Supporting Information

Controlling Primary Chain Dispersity in Network Polymers: Elucidating the Effect of Dispersity on Degradation

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Contents

Materials and Instrumentation

All materials were purchased from Sigma Aldrich or Fischer Scientific and used as received unless otherwise stated. All monomers were filtered through a column of basic alumina prior to usage.

Light irradiation was performed using a handmade photoreactor. RGB photodiode tape was coated around the inside of a glass cylinder (F 110 mm, H 180 mm). Reactions were irradiated with blue light (Light intensity 4.8 mW/cm^2).

^{1}H NMR spectra were recorded on a Bruker DPX-300 spectrometer in deuterated chloroform ($CDCl_3$). Chemical shifts are given in ppm downfield from tetramethylsilane referenced to residual $CHCl_3$ protons. Monomer conversions were determined via ^{1}H NMR spectroscopy by comparing the integrals of monomeric vinyl protons to monomer and polymer signals.

Size exclusion chromatography (SEC) analysis of polymer samples was performed using a Shimadzu modular system comprising of a CBM-20A system controller, an SIL-20A automatic injector, a 10.0 μm beadsize guard column (50 × 7.5 mm) followed by three KF-805L columns (300 × 8 mm, bead size: 10 μm, pore size maximum: 5000 Å), an SPD-20A ultraviolet detector, and an RID-20A differential refractive-index detector. The temperature of the columns was maintained at 40 °C using a CTO-20A oven. The eluent was N,N-dimethylacetamide (HPLC grade, with 0.03% w/v LiBr) and the flow rate was kept at 1 mL/minute using an LC-20AD pump. A molecular weight calibration curve was produced using commercial narrow molecular weight distribution poly(methyl methacrylate) standards with molecular weights ranging from 5000 to 1.5 × 10^6 Da.

UV-Vis spectrometry was performed on a JASCO V-730 spectrophotometer equipped with STR-773 water thermostated cell holder and stirrer. Spectra were typically recorded from 400 to 1000 nm at a rate of 400 nm min^{-1} at 25 °C.

General Procedures: Degradable crosslinker synthesis (N,N'-Cystaminebis(acrylamide))

In a 500 mL three-neck round bottomed flask, 11.3 g of cystamine dihydrochloride (50 mmol), 80 mL of water and 40 mL of 5M NaOH aq. 40 mL were added. The flask was placed under a continuous nitrogen atmosphere and cooled in an ice bath. Into a 100 mL dropping funnel, 10 mL of DCM and 16.2 mL of acryloyl chloride was added. This mixture was then added dropwise to the round bottom flask over 30 minutes. The reaction was stirred at 200 rpm overnight. A white solid formed which was collected via filtration. This solid was then dissolved in 200 mL of DCM and washed three times in water, before being dried with magnesium sulfate. The DCM was then removed under vacuum yielding 3.8g (29% yield) of white solid. ^{1}H NMR (300 MHz, DMSO-d6) d 8.51 (2H), 6.18 (4H), 5.62 (2H), 3.44 (4H), 2.85 (4H).

General Procedures: PET RAFT Polymerisation

Linear Polymer Synthesis

To a foil-wrapped 5 mL glass vial, 8.33 mg (1 eq.), 0.40 mL of dimethylacrylamide (120 eq.), 0.32 mL of DMF and 0.96 mL of water (80 vol% solvent) were added. A stock solution of eosin Y (EY) was prepared at 0.325 mg/ml and 0.32 mL (0.1046 mg, 0.005 eq.) was added to the glass vial. Various amounts of sulfuric acid (0, 0.43 µL, 0.86 µL and 5.16 µL) were then added, depending on the desired target dispersity. The vial was then capped with a septum and was then deoxygenated via nitrogen bubbling for 15 minutes. Then foil was removed and the vial was put into the photoreactor on a stirrer. The reaction was irradiated with blue light for 18 hours with 200 rpm stirring. The reaction was then sampled for ^{1}H NMR and SEC, with SEC samples passed through a basic alumina column prior to analysis.

Synthesis of PDMA/PCBA networks

A glove bag was inflated and flushed with nitrogen for 30 minutes prior to the experiment and a double glass plated mould (8 x 8 x 0.3 cm) was prepared after pretreatment with SigmaCote. In parallel, to a 5 mL foil wrapped glass vial, 8.75 mg of CTA (1 eq.), 50.5 mg of CBA (6 eq.), 0.40 mL of dimethylacrylamide (120 eq.), 0.32 mL of DMF and 0.96 mL of water were added. A stock solution of eosin Y (EY) was prepared at 0.325 mg/ml and 0.32 mL (0.1046 mg, 0.005 eq.) was added to the glass vial. Various amounts of sulfuric acid (0, 0.43 µL, 0.86 µL and 5.16 µL) were then added, depending on the desired target dispersity. The vial was then capped with a septum and deoxygenated by nitrogen bubbling for 15 minutes. The mixture was then transferred to the double glass plated mould with a silicone rubber spacer (1 or 3 mm in thickness) under a nitrogen atmosphere and sealed. The mould was then placed into the photoreactor and irradiated with blue light for 18 hours for gelation to occur.

General Procedures: Purification and Degradation

Purification of PDMA/PCBA gels

180 mg of gel was collected for DTT cleavage and equilibrium water content measurements. The remaining gel was placed into a petri dish containing 30 mL of distilled water and a lid was placed on it, allowing any eosin Y, sulfuric acid and DMF to diffuse out. After 24 hours, the water was replaced and this process was repeated twice. 0.3 mL of the extracted solutions were mixed with 0.3 mL of deuterated water, and this was analysed by ^{1}H NMR to determine the extent of monomer and polymer incorporation.

Equilibrium Water Content

150 mg of unpurified gel was extracted for 24 hours, 3 times in 3 mL of water to remove any unreacted species and swell the gel to its maximum. The gel was then freeze-dried to remove all water. By weighing before and after drying, EWC was calculated using the following equation. EWC (%) = $(W_s\text{-}W_d)/W_s \times 100$, where W_s and W_d are the weights of the swollen and dried gel, respectively.

Swelling Ratio

Swelling ratio (SR) was calculated using the following equations: SR = (W_s/W_d)-1 or SR = (1/(1-EWC)-1), where EWC is the equilibrium water content given as a decimal, rather than a percentage.

Gel Cleavage using DTT

In a 5 mL glass vial, 10 mg of DTT was dissolved in 2 mL of dimethylacetamide. The vial was then sealed with a septum and deoxygenated by bubbling with nitrogen for 15 minutes before the addition of 9.1 µL of trimethylamine. In parallel, 30 mg of unpurified gel (1 equiv. of disulfide) and a stirrer bar was placed into a second vial. The vial was sealed with a septum and put under a nitrogen atmosphere for 15 minutes. 1.5 mL of the solution of DTT (16 equiv.) and TEA (16 equiv.) was then transferred into the vial containing the gel and the reaction commenced at 60˚C for 24 hours. The solution was then passed through a column of alumina prior to size exclusion chromatography (SEC) analysis.

Gel Degradation Test with Glutathione

Three discs of 1 mm thickness and 10 mm diameter were punched out of the purified gel and each placed in a separate glass vial. In a separate vial, a 10 mM glutathione solution was prepared with 123 mg of glutathione dissolved in 40 mL of 0.1M PBS solution. 3 mL of this solution was added to each of the gels and the vials were stored at room temperature under full dissolution had occurred. The diameters of the gels were recorded periodically using a Vernier Calliper.

Additional Characterization Data

Dispersity Control in Linear Polymers

Table S1: ^{1}H NMR and SEC data illustrating the polymerization of DMA with various amounts of Eosin Y (EY).

Entry[a]	[EY]	Time (h)	Conversion (%)[b]	$M_{n\ (Theo.)}$ (Da)[c]	$M_{n\ (SEC)}$	$M_{w\ (SEC)}$	$M_{P\ (SEC)}$	$Đ$[d]
1	None	4	**0**	-	-	-	-	**-**
2	0.005	4	**95**	9700	10500	16400	16100	**1.56**
3	0.02	4	**94**	9600	10100	15800	15400	**1.58**
4	0.04	4	**75**	7700	8400	14200	14000	**1.69**

[a] Reactions were performed with a target DP of 100. The volume ratio of H_2O:DMF (4:1) to DMA was maintained at 4:1 for all entries. [b] Conversion was measured by ^{1}H NMR. [c] Theoretical M_n was calculated based on conversion and the target DP. [d] Molecular weight and dispersity values were determined by SEC.

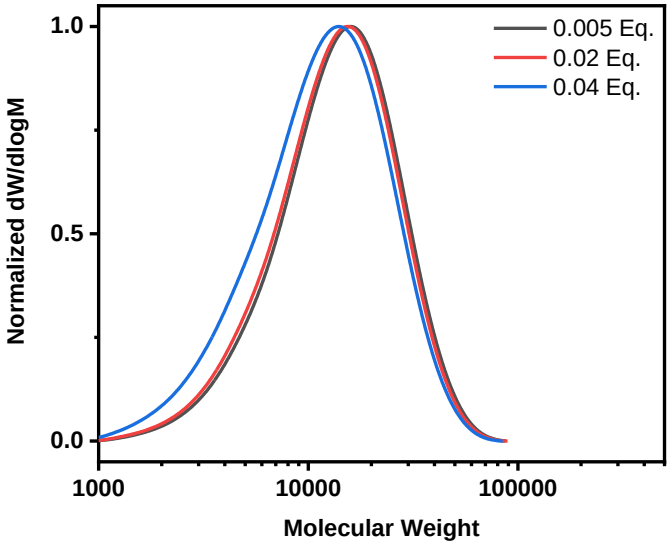


Figure S1: SEC data illustrating the polymerization of DMA with various amounts of Eosin Y. This data corresponds to entries 2, 3 and 4 in Table 1.

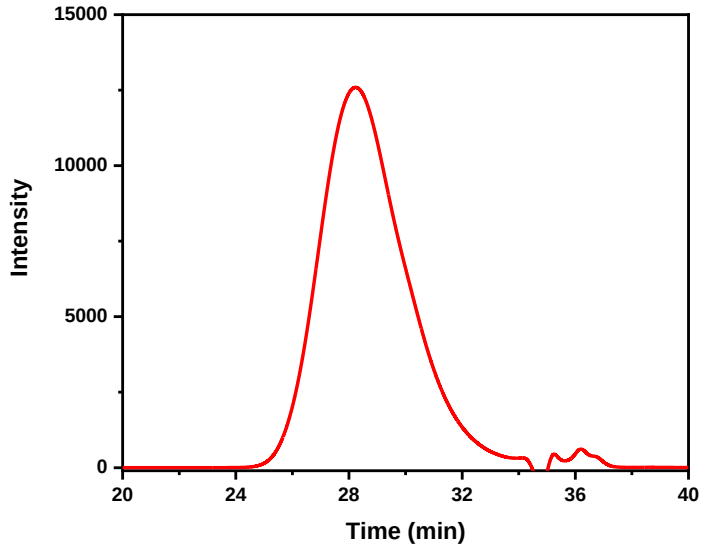


Figure S2: UV detector for high dispersity PDMA (Đ=1.60) demonstrating that all raft agent was consumed.

Table S2: ^{1}H NMR and SEC data illustrating the chain extension of PDMA with DMA at various time points.

Entry[a]	Polymer	Time (h)	Conversion (%)[b]	M_n *(Theo.)* (Da)[c]	M_n *(SEC)*	M_w *(SEC)*	M_P *(SEC)*	$Đ$[d]
1	PDMA macroCTA	-	**98**	10000	10100	15800	15400	**1.57**
2	P(DMA-*b*-DMA)	2	**13**	11300	11400	17300	16800	**1.51**
3		5	**36**	13600	14400	20000	18900	**1.40**
4		12	**82**	18100	18800	24500	22900	**1.30**
5		27	**>99**	20100	20900	26700	24600	**1.28**

[a] Reaction was performed with a target DP of 100. The volume ratio of H_2O:DMF (4:1) to DMA was maintained at 4:1 for all entries. [b] Conversion was measured by ^{1}H NMR. [c] Theoretical M_n was calculated based on conversion and the target DP. [d] Molecular weight and dispersity values were determined by SEC.

Table S3: ^{1}H NMR and SEC data illustrating the polymerization of DMA with 3 equivalents of acid and various amounts of Eosin Y (EY).

Entry	[EY]	Time (h)	Conversion (%)	M_n *(Theo.)* (Da)	M_n *(SEC)*	M_w *(SEC)*	M_P *(SEC)*	*Đ*
1	0.005	2	**11**	1400	-	-	-	-
2		4	**17**	2000	-	-	-	-
3		24	**99**	10100	10800	12700	12400	**1.18**
4	0.02	2	**9**	1200	-	-	-	-
5		4	**11**	1400	-	-	-	-
6		19	**60**	6200	6100	7700	7700	**1.26**
7		44	**99**	10200	11000	13300	12900	**1.20**
8	0.04	2	**13**	1600	-	-	-	-
9		4	**14**	1700	-	-	-	-
10		21	**22**	2500	-	-	-	-

[a] Reactions were performed with a target DP of 100. The volume ratio of H_2O:DMF (4:1) to DMA was maintained at 4:1 for all entries. [b] Conversion was measured by ^{1}H NMR. [c] Theoretical M_n was calculated based on conversion and the target DP. [d] Molecular weight and dispersity values were determined by SEC.

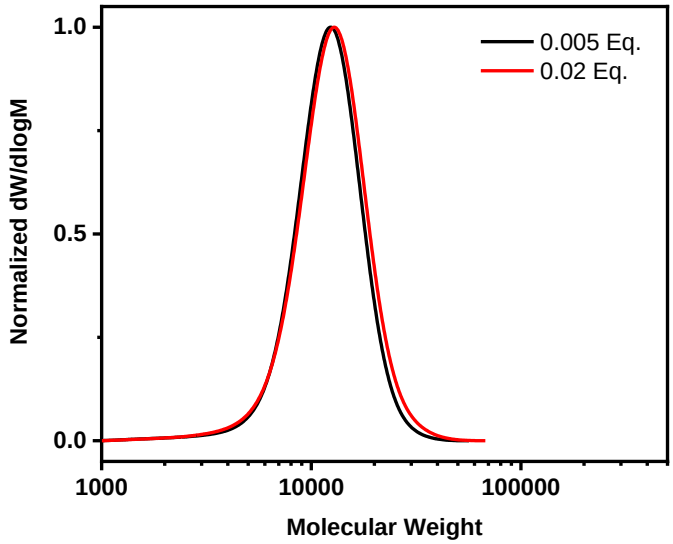


Figure S3: SEC data illustrating the polymerization of DMA with 3 equivalents of acid and various amounts of Eosin Y. This data corresponds to entries 3 and 7 in Table 2.

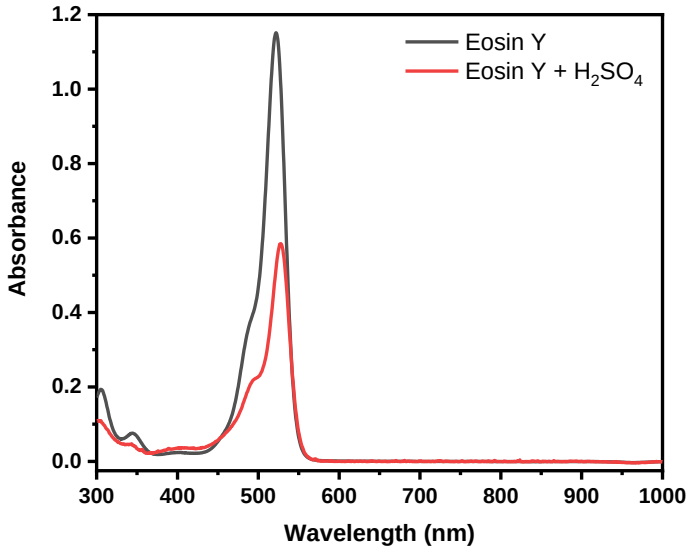


Figure S4: UV-Vis Spectrometry showing a reduced absorption of EY in the presence of sulphuric acid (150 equiv.)

Table S4: ^{1}H NMR and SEC data illustrating dispersity control for the polymerization of DMA with various amounts of acid.

Entry[a]	[H_2SO_4]	Conversion (%)[b]	$M_{n\ (Theo.)}$ (Da)[c]	$M_{n\ (SEC)}$	$M_{w\ (SEC)}$	$M_{P\ (SEC)}$	$Đ$[d]
1	0	**>99**	12700	13200	20900	19800	**1.58**
2	0.5	**97**	12300	13300	17900	17100	**1.34**
3	1.0	**97**	12300	13200	15900	15400	**1.20**
4	1.5	**97**	12300	12700	14900	14500	**1.18**
5	3.0	**97**	12300	12500	14800	14400	**1.18**

[a] Reactions were performed with a target DP of 125 and 0.005 equivalents of EY. The volume ratio of H_2O:DMF (4:1) to DMA was maintained at 4:1 for all entries. [b] Conversion was measured by ^{1}H NMR. [c] Theoretical M_n was calculated based on conversion and the target DP. [d] Molecular weight and dispersity values were determined by SEC.

Crosslinker Concentration Optimisation

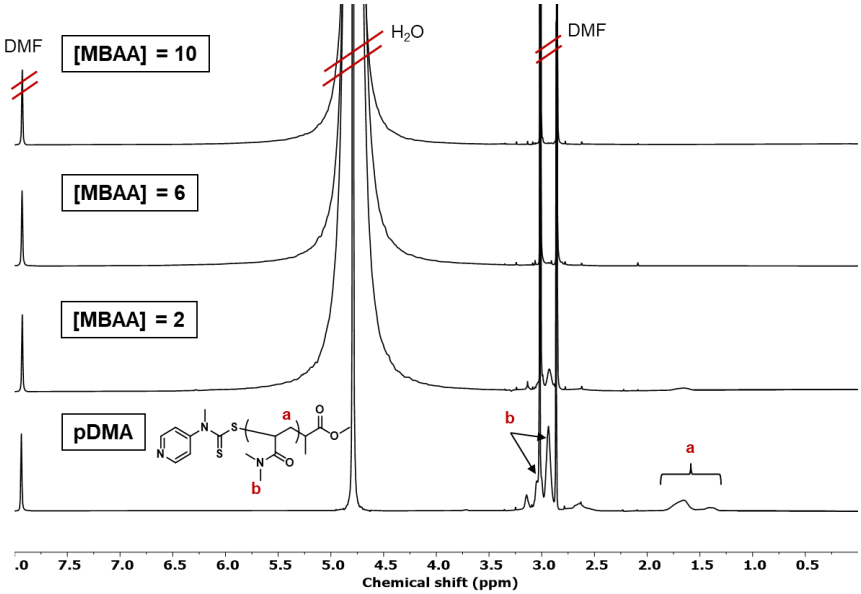
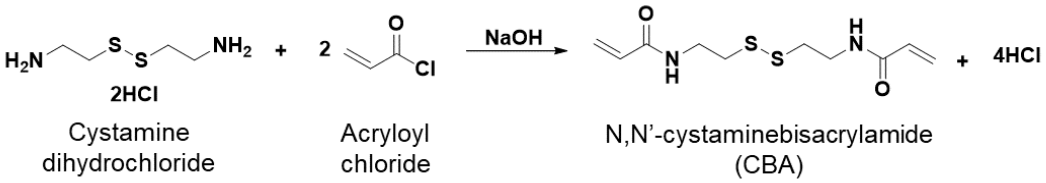


Figure S5: Full ^{1}H NMR spectra of the extracted solutions obtained from the gels prepared with various amounts of crosslinker (CL). These are compared to a linear homopolymer of PDMA. This data corresponds to Figure 2 and demonstrates that all monomer or crosslinker had reacted.



Scheme S1: The synthesis of the degradable crosslinker.

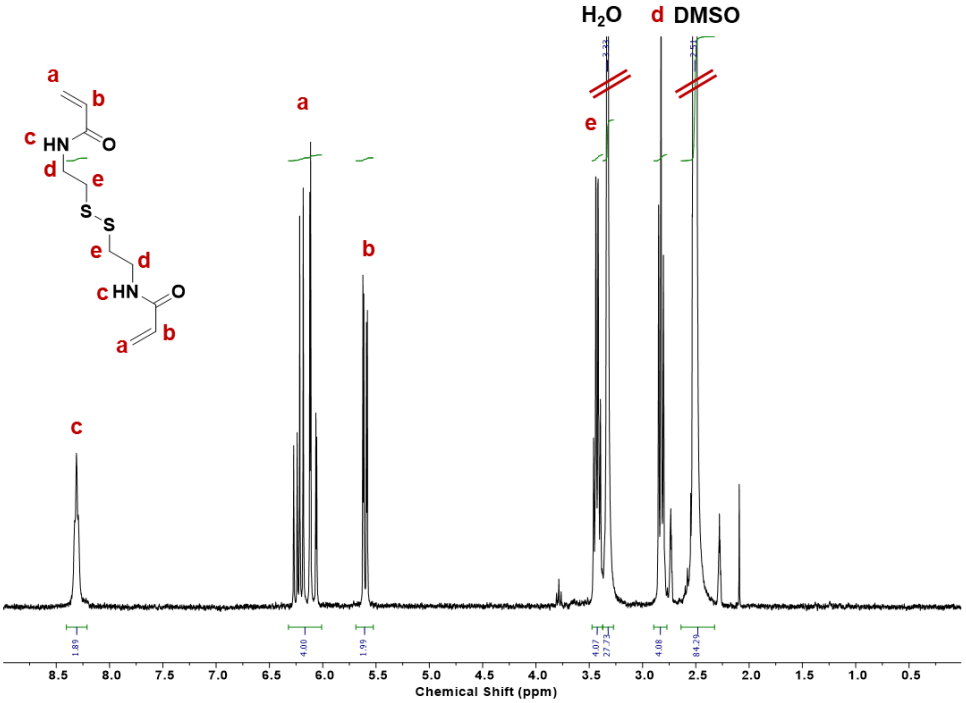


Figure S6: 1H NMR illustrating the synthesis of the degradable crosslinker (CBA)

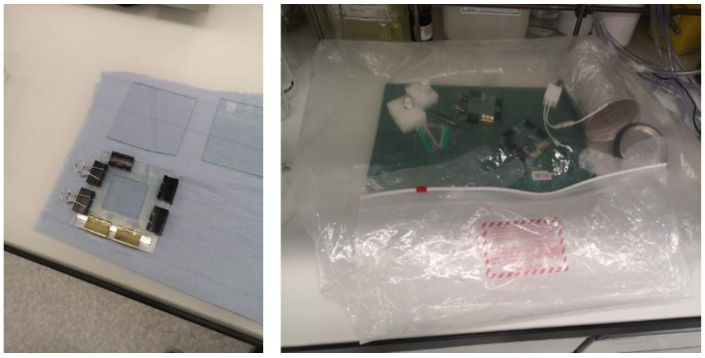


Figure S7: Photos illustrating the double-plated glass mould and the reaction set-up within the glove bag.

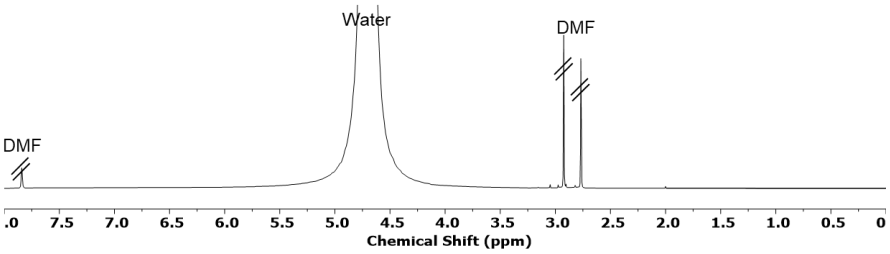
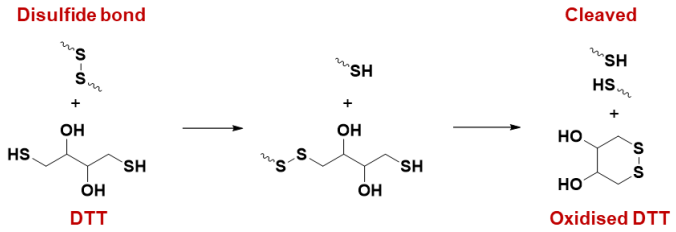


Figure S8: Full ^{1}H NMR spectra of the extracted solutions obtained from the high primary dispersity gel. 6 equivalents of crosslinker were used for the synthesis.

Figure S9: A photo of a purified gel, illustrating an absence of acid or photocatalyst.

Dispersity Controlled Network Degradation



Scheme S2: A scheme illustrating how DTT degrades a disulphide bond.

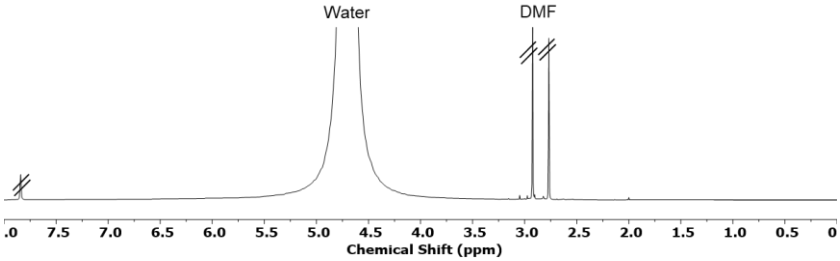


Figure S10: Full ^{1}H NMR spectra of the extracted solutions obtained from the low primary dispersity gel. 6 equivalents of crosslinker and 3 equivalents of acid were used for the synthesis.

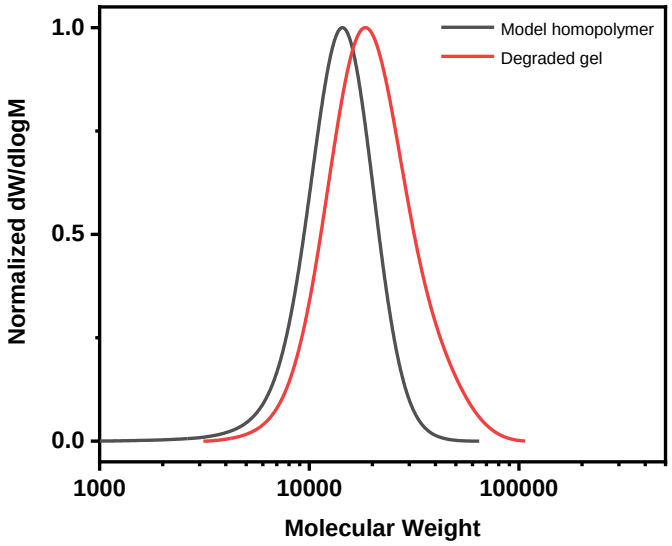


Figure S11: A comparison between a directly synthesised linear homopolymer (DP120, *Đ* = 1.20) and the corresponding linear polymer obtained after network degradation (DP120 +DP6 Crosslinker, *Đ* = 1.28).

Table S5: Data obtained from the degradation of high primary chain dispersity (*Đ* = 1.60) network polymer in glutathione. The target DP was 120.

Đ = 1.60, Target DP120

Day	Run 1	Run 2	Run 3	Average	Standard deviation
0	9.40	9.70	9.66	9.59	0.16
1	9.62	9.80	9.80	9.74	0.10
2	9.80	9.82	9.84	9.82	0.02
3	10.10	10.28	10.12	10.17	0.10
4	10.42	10.40	10.30	10.37	0.06
7	11.02	11.00	11.00	11.01	0.01
8	11.32	11.40	11.32	11.35	0.05
9	11.60	11.74	11.60	11.65	0.08
10	11.88	11.80	11.88	11.85	0.05
11	12.12	12.00	12.10	12.07	0.06
14	12.90	13.06	12.96	12.97	0.08
15	13.34	13.30	13.28	13.31	0.03
16	13.74	13.62	13.80	13.72	0.09

Table S6: Data obtained from the degradation of medium primary chain dispersity (*Đ* = 1.55) network polymer in glutathione. The target DP was 120.

Đ = 1.55, Target DP120

Day	Run 1	Run 2	Run 3	Average	Standard deviation
0	9.60	9.60	9.60	9.60	0.00
1	10.02	9.82	9.90	9.91	0.10
2	10.20	10.12	10.18	10.17	0.04
3	10.60	10.40	10.44	10.48	0.11
6	11.20	11.28	11.12	11.20	0.08
7	11.40	11.40	11.28	11.36	0.07
8	11.52	11.56	11.60	11.56	0.04
9	11.70	11.88	11.76	11.78	0.09
10	11.98	12.26	11.98	12.07	0.16
13	12.92	13.30	12.90	13.04	0.23
14	13.42	13.90	13.38	13.57	0.29

Table S7: Data obtained from the degradation of medium primary chain dispersity (*Đ* = 1.40) network polymer in glutathione. The target DP was 120.

Đ = 1.40, Target DP120

Day	Run 1	Run 2	Run 3	Average	Standard deviation
0	9.60	9.64	9.62	9.62	0.02
1	9.72	9.72	9.78	9.74	0.03
2	9.90	10.00	10.08	9.99	0.09
3	10.20	10.38	10.30	10.29	0.09
4	10.46	10.68	10.70	10.61	0.13
7	11.30	11.80	11.70	11.60	0.26
8	11.70	11.90	12.08	11.89	0.19
9	12.16	12.34	12.56	12.35	0.20
10	12.70	12.88	12.96	12.85	0.13
11	13.50	13.68	13.70	13.63	0.11

Table S8: Data obtained from the degradation of low primary chain dispersity (*Đ* = 1.28) network polymer in glutathione. The target DP was 120.

Đ = 1.28, Target DP120

Day	Run 1	Run 2	Run 3	Average	Standard deviation
0	9.38	9.50	9.24	9.37	0.13
3	10.26	10.42	10.40	10.36	0.09
4	10.60	10.70	10.80	10.70	0.10
5	10.98	11.10	11.02	11.03	0.06
6	11.24	11.60	11.32	11.39	0.19
7	11.48	12.02	11.80	11.77	0.27
10	13.20	13.41	13.60	13.41	0.20

Table S9: Data obtained from the degradation of low primary chain dispersity (*Đ* = 1.28) network polymer in glutathione. The target DP was 132.

Đ = 1.28, Target DP132

Day	Run 1	Run 2	Run 3	Average	Standard deviation
0	9.54	9.52	9.44	9.50	0.05
3	10.34	10.40	10.48	10.41	0.07
4	10.60	10.80	10.80	10.73	0.12
5	10.96	11.00	11.06	11.01	0.05
6	11.22	11.44	11.46	11.37	0.13
7	11.68	12.02	11.96	11.89	0.18
10	13.30	13.80	13.78	13.63	0.28

Table S10: Data obtained from the degradation of low primary chain dispersity (*Đ* = 1.28) network polymer in glutathione. The target DP was 140.

Đ = 1.28, Target DP140

Day	Run 1	Run 2	Run 3	Average	Standard deviation
0	9.54	9.52	9.56	9.54	0.02
3	10.30	10.40	10.50	10.40	0.10
4	10.62	10.70	10.80	10.71	0.09
5	10.94	10.94	11.02	10.97	0.05
6	11.12	11.42	11.56	11.37	0.22
7	11.56	11.96	12.04	11.85	0.26
10	12.94	13.50	13.60	13.35	0.36

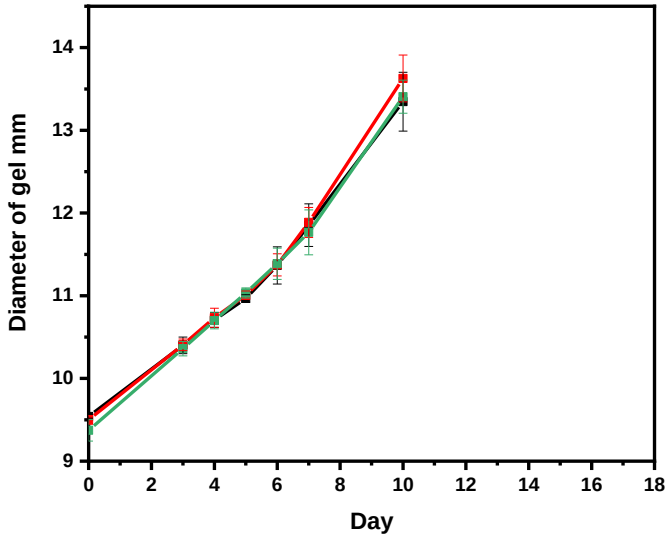


Figure S12: Line graphs showing the degradation of network polymers with consistent dispersity (*Đ* = 1.28) and various DPs (120 is green, 132 is black and 144 is red)

Table S11: Data obtained from the degradation of medium primary chain dispersity (*Đ* = 1.40) network polymer in glutathione. The target DP was 132.

Đ = 1.40, Target DP132

Day	Run 1	Run 2	Run 3	Average	Standard deviation
0	9.52	9.70	9.64	9.62	0.09
1	9.80	9.70	9.70	9.73	0.06
2	9.92	10.10	10.08	10.03	0.10
3	10.38	10.42	10.52	10.44	0.07
4	10.90	10.78	10.90	10.86	0.07
7	11.30	11.66	11.94	11.63	0.32
8	11.70	12.12	12.38	12.07	0.34
9	12.10	12.86	12.66	12.54	0.39
10	12.70	13.46	13.24	13.13	0.39
11	13.20	Dissolved	Dissolved		

Table S12: Data obtained from the degradation of medium primary chain dispersity (*Đ* = 1.40) network polymer in glutathione. The target DP was 140.

Đ = 1.40, Target DP140

Day	Run 1	Run 2	Run 3	Average	Standard deviation
0	9.52	9.46	9.80	9.59	0.18
1	9.76	9.84	9.84	9.81	0.05
2	9.84	10.08	10.04	9.99	0.13
3	10.50	10.72	10.62	10.61	0.11
4	10.60	10.80	10.86	10.75	0.14
7	11.62	11.98	11.96	11.85	0.20
8	12.14	12.20	12.34	12.23	0.10
9	12.42	12.96	12.88	12.75	0.29
10	13.32	13.98	13.90	13.73	0.36
11	13.4	Dissolved	Dissolved		

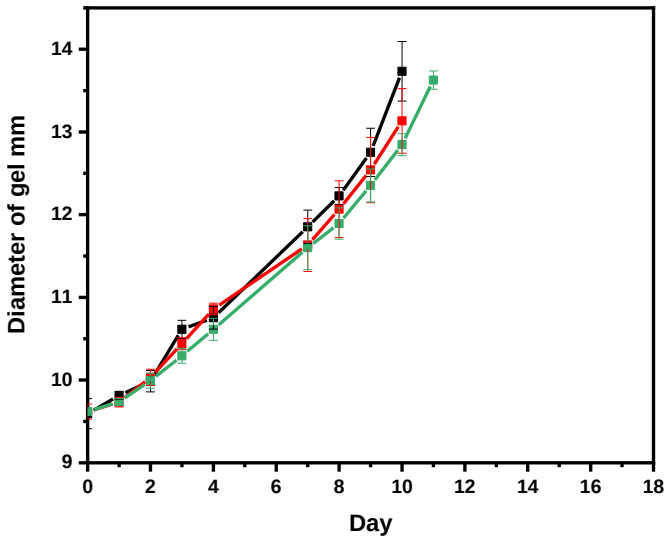


Figure S13: Line graphs showing the degradation of network polymers with consistent dispersity (*Đ* = 1.28) and various DPs (120 is green, 132 is red and 144 is black)

Table S13: Anova analysis comparing days 8, 9 and 10 of various primary chain dispersity networks (*Đ* = 1.28, 1.40, 1.55 and 1.60). All target DP of 120. P Values are less than 0.01, suggesting a negligible chance of this variation being due to chance.

ANOVA, Day 8

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.455467	2	0.227733333	17.13712375	0.003307	5.143253
Within Groups	0.079733	6	0.013288889			
Total	0.5352	8				

ANOVA, Day 9

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.845867	2	0.422933	23.04116	0.001528913	5.14325285
Within Groups	0.110133	6	0.018356			
Total	0.956	8				

ANOVA, Day 10

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4.603033	3	1.534344	71.25438596	4.11E-06	4.066181
Within Groups	0.172267	8	0.021533			
Total	4.7753	11				

Table S14: Anova analysis comparing days 6, 7 and 10 of various primary molecular weight networks of *Đ* = 1.28. P Values are high, suggesting a high chance of this variation being due to chance.

ANOVA, Day 6

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.000622	2	0.000311	0.008974	0.991079	5.143253
Within Groups	0.208	6	0.034667			
Total	0.208622	8				

ANOVA, Day 7

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.023022	2	0.011511	0.199846	0.824094	5.143253
Within Groups	0.3456	6	0.0576			
Total	0.368622	8				

ANOVA, Day 10

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.1304	2	0.0652	0.792545	0.494962	5.143253
Within Groups	0.4936	6	0.082267			
Total	0.624	8				

Table S15: Anova analysis comparing days 6, 7 and 10 of various primary molecular weight networks of *Đ* = 1.40. P Values are high, suggesting a high chance of this variation being due to chance.

ANOVA, Day 8

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.166756	2	0.083378	1.521492	0.292091	5.143253
Within Groups	0.3288	6	0.0548			
Total	0.495556	8				

ANOVA, Day 9

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.240356	2	0.120178	1.286394	0.342837	5.143253
Within Groups	0.560533	6	0.093422			
Total	0.800889	8				

ANOVA, Day 10

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*

Between Groups	1.228356	2	0.614178	6.1336	0.035435	5.143253
Within Groups	0.6008	6	0.100133			
Total	1.829156	8				

Gel Degradation Simulation with Datasets from SEC

3 datasets were considered: a high dispersity system, a low dispersity system, and a monodisperse system. The high and low dispersity data sets were obtained directly from SEC files, before being directly unweighted and rounded. This generated frequency tables with molecular weight vs. frequency. The data was then weighted based on an average of 6 crosslinkers per chain, in each case, to give a total of ~1000000 chains. The monodisperse data set was generated by setting the number of crosslinkers per chain as 6 and the frequency as 1000000.

Gel degradation was simulated using a simple Python program, whereby crosslinks in the sample are chosen at random and 'broken'. The frequency table was imported into Python and converted into a list where each individual chain was represented by an integer denoting its number of crosslinks. Degradation was simulated in an iterative manner as follows:

1. A random index in the list is chosen (one chain is selected)
2. If the integer value at this index is below 1, a new index is selected (if a chain has no crosslinks, another is chosen)
3. 1 is subtracted from the integer value at this index (one crosslink is broken)
4. A new index is chosen and the process iterates until all crosslinks are broken.

As the total number of crosslinks in the data decreases, a 'snapshot' of the distribution of crosslinks in the sample is taken at increments of 5%.

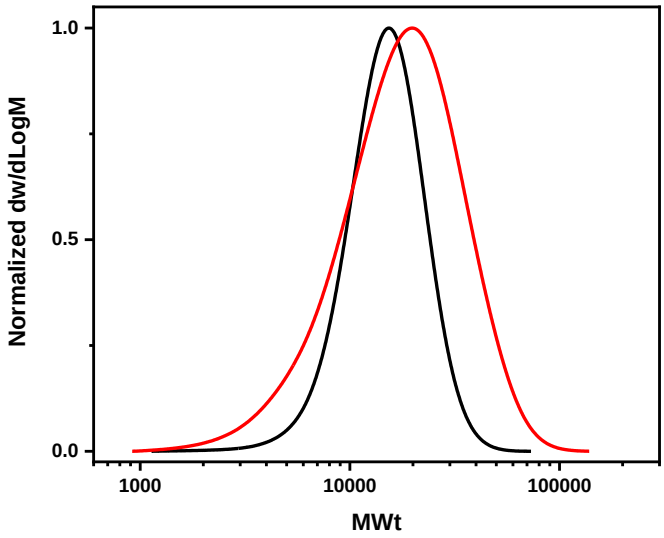


Figure S14: SEC traces of high and low dispersity PDMA (1.18 and 1.60) obtained from PET-RAFT polymerization that were subsequently used for the simulations.

Table S16: Data obtained from the simulated degradation of high dispersity PDMA. Rows in the table give the number of chains with more than x crosslinkers, for various degradation percentages.

	0%	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	55%	60%	65%	70%	75%	80%	85%	90%
≥1	999997	970871	937985	902088	863199	822049	778091	732683	684759	635448	584520	532034	477966	422303	365119	306492	247034	186154	124378
≥2	909948	870333	830439	789855	748036	705792	662871	619155	574866	529726	483748	437504	390647	342903	295039	246599	197707	148248	98503
≥3	780648	742642	704506	666535	628135	589540	550740	511623	472829	433725	394416	354901	315415	275887	236334	196993	157329	117745	78082
≥4	655306	620915	586419	551747	517646	483870	450541	417180	383993	350932	318295	285335	252803	220567	188478	156526	124706	93313	61868
≥5	539777	509404	479389	449693	420800	392130	364173	336119	308772	281687	254597	227743	201392	175379	149631	123961	98744	73796	48801
≥6	437909	412060	386821	362301	338145	314647	291527	268681	246335	224018	202323	180896	159844	138901	118305	98171	78236	58163	38592
≥7	350784	329756	309196	289326	269982	250787	232203	213974	195759	178071	160621	143478	126584	109967	93646	77688	61766	46131	30739
≥8	280320	263338	246725	230545	214847	199402	184263	169532	155100	140943	127046	113487	99969	87010	74177	61459	49000	36602	24633
≥9	223143	209009	195502	182562	170018	157643	145710	134100	122615	111355	100523	89685	79158	68840	58639	48592	38769	29170	19647
≥10	175239	164626	154263	144070	134206	124508	115048	105786	96617	87956	79353	71034	62736	54487	46417	38546	30806	23214	15682
≥11	139558	130745	122381	114251	106400	98683	91077	83698	76633	69677	62857	56195	49623	43227	36844	30607	24480	18491	12479
≥12	109862	103083	96424	89994	83920	77845	71851	66215	60597	55111	49737	44590	39354	34284	29329	24390	19556	14737	10021
≥13	86856	81388	76186	71206	66401	61674	57055	52397	47940	43644	39396	35325	31306	27337	23447	19566	15602	11805	8031
≥14	68338	64263	60355	56414	52543	48861	45139	41568	38112	34687	31415	28205	25018	21881	18711	15535	12410	9462	6393
≥15	54479	51201	48114	44951	41843	38921	36017	33190	30414	27733	25137	22574	19961	17482	14933	12464	10005	7515	5127
≥16	43507	40793	38198	35716	33332	31035	28723	26478	24345	22243	20077	17940	15925	13964	11908	9962	7934	5978	4022
≥17	34268	32297	30333	28413	26520	24707	22900	21159	19376	17655	15948	14300	12734	11129	9517	7870	6343	4798	3138
≥18	27602	25943	24330	22789	21285	19752	18264	16818	15456	14089	12733	11426	10119	8789	7596	6315	4998	3783	2498
≥19	21972	20681	19402	18158	16930	15693	14550	13470	12369	11299	10203	9149	8107	7070	6067	5041	4005	2975	1994
≥20	17625	16534	15473	14463	13454	12536	11655	10826	9967	9078	8198	7340	6501	5686	4827	4001	3177	2372	1595
≥21	13977	13132	12333	11529	10767	10039	9343	8637	7925	7190	6544	5863	5166	4505	3806	3182	2535	1909	1293
≥22	11197	10549	9903	9293	8671	8077	7460	6907	6314	5749	5184	4634	4086	3545	3043	2532	2003	1524	1040
≥23	8870	8338	7896	7403	6924	6444	5965	5474	5017	4548	4068	3661	3231	2827	2411	2020	1624	1219	842
≥24	7121	6690	6289	5877	5472	5060	4682	4321	3987	3614	3264	2940	2601	2282	1954	1614	1292	991	675
≥25	5660	5310	4986	4656	4341	4016	3732	3452	3168	2907	2641	2360	2083	1787	1537	1295	1063	816	551
≥26	4452	4197	3969	3688	3444	3213	2957	2757	2547	2308	2087	1860	1632	1419	1231	1044	870	645	418
≥27	3564	3374	3159	2965	2748	2573	2379	2199	1998	1823	1649	1488	1315	1143	993	834	688	498	323
≥28	2827	2687	2520	2370	2211	2058	1904	1755	1590	1461	1328	1188	1052	925	785	663	544	406	272
≥29	2293	2157	2036	1898	1768	1634	1521	1395	1286	1165	1059	942	846	745	646	548	433	312	216
≥30	1845	1742	1635	1526	1406	1301	1205	1114	1030	934	860	758	683	602	518	436	332	246	170
≥31	1475	1386	1300	1214	1132	1051	981	895	818	736	662	606	544	478	425	345	259	192	129
≥32	1170	1110	1049	984	908	845	782	717	660	591	526	485	439	387	331	265	199	149	108
≥33	919	867	819	766	715	662	622	570	521	477	429	391	351	301	257	205	163	123	88
≥34	742	701	662	624	578	539	500	452	404	373	341	314	272	234	198	170	135	105	66
≥35	597	561	521	486	458	417	386	349	322	296	270	248	215	190	166	136	107	81	50
≥36	477	448	420	390	356	326	304	272	259	241	218	194	174	153	133	108	85	61	38
≥37	378	353	330	306	281	265	251	233	219	196	173	147	131	117	98	79	67	49	32
≥38	297	280	262	241	228	214	202	185	169	148	133	113	101	93	82	65	55	34	22
≥39	242	228	213	198	181	170	160	147	129	121	106	92	85	75	61	53	40	31	19
≥40	187	175	169	157	148	136	128	113	106	95	86	77	68	59	47	39	30	21	12
≥41	150	140	132	121	117	105	96	89	81	72	67	61	54	46	38	31	26	16	6
≥42	119	111	102	94	90	82	73	68	64	58	56	48	38	34	28	25	18	11	6
≥43	94	89	80	77	72	68	61	56	53	47	43	38	29	27	22	17	13	8	5
≥44	74	69	64	61	55	53	44	41	38	36	34	28	24	21	16	13	12	6	3
≥45	57	53	52	47	42	41	36	32	28	25	21	20	19	15	12	11	8	5	1
≥46	45	45	38	34	30	27	26	23	20	18	18	13	12	9	9	6	4	2	0
≥47	35	33	28	28	27	23	20	17	15	15	13	9	8	7	7	5	3	0	0
≥48	27	23	21	19	18	17	15	11	11	9	9	9	6	6	4	2	1	0	0
≥49	19	17	17	17	15	14	11	9	8	8	7	7	5	3	3	0	0	0	0
≥50	15	14	12	11	11	9	8	8	7	6	2	2	1	1	0	0	0	0	0
≥51	11	10	9	8	5	4	4	3	2	2	1	1	0	0	0	0	0	0	0
≥52	7	7	7	5	4	3	2	1	0	0	0	0	0	0	0	0	0	0	0
≥53	3	2	2	2	2	2	1	1	0	0	0	0	0	0	0	0	0	0	0

Table S18: Data obtained from the simulated degradation of low dispersity PDMA. Rows in the table give the number of chains with more than x crosslinkers, for various degradation percentages.

	0%	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	55%	60%	65%	70%	75%	80%	85%	90%
≥1	999991	993288	983391	969854	952185	930271	903701	872648	836778	796298	750407	700012	644401	584145	518672	447972	371716	289599	201588
≥2	982796	966454	945436	919786	889523	855156	817149	775239	730196	681878	630652	577005	520679	461944	401350	338677	274128	208286	140164
≥3	936261	904499	868748	829792	787908	743191	696997	649343	599978	550050	499493	448345	397340	346105	294844	244028	193486	143469	94103
≥4	838502	792968	746301	698587	650688	602919	555623	508730	462744	417254	373280	330005	287634	246270	206532	168429	131116	95556	61440
≥5	690055	640372	591818	544542	499147	455526	413792	373611	335288	298484	263492	230075	198354	168085	139183	111796	86105	61692	39195
≥6	522440	477568	435312	395585	358417	323623	290625	259630	230778	203739	178077	154010	131396	110417	90759	72186	55140	39379	24870
≥7	367989	333243	300919	271393	243903	218539	194755	172873	152458	133501	116277	99954	84853	70933	58052	45779	34906	24630	15275
≥8	248210	223026	200090	179158	160043	142617	126514	111781	98221	85698	74144	63511	53744	44734	36278	28585	21551	15170	9482
≥9	161821	144589	129054	114977	102303	90692	80257	70615	61861	53839	46381	39629	33396	27745	22479	17676	13273	9304	5836
≥10	100808	90351	80721	71930	63872	56680	49978	44054	38570	33564	28768	24522	20671	17083	13828	10785	8087	5685	3562
≥11	63719	56727	50442	44874	39792	35152	30976	27171	23686	20465	17568	14977	12639	10419	8381	6608	5031	3539	2237
≥12	38977	34615	30916	27477	24308	21462	18844	16467	14335	12405	10707	9144	7706	6337	5164	4089	3116	2170	1389
≥13	23888	21199	18797	16696	14786	13078	11509	10078	8779	7666	6611	5568	4687	3886	3139	2506	1912	1329	855
≥14	14420	12887	11445	10103	8989	7940	6966	6136	5347	4683	4040	3441	2922	2433	1997	1591	1187	852	540
≥15	8920	7921	7045	6246	5577	4931	4323	3823	3333	2897	2496	2151	1803	1530	1249	986	740	524	329
≥16	5524	4885	4332	3859	3423	3042	2686	2384	2076	1835	1604	1371	1168	974	781	628	462	327	190
≥17	3318	2971	2684	2389	2129	1905	1706	1512	1324	1134	978	843	722	609	498	399	283	194	110
≥18	2088	1859	1679	1495	1353	1192	1061	922	807	693	609	520	450	384	310	246	171	111	56
≥19	1282	1145	1013	918	829	751	664	580	508	447	391	335	288	243	194	134	85	57	36
≥20	799	716	636	569	496	444	406	356	319	274	234	198	165	132	103	66	45	38	23
≥21	484	433	382	337	300	266	245	220	189	156	133	112	90	70	54	42	33	23	14
≥22	299	270	237	217	194	164	147	133	115	101	83	64	54	42	31	25	17	10	6
≥23	179	167	142	127	113	106	92	80	62	52	47	37	25	21	16	12	8	4	0
≥24	107	96	80	66	62	57	47	41	32	28	22	18	12	8	5	5	2	2	0
≥25	62	54	44	39	35	28	23	16	12	7	4	3	1	1	1	0	0	0	0
≥26	34	26	22	22	17	12	9	4	3	2	2	0	0	0	0	0	0	0	0
≥27	18	15	10	8	5	4	4	2	1	0	0	0	0	0	0	0	0	0	0
≥28	8	6	4	4	3	2	1	1	0	0	0	0	0	0	0	0	0	0	0
≥29	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table S19: Data obtained from the simulated degradation of monodisperse PDMA. Rows in the table give the number of chains with more than x crosslinkers, for various degradation percentages.

	0%	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	55%	60%	65%	70%	75%	80%	85%	90%
≥1	1000000	1000000	999952	999647	998531	995626	989677	979369	963500	940761	910401	871685	823738	765747	696996	617653	526827	422143	303575
≥2	1000000	999984	999584	997671	992368	981591	963673	937172	902047	858169	806011	745759	678177	604337	525744	442833	355381	265958	175236
≥3	1000000	999694	996606	986615	965992	934053	890839	837135	775245	707223	634663	559508	484233	409687	337043	266524	200056	138691	83000
≥4	1000000	996365	976870	937152	879564	808851	729541	647495	565322	485664	410826	341488	278114	220896	170098	125611	87630	55826	29929
≥5	1000000	963049	878323	772776	662901	557441	461791	377408	304860	243120	191250	148050	112309	83165	59442	40728	26146	15282	7340
≥6	999999	740907	548664	406138	300643	222437	164478	121420	89025	65062	46848	33509	23428	16167	10676	6650	3959	2099	919