## **Supporting Information**

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

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### **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<sup>2</sup>).

<sup>1</sup>**H NMR** spectra were recorded on a Bruker DPX-300 spectrometer in deuterated chloroform (CDCl<sub>3</sub>). Chemical shifts are given in ppm downfield from tetramethylsilane referenced to residual CHCl<sub>3</sub> protons. Monomer conversions were determined via <sup>1</sup>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  $\mu$ m beadsize guard column (50 × 7.5 mm) followed by three KF-805L columns (300 × 8 mm, bead size: 10  $\mu$ m, 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<sup>6</sup> 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<sup>-1</sup> 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. <sup>1</sup>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  $\mu$ L, 0.86  $\mu$ L and 5.16  $\mu$ L) 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 <sup>1</sup>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  $\mu$ L, 0.86  $\mu$ L and 5.16  $\mu$ L) 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 <sup>1</sup>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 (%) =  $(W_s-W_d)/W_s \times 100$ , 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  $\mu$ L 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**

Entry <sup>[a]</sup>	[EY]	Time (h)	Conversion (%) <sup>[b]</sup>	М <sub>п (Theo.)</sub> (Da) <sup>[с]</sup>	<b>M</b> <sub>n (SEC)</sub>	M <sub>w (SEC)</sub>	<b>М<sub>Р (SEC)</sub></b>	$\boldsymbol{ ilde{ heta}}^{[d]}$
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

Table S1: <sup>1</sup>H NMR and SEC data illustrating the polymerization of DMA with various amounts of Eosin Y (EY).

<sup>[a]</sup> Reactions were performed with a target DP of 100. The volume ratio of H<sub>2</sub>O:DMF (4:1) to DMA was maintained at 4:1 for all entries. <sup>[b]</sup> Conversion was measured by <sup>1</sup>H NMR. <sup>[c]</sup> Theoretical *M<sub>n</sub>* was calculated based on conversion and the target DP. <sup>[d]</sup> 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**: <sup>1</sup>H NMR and SEC data illustrating the chain extension of PDMA with DMA at various time points.

Entry <sup>[a]</sup>	Polymer	Time (h)	Conversion (%) <sup>[b]</sup>	<i>М</i> <sub>n</sub> (Theo.) (Da) <sup>[С]</sup>	M <sub>n</sub> (SEC)	M <sub>w</sub> (sec)	<b>M</b> <sub>P</sub> (SEC)	Đ <sup>[d]</sup>
1	PDMA macroCTA	-	98	10000	10100	15800	15400	1.57
2		2	13	11300	11400	17300	16800	1.51
3	P(DMA- <i>b</i> -	5	36	13600	14400	20000	18900	1.40
4	DMA)	12	82	18100	18800	24500	22900	1.30
5		27	>99	20100	20900	26700	24600	1.28

<sup>[a]</sup> Reaction was performed with a target DP of 100. The volume ratio of H<sub>2</sub>O:DMF (4:1) to DMA was maintained at 4:1 for all entries. <sup>[b]</sup> Conversion was measured by <sup>1</sup>H NMR. <sup>[c]</sup> Theoretical *M<sub>n</sub>* was calculated based on conversion and the target DP. <sup>[d]</sup> Molecular weight and dispersity values were determined by SEC.

Entry	[EY]	Time (h)	Conversion (%)	<i>М</i> <sub>n</sub> <sup>(Theo.)</sup> (Da)	M <sub>n</sub> (SEC)	M <sub>w</sub> (SEC)	M <sub>P</sub> (SEC)	Ð
1		2	11	1400	-	-	-	-
2	0.005	4	17	2000	-	-	-	-
3		24	99	10100	10800	12700	12400	1.18
4		2	9	1200	-	-	-	-
5	0.02	4	11	1400	-	-	-	-
6		19	60	6200	6100	7700	7700	1.26
7		44	99	10200	11000	13300	12900	1.20
8		2	13	1600	-	-	-	-
9	0.04	4	14	1700	-	-	-	-
10		21	22	2500	-	-	-	-

**Table S3**: <sup>1</sup>H NMR and SEC data illustrating the polymerization of DMA with 3 equivalents of acid and various amounts of Eosin Y (EY).

<sup>[a]</sup> Reactions were performed with a target DP of 100. The volume ratio of H<sub>2</sub>O:DMF (4:1) to DMA was maintained at 4:1 for all entries. <sup>[b]</sup> Conversion was measured by <sup>1</sup>H NMR. <sup>[c]</sup> Theoretical *M<sub>n</sub>* was calculated based on conversion and the target DP. <sup>[d]</sup> 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:	<sup>1</sup> H NMR	and SEC	data illustra	ating dispe	ersity cont	rol for the	e polyme	erization of	DMA	with	various
amounts o	f acid.										

Entry <sup>[a]</sup>	[H2SO4]	Conversion (%) <sup>[b]</sup>	М <sub>п (Theo.)</sub> (Da) <sup>[с]</sup>	M <sub>n (SEC)</sub>	M <sub>w (SEC)</sub>	<b>M</b> <sub>P</sub> (SEC)	<b>Đ</b> <sup>[d]</sup>
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

<sup>[a]</sup> Reactions were performed with a target DP of 125 and 0.005 equivalents of EY. The volume ratio of H<sub>2</sub>O:DMF (4:1) to DMA was maintained at 4:1 for all entries. <sup>[b]</sup> Conversion was measured by <sup>1</sup>H NMR. <sup>[c]</sup> Theoretical  $M_n$  was calculated based on conversion and the target DP. <sup>[d]</sup> Molecular weight and dispersity values were determined by SEC.

#### **Crosslinker Concentration Optimisation**



**Figure S5**: Full <sup>1</sup>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 <sup>1</sup>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 <sup>1</sup>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, D = 1.20) and the corresponding linear polymer obtained after network degradation (DP120 +DP6 Crosslinker, D = 1.28).

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

D = 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

*Đ* = 1.60, Target DP120

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

D = 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 (D = 1.40) network polymer in glutathione. The target DP was 120.

<i>Ð</i> = 1.40, <sup>-</sup>	Target DP120	1			
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 (D = 1.28) network polymer in glutathione. The target DP was 120.

<i>Ð</i> = 1.28, Ta	arget 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 (D = 1.28) network polymer in glutathione. The target DP was 132.

<i>Đ</i> = 1	.28, Target D	P132			
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 (D = 1.28) network polymer in glutathione. The target DP was 140.

<i>Đ</i> = 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 (D = 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 (D = 1.40) network polymer in glutathione. The target DP was 132.

<i>Ð</i> = 1.40, Ta	<i>D</i> = 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 (D = 1.40) network polymer in glutathione. The target DP was 140.

<i>Ð</i> = 1.40, T	<i>Đ</i> = 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 (D = 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 (D = 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	3 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 D = 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 D = 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
Determent Oregona						
Between Groups	0.240356	2	0.120178	1.286394	0.342837	5.143253
Within Groups	0.240356 0.560533	2 6	0.120178 0.093422	1.286394	0.342837	5.143253
Within Groups Total	0.240356 0.560533 0.800889	2 6 8	0.120178 0.093422	1.286394	0.342837	5.143253
Within Groups Total ANOVA, Day 10	0.240356 0.560533 0.800889	2 6 8	0.120178 0.093422	1.286394	0.342837	5.143253

Potwoon Croups	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.

11         99907         9700         970		0%	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	55%	60%	65%	70%	75%	80%	85%	90%
12         10000         1	≥1	999997	970871	937985	902088	863199	822049	778091	732683	684759	635448	584520	532034	477966	422303	365119	306492	247034	186154	124378
1         1	≥2	909948	870333	830439	789855	748036	705792	662871	619155	574866	529726	483748	437504	390647	342903	295039	246599	197707	148248	98503
i         68508         6804         6804         6804         6808         5808        5808        580	≥3	780648	742642	704506	666535	628135	589540	550740	511623	472829	433725	394416	354901	315415	275887	236334	196993	157329	117745	78082
b         59877         59848         69878         5988         5988        5988         598	≥4	655306	620915	586419	551747	517646	483870	450541	417180	383993	350932	318295	285335	252803	220567	188478	156526	124706	93313	61868
int         47300         4700         4900         4900         1000 <th< td=""><td>≥5</td><td>539777</td><td>509404</td><td>479389</td><td>449693</td><td>420800</td><td>392130</td><td>364173</td><td>336119</td><td>308772</td><td>281687</td><td>254597</td><td>227743</td><td>201392</td><td>175379</td><td>149631</td><td>123961</td><td>98744</td><td>73796</td><td>48801</td></th<>	≥5	539777	509404	479389	449693	420800	392130	364173	336119	308772	281687	254597	227743	201392	175379	149631	123961	98744	73796	48801
17         3078         5078         5	26	437909	412060	386821	362301	338145	314647	291527	268681	246335	224018	202323	180896	159844	138901	118305	98171	78236	58163	38592
bit         20202         20203         40202         20202         12522         11560         1	≥7	350784	329756	309196	289326	269982	250787	232203	213974	195759	178071	160621	143478	126584	109967	93646	77688	61766	46131	30739
bit         22110         00000         16500         16700         1	≥8	280320	263338	246725	230545	214847	199402	184263	169532	155100	140943	127046	113487	99969	87010	74177	61459	49000	36602	24633
int         int <td>≥9</td> <td>223143</td> <td>209009</td> <td>195502</td> <td>182562</td> <td>170018</td> <td>157643</td> <td>145710</td> <td>134100</td> <td>122615</td> <td>111355</td> <td>100523</td> <td>89685</td> <td>79158</td> <td>68840</td> <td>58639</td> <td>48592</td> <td>38769</td> <td>29170</td> <td>19647</td>	≥9	223143	209009	195502	182562	170018	157643	145710	134100	122615	111355	100523	89685	79158	68840	58639	48592	38769	29170	19647
11         19868         10708         6870         6770         6870         6770         6870         6770        6770        6	≥10	175239	164626	154263	144070	134206	124508	115048	105786	96617	87956	79353	71034	62736	54487	46417	38546	30806	23214	15682
11         10882         10884         1888         7884         7884         7885         7895        7895        7	≥11	139558	130745	122381	114251	106400	98683	91077	83698	76633	69677	62857	56195	49623	43227	36844	30607	24480	18491	12479
11         8885         8186         7136         7237         2347         1686         1692         1695         8333         8335         8735         2345         1245         1	≥12	109862	103083	96424	89994	83920	77845	71851	66215	60597	55111	49737	44590	39354	34284	29329	24390	19556	14737	10021
int         B333         B436         B530         4168         3912         3469         2733         2734         2734         180         1744         1803         1404         000         7516           1760         4070         0730         3819         5776         3322         3105         2107         2733         2130         1740         1224         1108         1962         7848         673         7848         784         785         7848         7850         1744         1129         1750         1750         1751         1750         1751         1750         1751         1750         1751         1750         1751         1750         1751 <td>≥13</td> <td>86856</td> <td>81388</td> <td>76186</td> <td>71206</td> <td>66401</td> <td>61674</td> <td>57055</td> <td>52397</td> <td>47940</td> <td>43644</td> <td>39396</td> <td>35325</td> <td>31306</td> <td>27337</td> <td>23447</td> <td>19566</td> <td>15602</td> <td>11805</td> <td>8031</td>	≥13	86856	81388	76186	71206	66401	61674	57055	52397	47940	43644	39396	35325	31306	27337	23447	19566	15602	11805	8031
bit         54/79         51/70         48/74         48/74         48/74         48/74         48/74         48/74         48/74         48/74         48/74         48/74         48/74         48/74         2274         2071         1794         18/25         18/84         18/85         18/8	≥14	68338	64263	60355	56414	52543	48861	45139	41568	38112	34687	31415	28205	25018	21881	18711	15535	12410	9462	6393
infe       4307       4308       3238       9319       3332       9310       3273       2473       2139       2307       1780       1682       1984       1984       1984       1984       1987       9784       6781	≥15	54479	51201	48114	44951	41843	38921	36017	33190	30414	27733	25137	22574	19961	17482	14933	12464	10005	7515	5127
111         34288         2294         2333         2841         2820         24107         21200         2115         1153         1546         1123         1123         1173         9717         6831         4783         2488           219         21972         20641         14302         1153 <t< td=""><td>≥16</td><td>43507</td><td>40793</td><td>38198</td><td>35716</td><td>33332</td><td>31035</td><td>28723</td><td>26478</td><td>24345</td><td>22243</td><td>20077</td><td>17940</td><td>15925</td><td>13964</td><td>11908</td><td>9962</td><td>7934</td><td>5978</td><td>4022</td></t<>	≥16	43507	40793	38198	35716	33332	31035	28723	26478	24345	22243	20077	17940	15925	13964	11908	9962	7934	5978	4022
11         27002         2681         1942         1972         1824         1946         1949         1723         1142         1014         1979         1975         6754         4750         2773         1942           17025         1654         15473         1533         1533         1533         1535         1656         466         566         566         465         303         312         225         190         123           1717         1715         1733         1767         1070         607         614         576         454         466         356         356         352         220         1	≥17	34268	32297	30333	28413	26520	24707	22900	21159	19376	17655	15948	14300	12734	11129	9517	7870	6343	4798	3138
110         1107         1108         11082         11083         11084         11020         11020         11020         11020         11070         10707         1070         10707         1070         1070         10707         1070         1070         10707         1070         1070         10707         1070         1070         1070         1070         1070         1070     <	≥18	27602	25943	24330	22789	21285	19752	18264	16818	15456	14089	12733	11426	10119	8789	7596	6315	4998	3783	2498
120         17825         1683         15473         11448         1238         1125         11057         1313         1233         1123         1123         1123         1123         1123         1123         1123         1123         1123         1123         1117         1044         903         8238         8071         8071         6314         6514         6454         6454         5464         5454         3232         2203         1524         1107           224         8701         6838         9667         6281         6314         624         510         4684         344         324         327         218         127         218         1444         122         914         128         1413         128         1414         122         914         4164         323         227         218         453         328         2067         1800         1825         1413         928         544         466         323         123         1414         120         918         125         148         1315         1414         120         918         123         1416         124         124         124         124         124         124         124	≥19	21972	20681	19402	18158	16930	15693	14550	13470	12369	11299	10203	9149	8107	7070	6067	5041	4005	2975	1994
221         1997         1938         1233         1123	≥20	17625	16534	15473	14463	13454	12536	11655	10826	9967	9078	8198	7340	6501	5686	4827	4001	3177	2372	1595
11197         10140         9030         6271         677         740         6740         5740         5740         4534         4056         3541         2201         1220         1620         1220         1620         1220         1620         1220         1620         1220         1620         1620         1620         2827         2861         2221         1660         6286         4341         4310         2877         2370         2361         3160         2861         2221         1651         1632         1614         1231         1646         4314           228         560         5310         4886         4841         213         2977         2547         2306         2081         1480         1313         1434         688         486         327           228         2827         2867         3570         2570         1261         1461         1328         1188         1032         144         468         337         345         345         232         246         745         643         433         345         345         345         345         345         345         345         345         345         345         345         345	≥21	13977	13132	12333	11529	10767	10039	9343	8637	7925	7190	6544	5863	5166	4505	3806	3182	2535	1909	1293
b23         8870         8830         7898         7493         6024         5444         5965         5474         5070         4548         4089         3881         3231         2827         2411         2000         1624         121         6400         575           225         5660         5510         4886         4656         4314         4018         3732         3452         3187         2500         2681         1231         1031         1231         1034         663         544         566           226         4457         2500         2270         2214         2372         2379         2179         1366         1680         1518         1435         143         662         546         433         312         216           223         2157         2364         1530         1245         1141         1336         126         1660         158         662         546         433         322         246         170           230         1497         1330         1562         158         456         459         357         353         352         150         451         450         451         450         451         450	≥22	11197	10549	9903	9293	8671	8077	7460	6907	6314	5749	5184	4634	4086	3545	3043	2532	2003	1524	1040
AA         PA         BAP         SA/A	≥23	8870	8338	7896	7403	6924	6444	5965	5474	5017	4548	4068	3661	3231	2827	2411	2020	1624	1219	842
bed         bed <td>224</td> <td>7121</td> <td>6690</td> <td>6289</td> <td>58/7</td> <td>54/2</td> <td>5060</td> <td>4682</td> <td>4321</td> <td>3987</td> <td>3614</td> <td>3264</td> <td>2940</td> <td>2601</td> <td>2282</td> <td>1954</td> <td>1614</td> <td>1292</td> <td>991</td> <td>6/5</td>	224	7121	6690	6289	58/7	54/2	5060	4682	4321	3987	3614	3264	2940	2601	2282	1954	1614	1292	991	6/5
4482         4487         4487         3568         3608         273         253         273         2508         2508         1632         1632         1639         1632         1639         1632         1639         1634         670         670         683         480         3774           228         2827         2667         2520         2370         2211         2026         1049         1755         1165         1135         1143         633         634         644         406         2772           228         2157         2261         1026         1146         1032         1465         1086         646         646         643         433         32         216           1845         1742         1630         124         1326         660         544         478         425         436         322         226         120           233         919         667         661         662         570         521         477         426         436         437         331         265         153         146         133         131         135         136         136         107         135         148         133 <t< td=""><td>≤25 &gt;00</td><td>5660</td><td>5310</td><td>4900</td><td>4050</td><td>4341</td><td>4016</td><td>3732</td><td>3452</td><td>3100</td><td>2907</td><td>2041</td><td>2360</td><td>2063</td><td>1/0/</td><td>1537</td><td>1295</td><td>1063</td><td>010</td><td>551</td></t<>	≤25 >00	5660	5310	4900	4050	4341	4016	3732	3452	3100	2907	2041	2360	2063	1/0/	1537	1295	1063	010	551
Lat         Lat <thlat< th=""> <thlat< th=""> <thlat< th=""></thlat<></thlat<></thlat<>	>27	3564	3374	3150	2065	2748	2573	2370	2100	1008	1823	1649	1488	1315	1143	003	834	688	408	323
223         2157         2036         1988         1768         1634         1521         1985         1185         1099         942         646         746         646         548         433         312         216           330         1144         11302         1146         1301         1205         1114         1030         944         860         758         633         602         518         436         332         246         1707           331         1477         1386         1000         1244         1012         051         652         670         534         439         433         342         246         170           339         987         591         672         777         660         591         526         439         439         331         265         199         140         108         108         108         108         108         108         141         174         130         133         105         661         53         105         661         53         105         661         53         40         131         113         101         93         62         65         54         43 <td< td=""><td>≥28</td><td>2827</td><td>2687</td><td>2520</td><td>2370</td><td>2211</td><td>2058</td><td>1904</td><td>1755</td><td>1590</td><td>1461</td><td>1328</td><td>1188</td><td>1052</td><td>925</td><td>785</td><td>663</td><td>544</td><td>406</td><td>272</td></td<>	≥28	2827	2687	2520	2370	2211	2058	1904	1755	1590	1461	1328	1188	1052	925	785	663	544	406	272
1846         1742         1635         1526         1466         1216         1144         103         934         860         768         663         662         518         436         332         246         170           131         1475         1360         1300         124         110         1049         984         908         681         626         666         449         345         345         249         149         100           333         919         687         819         766         715         682         622         570         521         477         429         381         361         301         257         205         163         153         667           587         567         561         521         682         620         570         521         473         311         314         316         316         130         163         16	≥29	2293	2157	2036	1898	1768	1634	1521	1395	1286	1165	1059	942	846	745	646	548	433	312	216
13.1         14.75         13.86         10.00         12.14         11.12         10.15         981         680         78         662         666         6.44         4.76         4.25         4.56         2.99         14.9         14.9           23.2         11170         1100         10.49         984         908         87         77         620         526         439         387         331         255         199         14.9         14.9           23.4         742         701         662         67.6         51         432         341         314         272         234         138         105         135         105         662         67.6         51         48.5         34.7         37.8         341         314         272         234         138         107         135         105         136         136         137         137         135         106         137         137         138         130         316         317         138         130         136         137         138         130         138         131         131         131         136         137         140         132         131         131         131	≥30	1845	1742	1635	1526	1406	1301	1205	1114	1030	934	860	758	683	602	518	436	332	246	170
1170         1110         1040         964         908         845         752         777         650         591         526         430         430         337         231         265         199         140         108           233         919         667         819         766         715         662         622         570         521         477         420         331         225         163 <td>≥31</td> <td>1475</td> <td>1386</td> <td>1300</td> <td>1214</td> <td>1132</td> <td>1051</td> <td>981</td> <td>895</td> <td>818</td> <td>736</td> <td>662</td> <td>606</td> <td>544</td> <td>478</td> <td>425</td> <td>345</td> <td>259</td> <td>192</td> <td>129</td>	≥31	1475	1386	1300	1214	1132	1051	981	895	818	736	662	606	544	478	425	345	259	192	129
333         919         867         819         766         715         662         622         670         621         477         429         331         331         331         237         236         153         123         861           234         742         701         662         624         539         561         521         486         446         339         349         322         266         270         248         275         190         166         133         106         661         561           238         477         484         420         390         356         304         272         226         270         248         174         163         103         108         67         49         222           288         297         280         282         241         202         185         132         147         148         133         101         69         65         34         222           288         297         230         221         140         132         161         161         161         161         161         161         161         161         161         161 <td< td=""><td>≥32</td><td>1170</td><td>1110</td><td>1049</td><td>984</td><td>908</td><td>845</td><td>782</td><td>717</td><td>660</td><td>591</td><td>526</td><td>485</td><td>439</td><td>387</td><td>331</td><td>265</td><td>199</td><td>149</td><td>108</td></td<>	≥32	1170	1110	1049	984	908	845	782	717	660	591	526	485	439	387	331	265	199	149	108
b24         742         701         662         624         576         500         452         440         373         341         341         272         234         188         170         135         105         666           555         567         551         521         486         470         386         304         222         226         20         245         100         166         138         107         13         37           378         330         300         366         281         262         212         230         17         147         131         117         98         79         67         49         327           378         378         230         262         214         228         213         130         131	≥33	919	867	819	766	715	662	622	570	521	477	429	391	351	301	257	205	163	123	88
bit         597         691         521         486         448         447         386         349         322         296         270         286         215         190         166         136         107         81         507           586         477         486         420         300         366         326         326         259         216         173         147         131         117         98         79         67         49         327           378         353         300         306         281         282         259         214         133         117         191         193         163         65         55         34         227           388         247         228         242         228         241         202         185         169         140         92         65         61         53         34         101         98         92         65         64         38         34         28         25         18         11         93         93         21         16         66         66         66         66         66         66         66         66         67         68	≥34	742	701	662	624	578	539	500	452	404	373	341	314	272	234	198	170	135	105	66
288         477         448         420         390         356         304         272         280         241         216         144         174         153         133         108         85         61         383           377         378         330         300         281         251         223         29         147         147         111         117         18         79         853         304         306         281         226         282         241         228         221         228         18         170         183         117         18         75         61         53         30         21         121           242         228         231         169         157         148         138         166         92         67         61         53         40         21         16         11         11         101         11         11         11         11         11         11         11         11         11         11         11         11         11         11         11         11         11         12         12         11         11         11         11         11         11	≥35	597	561	521	486	458	417	386	349	322	296	270	248	215	190	166	136	107	81	50
378       378       333       330       306       281       173       181       113       117       98       79       67       49       32         283       242       228       213       198       181       170       169       121       106       92       65       61       53       40       31       13         401       150       169       161       162       113       166       65       66       67       68       50       67       98       63       40       31       16       16       16       66       66       66       67       68       50       47       38       36       38       38       38       38       38       38       38       36       36       36       36       36       36       36       38       36       25       11       68       37       38       36       31       3	≥36	477	448	420	390	356	326	304	272	259	241	218	194	174	153	133	108	85	61	38
base         297         280         282         241         282         242         282         243         196         140         133         101         901         92         65         65         34         22           289         242         228         228         228         228         238         198         181         170         106         147         129         121         106         92         85         75         61         53         40         31         19           400         167         148         170         105         147         129         121         105         85         75         61         53         47         39         30         21         12           410         132         132         147         105         86         61         55         36         47         43         38         29         27         22         17         13         8         5           443         94         94         80         77         72         68         61         55         34         47         43         38         29         27         22         17 </td <td>≥37</td> <td>378</td> <td>353</td> <td>330</td> <td>306</td> <td>281</td> <td>265</td> <td>251</td> <td>233</td> <td>219</td> <td>196</td> <td>173</td> <td>147</td> <td>131</td> <td>117</td> <td>98</td> <td>79</td> <td>67</td> <td>49</td> <td>32</td>	≥37	378	353	330	306	281	265	251	233	219	196	173	147	131	117	98	79	67	49	32
S39       242       228       213       199       181       170       160       147       120       121       106       92       85       75       61       53       40       31       199         440       187       175       169       157       148       136       136       166       65       86       77       68       59       47       39       30       21       12         k11       150       140       132       121       117       105       66       89       66       48       38       34       28       25       16       11       66       53       47       43       38       24       24       12       13       8       5       53       47       43       38       24       24       12       13       8       5       53       47       43       38       24       24       21       16       13       12       6       38       34       28       24       21       13       48       5       11       8       5       13       14       13       28       24       24       24       24       24       24	≥38	297	280	262	241	228	214	202	185	169	148	133	113	101	93	82	65	55	34	22
Add       187       1175       169       157       143       128       113       106       165       166       167       168       50       47       39       30       21       127         441       150       140       132       121       117       105       66       86       72       67       61       54       46       38       34       28       25       18       11       66       61       56       53       47       43       38       24       28       25       18       11       66       53       34       38       28       24       21       16       13       12       6       3         244       74       69       64       61       55       53       44       11       38       36       34       28       21       16       13       12       6       3         245       57       53       52       47       42       41       36       32       28       21       10       13       12       14       18       3       22       21       16       13       12       6       3       3       0 <t< td=""><td>≥39</td><td>242</td><td>228</td><td>213</td><td>198</td><td>181</td><td>170</td><td>160</td><td>147</td><td>129</td><td>121</td><td>106</td><td>92</td><td>85</td><td>75</td><td>61</td><td>53</td><td>40</td><td>31</td><td>19</td></t<>	≥39	242	228	213	198	181	170	160	147	129	121	106	92	85	75	61	53	40	31	19
A41       150       140       122       121       117       110       46       80       81       62       61       54       64       54       64       54       64       58       56       48       38       31       20       16       1       6         842       191       111       102       94       90       82       73       68       64       65       66       48       38       28       22       17       13       8       5         844       74       69       64       61       55       53       44       41       38       38       24       21       16       13       12       6       3       34       5       14       14       38       36       24       24       21       16       13       12       6       3       3       20       13       14       12       14       8       5       1       14       12       14       18       17       15       11       11       9       13       9       8       7       7       5       3       0       0       0       0       0       0       0	≥40	187	175	169	157	148	136	128	113	106	95	86	77	68	59	47	39	30	21	12
ava:       119       111       102       94       80       61       56       50       90       50       50       50       50       20       20       20       10       11       60         43       94       80       80       77       72       68       61       55       53       47       43       38       29       27       22       17       13       8       5         b44       74       68       61       55       53       44       41       38       26       24       21       16       13       12       6       3         b45       57       53       52       47       42       41       36       32       28       24       21       16       13       12       6       3	241	150	140	132	121	117	105	96	89	81	72	67	61	54	46	38	31	26	16	6
basis       basis <th< td=""><td>&gt;42</td><td>04</td><td>90</td><td>102</td><td>94 77</td><td>90</td><td>62</td><td>73 61</td><td>60 EE</td><td>64 E2</td><td>30</td><td>42</td><td>40</td><td>20</td><td>34</td><td>20</td><td>20</td><td>10</td><td></td><td>6</td></th<>	>42	04	90	102	94 77	90	62	73 61	60 EE	64 E2	30	42	40	20	34	20	20	10		6
Arr       Br       Br <t< td=""><td>544</td><td>74</td><td>60</td><td>64</td><td>61</td><td>55</td><td>60 E2</td><td>44</td><td>41</td><td>29</td><td></td><td>43</td><td>20</td><td>2.5</td><td>21</td><td>16</td><td>12</td><td>13</td><td>6</td><td>3</td></t<>	544	74	60	64	61	55	60 E2	44	41	29		43	20	2.5	21	16	12	13	6	3
Add       A	>45	57	53	52	47	42	41	36	32	28	25	21	20	19	15	12	11	8	5	1
Air       Air       Air       Bit       Company       Company <thcompany< th="">       Company       <thcompany< <="" td=""><td>&gt;46</td><td>45</td><td>45</td><td>38</td><td>34</td><td>30</td><td>27</td><td>26</td><td>23</td><td>20</td><td>18</td><td>18</td><td>13</td><td>12</td><td>0</td><td>9</td><td>6</td><td>4</td><td>2</td><td>0</td></thcompany<></thcompany<>	>46	45	45	38	34	30	27	26	23	20	18	18	13	12	0	9	6	4	2	0
x48       2       21       19       18       17       17       17       15       11       11       19       9       9       6       6       4       2       1       0       0         x49       19       17       17       17       15       14       11       9       9       9       6       6       4       2       1       0 </td <td>≥47</td> <td>35</td> <td>33</td> <td>28</td> <td>28</td> <td>27</td> <td>23</td> <td>20</td> <td>17</td> <td>15</td> <td>15</td> <td>13</td> <td>9</td> <td>8</td> <td>7</td> <td>7</td> <td>5</td> <td>3</td> <td>0</td> <td>0</td>	≥47	35	33	28	28	27	23	20	17	15	15	13	9	8	7	7	5	3	0	0
x49       19       17       17       17       15       14       11       9       8       8       7       7       5       3       3       0       0       0       0         250       15       14       12       11       11       9       8       7       6       2       2       1       1       0	≥48	27	23	21	19	18	17	15	11	11	9	9	9	6	6	4	2	1	0	0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	≥49	19	17	17	17	15	14	11	9	8	8	7	7	5	3	3	0	0	0	0
251     11     10     9     8     5     4     4     3     2     2     1     1     0     0     0     0     0     0       252     7     7     7     5     4     3     2     1     0     0     0     0     0     0     0     0     0       253     3     2     2     1     1     0     0     0     0     0     0     0     0     0	≥50	15	14	12	11	11	9	8	8	7	6	2	2	1	1	0	0	0	0	0
352         7         7         7         5         4         3         2         1         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