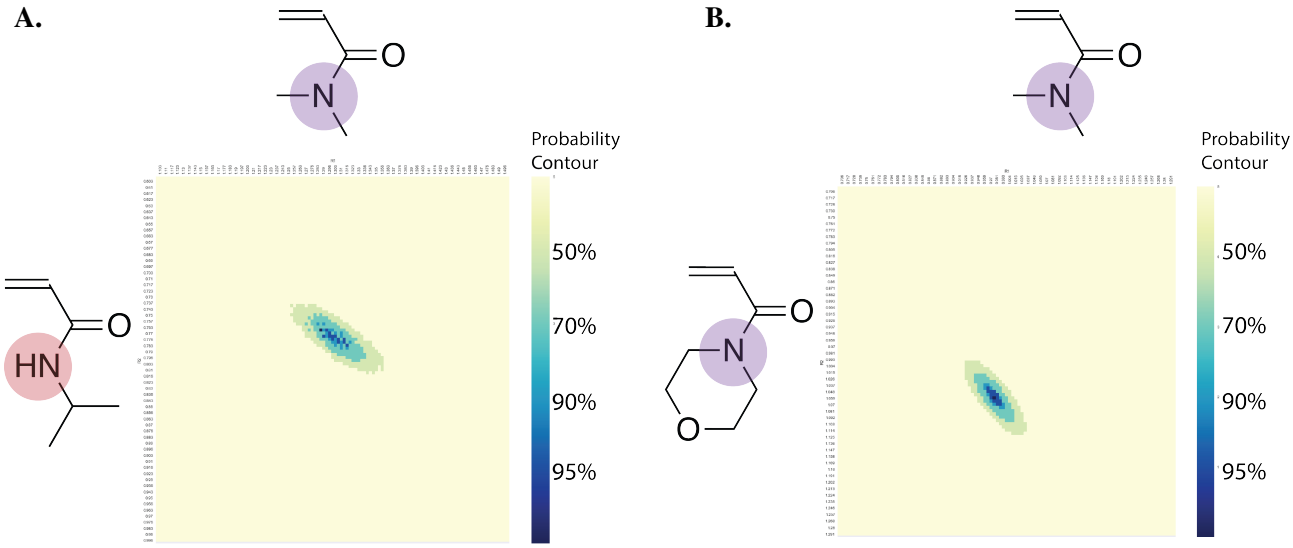

Figure S4: Reactivity ratio heat-maps for the copolymerization of **A.** DMA and NIPAM and **B.** DMA and MORPH calculated using the Meyer-Lowry method. Heat-map values correspond to probability contours fitting these reactivity ratios to the experimentally derived conversions compared to best fist (darkest dot). A probably contour of 95% indicates that, statistically, there is a 5% chance that this value has a different sum of squared errors than the global minimum. Color coding on vinyl monomers correspond to acrylamide class as secondary (red) or tertiary (purple).

Table S3: Reactivity Ratio calculated for the copolymerization of DMA and NIPAM and DMA and MORPH using the Meyer-Lowry method.

Monomer A	r_A	Monomer B	r_B
DMA	1.29	NIPAM	0.77
DMA	0.98	MORPH	1.06

2.4 Characterization Table of Branched Polymers

Table S4: Table of relevant characterization data for branched copolymers synthesized during this study.

Time	% Conversion[a]	DP	VM	[VM]	MVM	$\frac{[MVM]}{CTA}$	$\frac{[MVM]_{GP}}{CTA}$	M_p[b]	M_n[c]	M_w[c]	$\frac{M_n}{M_p}$	$\frac{M_w}{M_p}$	$\frac{[MVM]}{[MVM]_{GP}}$
24		50	MORPH	2.5	MBAM	0.25	1.8	8.5	8.75	13.1	1.02	1.54	0.14
24		50	MORPH	2.5	MBAM	0.5	1.8	8.5	10	15.6	1.17	1.83	0.28
24	99%+	50	MORPH	2.5	MBAM	0.75	1.8	8.5	13.3	23.9	1.56	2.81	0.42
24		50	MORPH	2.5	MBAM	1	1.8	8.5	15.2	38.6	1.78	4.54	0.56
24		50	MORPH	2.5	MBAM	1.3	1.8	8.5	24.9	97	2.92	11.4	0.72
24		50	MORPH	2.5	MBAM	1.5	1.8	8.5	34.2	198	4.02	23.3	0.83
24		50	MORPH	2.5	MBAM	1.7	1.8	8.5	96.4	393	11.3	46.2	0.94
24		50	MORPH	3.5	MBAM	0.25	1.4	8.2	9.4	11.3	1.14	1.38	0.18
24		50	MORPH	3.5	MBAM	0.5	1.4	8.2	11.4	18.2	1.39	2.22	0.36
24	99%+	50	MORPH	3.5	MBAM	0.75	1.4	8.2	13.4	29.1	1.63	3.54	0.54
24		50	MORPH	3.5	MBAM	0.9	1.4	8.2	14.8	45	1.80	5.48	0.64
24		50	MORPH	3.5	MBAM	1	1.4	8.2	22	86.8	2.68	10.58	0.71
24		50	MORPH	3.5	MBAM	1.2	1.4	8.2	49.3	246.9	6.01	30.11	0.86
24		50	MORPH	3.5	MBAM	1.3	1.4	8.2	583	1197	71.1	145.6	0.93
24		50	MORPH	2.5	PIPBAM	0.25	1.4	8	9	11.8	1.12	1.47	0.18
24		50	MORPH	2.5	PIPBAM	0.5	1.4	8.7	13	21.7	1.49	2.49	0.36
24		50	MORPH	2.5	PIPBAM	0.75	1.4	8.7	18.1	34	2.08	3.91	0.54
24		50	MORPH	2.5	PIPBAM	1	1.4	8.7	25.8	53.3	2.97	6.13	0.71
24		50	MORPH	2.5	PIPBAM	1.25	1.4	8.7	153.2	244.9	17.6	28.1	0.89
24		50	MPAM	2.5	PIPBAM	0.25	1.4	7.2	9.5	13	1.31	1.81	0.18
24		50	MPAM	2.5	PIPBAM	0.5	1.4	7.2	15.2	21.6	2.11	3	0.36
24		50	MPAM	2.5	PIPBAM	0.75	1.4	7.2	18.9	33.9	2.63	4.71	0.54
24		50	MPAM	2.5	PIPBAM	1	1.4	7.2	23.1	77	3.21	10.7	0.71
24		50	MPAM	2.5	MBAM	0.5	3.2	6.9	7.3	9	1.05	1.3	0.16
24	99%+	50	MPAM	2.5	MBAM	0.75	3.2	7.9	9.9	17.3	1.25	2.19	0.23
24		50	MPAM	2.5	MBAM	1.5	3.2	7.9	13.3	26.4	1.68	3.34	0.47
24		50	MPAM	2.5	MBAM	2.4	3.2	7.9	23.2	115.8	2.94	14.65	0.75
24		50	MPAM	2.5	MBAM	2.8	3.2	7.9	43.9	350.2	5.55	44.3	0.88
24		50	MPAM	3.5	MBAM	0.25	2	6.5	5.8	7.3	0.89	1.12	0.13
24		50	MPAM	3.5	MBAM	0.5	2	7.5	8.6	11.9	1.14	1.58	0.25
24	99%+	50	MPAM	3.5	MBAM	0.75	2	7.5	8	16.1	1.06	2.15	0.38
24		50	MPAM	3.5	MBAM	1	2	7.5	9.5	15.8	1.25	2.10	0.5
24		50	MPAM	3.5	MBAM	1.5	2	7.5	20.5	65.2	2.73	8.69	0.75
24		50	MPAM	3.5	MBAM	1.8	2	7.5	21.4	94.5	2.85	12.6	0.9
24		50	DMA	2.5	MBAM	0.25	1.8	5.6	6.1	7.7	1.09	1.35	0.14
24		50	DMA	2.5	MBAM	0.5	1.8	5.6	7.1	10.1	1.27	1.80	0.28
24	99%+	50	DMA	2.5	MBAM	0.75	1.8	5.6	8.7	14.6	1.55	2.61	0.42
24		50	DMA	2.5	MBAM	1.6	1.8	5.6	62	344.1	11.1	61.4	0.89
24		50	DMA	2.5	MBAM	1.7	1.8	5.6	109.3	482.7	19.5	86.2	0.94
24		50	DMA	3.5	MBAM	0.25	1.4	5.9	7.2	9.9	1.22	1.67	0.18
24		50	DMA	3.5	MBAM	0.5	1.4	5.9	8.0	12.6	1.35	2.13	0.36
24	99%+	50	DMA	3.5	MBAM	0.75	1.4	5.9	11	22.1	1.86	3.74	0.54
24		50	DMA	3.5	MBAM	0.9	1.4	5.9	15.6	40.8	2.65	6.91	0.64
24		50	DMA	3.5	MBAM	1	1.4	5.9	19.4	61.8	3.3	10.5	0.71
24		50	DMA	3.5	MBAM	1.2	1.4	5.9	42.5	217.6	7.2	36.9	0.86
24		50	DMA	5	MBAM	0.25	1.1	5.8	6.9	9.3	1.19	1.60	0.23
24		50	DMA	5	MBAM	0.5	1.1	5.8	9.1	16.4	1.56	2.82	0.45
24	99%+	50	DMA	5	MBAM	0.75	1.1	5.8	14.9	42.7	2.56	7.36	0.68
24		50	DMA	5	MBAM	0.9	1.1	5.8	36.7	206.2	6.33	35.55	0.82
24		50	DMA	5	MBAM	1	1.1	5.8	172	476	29.7	82	0.91
24		25	DMA	3.5	MBAM	0.25	1.4	3.0	3.1	4.2	1.03	1.4	0.18
24		25	DMA	3.5	MBAM	0.5	1.4	3.0	4.4	7.7	1.46	2.6	0.36
24		25	DMA	3.5	MBAM	0.75	1.4	3.0	6.4	15.8	2.13	5.3	0.54
24		25	DMA	3.5	MBAM	1	1.4	3.0	13.7	58.4	4.56	19.5	0.71
24		25	DMA	3.5	MBAM	1.25	1.4	3.0	461	752	153	250	0.89
24		100	DMA	3.5	MBAM	0.3	1.4	13.3	17.6	24.7	1.32	1.85	0.21
24		100	DMA	3.5	MBAM	0.6	1.4	11.1	16.2	25.8	1.46	2.32	0.43
24		100	DMA	3.5	MBAM	0.9	1.4	11.1	24.2	53.6	2.18	4.82	0.64
24		100	DMA	3.5	MBAM	1.2	1.4	11.1	125	528	11.26	47.57	0.86

[a] Conversion determined via the post polymerization ratio of unconsumed VM (DMA (δ = 6.47, q), MORPH (δ = 6.43, q), and MPAM(δ = 5.58, d)) vinyl peak to the integrated polymerization signal via ^{1}H NMR spectroscopy. Due to the similarity in polymerization conditions and a kinetics

experiment completed we assume >99% for all other experiments.
[b] Absolute M_p determined via Multi Angle Laser Light Scattering and is reported as the Molecular Weight determined at the apex of primary chain elution volume. Units are kDa.
[c] Absolute M_n and M_w determined via Multi Angle Laser Light Scattering through integration of the entire chromatogram (primary chains included). Units are kDa.

2.5 Molecular Weights at Different DP_{PC}s

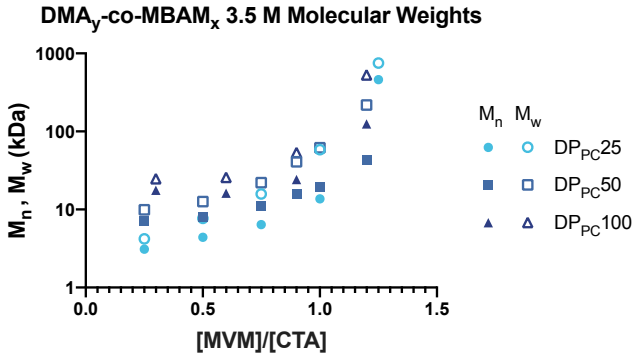

Figure S5: Number and weight average molecular weight scaling for DMA branched polymers copolymerized with MBAM at DP_{PC} 25, 50, and 100.

2.6 Alternate Scaling Analysis

Traditional polymer physics looks at the phenomena of percolation through scaling of ε rather than $\frac{[MVM]}{[MVM]_{GP}}$, where ε is the relative extent of reaction defined as $\frac{[MVM]-[MVM]_{GP}}{[MVM]_{GP}}$. We plot our data as a function of ε in SI Figure 6.

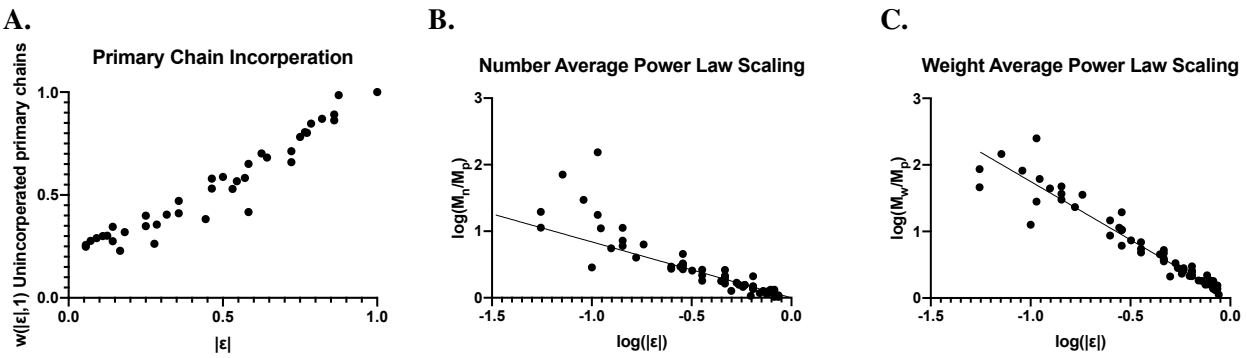

Figure S6: Three alternate plots of the scaling determined through our analysis where primary chain incorporation (**A.**), number average (**B.**) and weight average (**C.**) scaling are plotted as a function of ε. The slopes in **B** (-0.84) and **C** (-1.7) correspond to the exponent described in the main text's equation 4.

3 Rheology

3.1 Example of Oscillatory Sweep Data

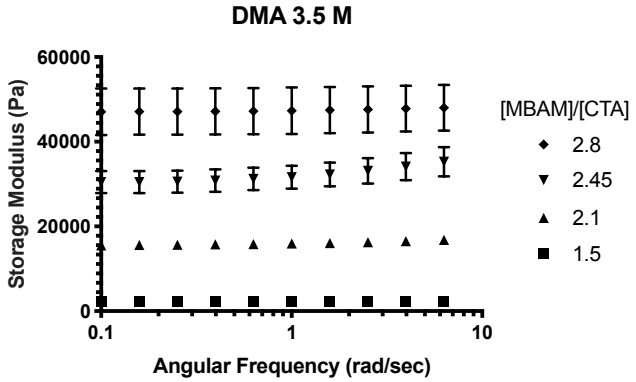

Figure S7: Shear storage modulus determined by oscillatory sweep (ε = 0.01) for the copolymerization of DMA (3.5 M) and MBAM targeting a $\frac{[\text{DMA}]}{[\text{CTA}]}$ = 50 at $\frac{[\text{MBAM}]}{[\text{CTA}]}$ of 1.5, 2.1, 2.45, and 2.8. n=3 for two sections of gel for each measurement (6 measurements).

3.2 The effect of DP_{PC} on Storage Modulus

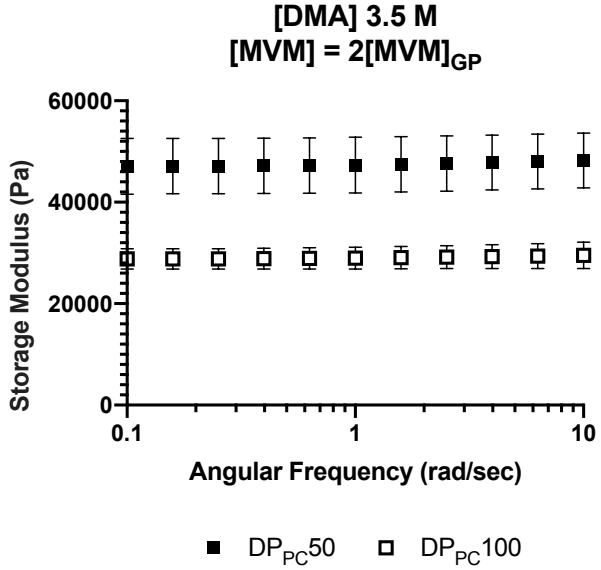

Figure S8: Shear storage modulus determined by oscillatory sweep (ε = 0.01) for the copolymerization of DMA (3.5 M) and MBAM targeting a $\frac{[\text{DMA}]}{[\text{CTA}]}$ = 50 at $\frac{[\text{MBAM}]}{[\text{CTA}]}$ of 2.8. n=3 for two sections of gel for each measurement (6 measurements).

3.3 Degree of Cure

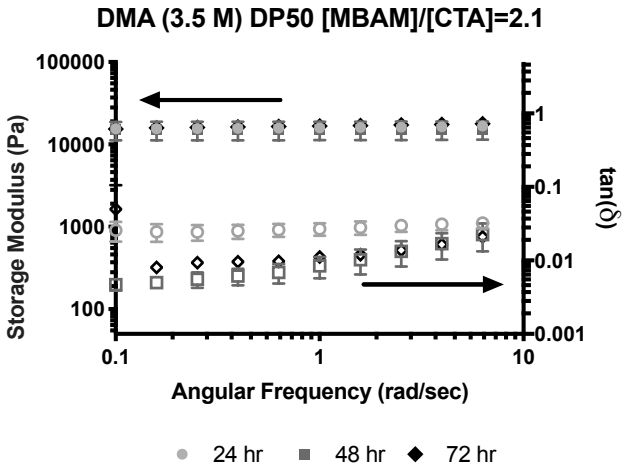

Figure S9: Shear storage modulus and tan(δ) determined by oscillatory sweep (ε = 0.01) for the copolymerization of DMA (3.5 M) and MBAM targeting a $\frac{[\text{MBAM}]}{[\text{CTA}]}$ = 2.1 and $\frac{[\text{DMA}]}{[\text{CTA}]}$ = 50 for 24, 48, and 72 hours. Identical oscillatory shear moduli for the three timepoints indicative of a full cure at 24 hrs. $\frac{[\text{MVM}]_{\text{GP}}}{[\text{CTA}]}$ for [DMA] = 3.5M is 1.4. n=3 for each measurement.

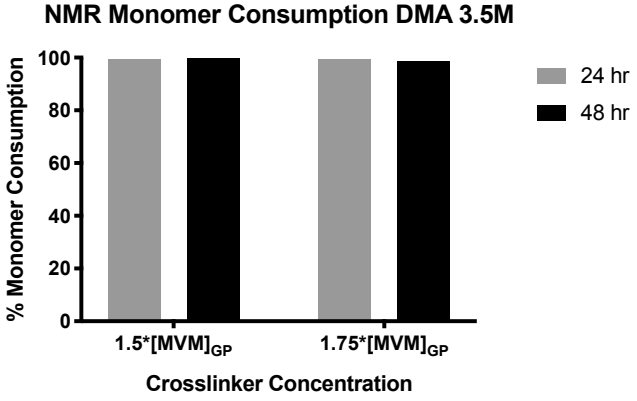

Figure S10: Vinyl Monomer consumption during the copolymerization of DMA (3.5 M) and MBAM targeting $\frac{[\text{DMA}]}{[\text{CTA}]}$ = 50 and $\frac{[\text{MBAM}]}{[\text{CTA}]}$ = 2.1 ($1.5 * [\text{MVM}]_{\text{GP}}$) and $\frac{[\text{MBAM}]}{[\text{CTA}]}$ = 2.45 ($1.75 * [\text{MVM}]_{\text{GP}}$) for cures of 24hrs and 48 hours. Vinyl Monomer consumption determined by addition of a1,3,5-trioxane (as an internal standard) to reaction mixture before polymerization, preforming a ^{1}H NMR of the reaction mixture before polymerization, swelling a section of gel in an excess of $CDCl_3$ for 48 hours with agitation, and preforming a ^{1}H NMR of the resulting $CDCl_3$. The pre and post polymerization ratios of $\frac{[\text{trioxane}]}{[\text{DMA}]}$ ((trioxane, δ = 5.08, s) and (DMA, δ = 6.54, q)) was used to determine the degree of conversion (Conversion = $\frac{\text{pre}-\text{post}}{\text{pre}}$). Very similar conversion are calculated when DMF (δ = 7.97, s) is employed as an internal standard. Actual conversion for $1.5 * [\text{MVM}]_{\text{GP}}$ at 24 and 48 hours are, respectively, 99.2, and 99.9. Actual conversion for $1.75 * [\text{MVM}]_{\text{GP}}$ at 24 and 48 hours are, respectively, 99.4, and 98.7, which we believe is within experimental error.

3.4 Setup

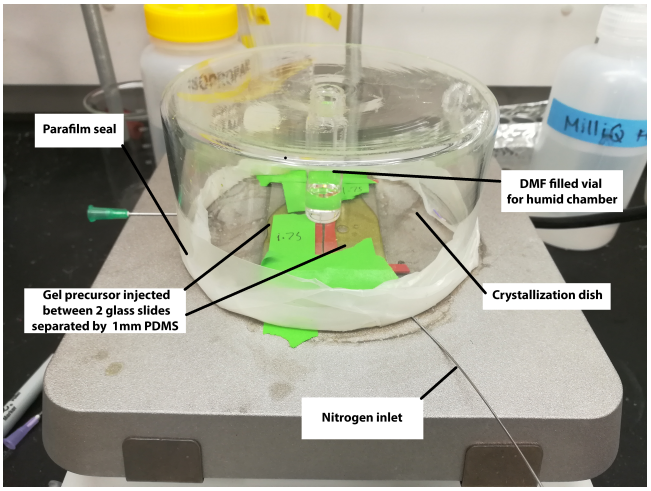

Figure S11: Gelation setup immediately after injecting RAFT gel precursor between the glass slides. During 24 hr polymerization the Nitrogen inlet and outlet are removed.