

Supplemental Information:

Unraveling polymer structures with RAFT polymerization and Diels-Alder chemistry

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Table S1. Relevant experimental conditions for preparation of NG/SL structures.

Sample ^a	DP ^b	%DA-Xlink ^c	[NIPAM]		Conversion (%) ^d		R_h (nm)	
			Initial	Final	Before DA-Xlink	Final	Pre-HT	Post-HT
1 (◆)	100	1.67%	3.97	3.20	46	82	11	42
2 (▲)	100	5.00%	3.71	3.03	62	79	34	28
3 (●)	200	0.50%	6.46	5.39	46	83	15	19
4 (◆)	200	0.50%	6.46	5.39	64	69	17	20
5 (■)	200	1.25%	6.32	5.30	78	86	15	22
6 (●)	200	1.25%	6.14	4.56	75	86	23	26
7 (■)	200	2.50%	6.09	4.44	70	83	34	69
8 (▲)	200	2.50%	4.90	4.44	79	84	40	69
9 (●)	200	2.50%	5.76	3.91	74	85	32	64
10 (●)	200	2.50%	5.76	3.49	75	80	39	54
11 (■)	200	2.50%	6.09	5.13	60	80	35	30
12 (■)	200	2.50%	6.24	4.52	63	72	42	32
13 (●)	200	5.00%	5.67	4.84	74	79	51	35
14 (●)	200	5.00%	5.67	4.22	76	84	57	52
15 (▲)	300	1.67%	7.70	6.66	67	85	23	23
16 (●)	300	5.00%	6.93	5.41	80	87	99	86
17	200	0.00% ^e	6.56	5.13	72	76	14	18
18	200	0.00% ^f	6.56	5.29	47	63	10	14
19	200	0.00%	5.76	5.76	n.a.	65	7	10

^a Symbol description : conversion upon addition of **DA-xlink** - diamond (◆) $\Delta > 30$, triangle (▲) for $15 < \Delta < 30$, square (■) for $9 < \Delta < 15$, and circle (●) for $\Delta < 9$ – See section entitled “**Other effects on Inter vs. Intra-molecular crosslinking**” for more explanation of symbols; Color description : black for $p_x < 50$, blue for $50 \leq p_x < 68$ and red for $p_x > 68$, where p_x is the conversion at which **DA-Xlink** was added. ^b DP was determined by the initial ratio of monomer to CTA. ^c %DA-xlink is relative the [NIPAM]. ^d Conversion determined by ¹H NMR. ^e 2.5% ethylene glycol dimethacrylate crosslinker was added; ^f 1.25% divinyl benzene crosslinker was added.

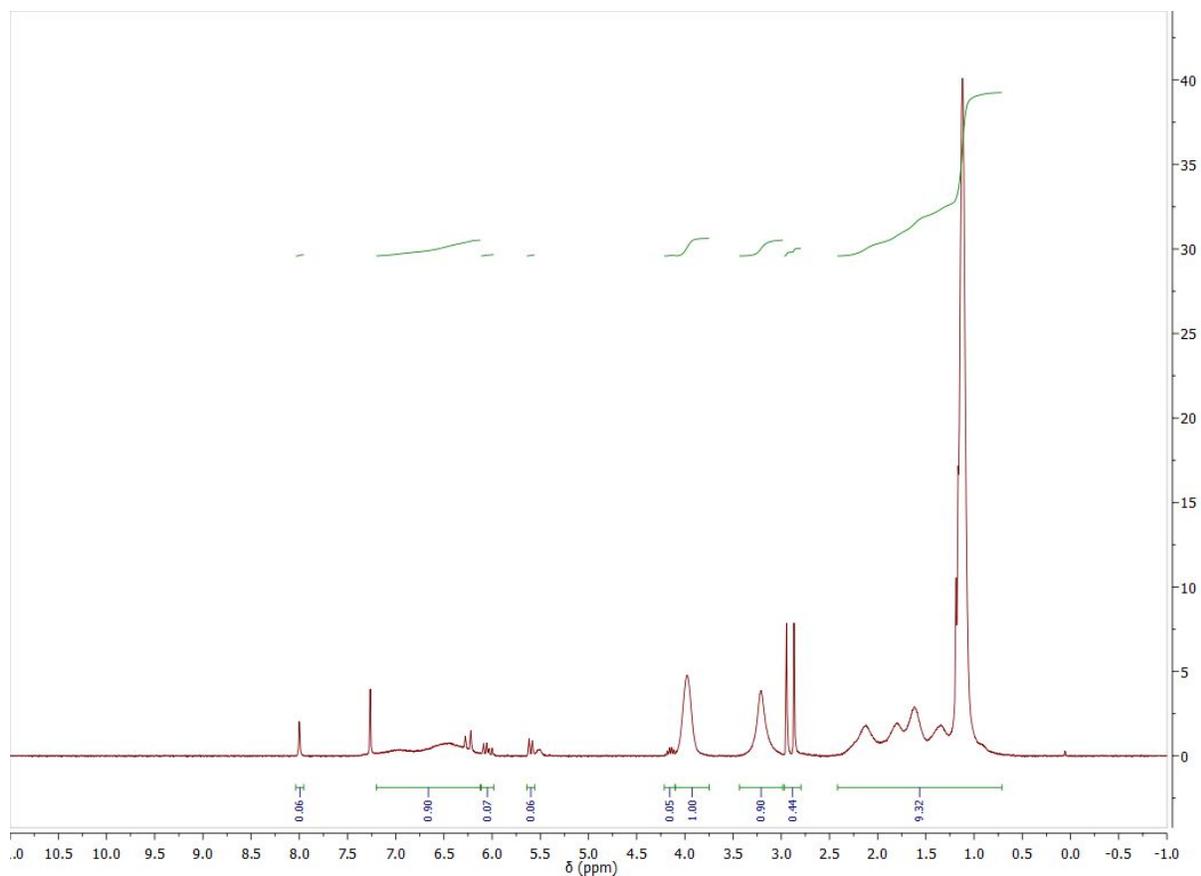


Figure S1. ¹H NMR analysis of **3** (Table S1) after purification. Residual vinylic signals can be seen from ~5.5 – 6.25 ppm.

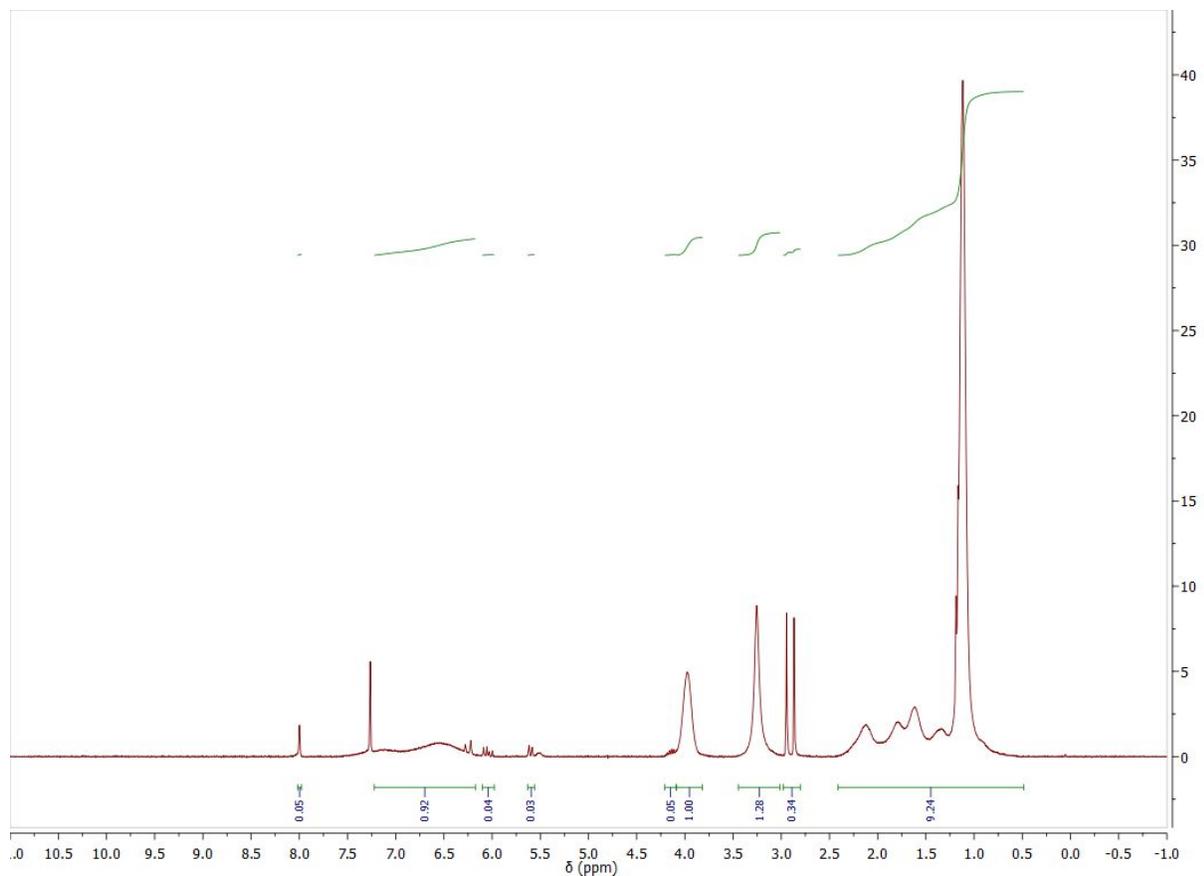


Figure S2. ^1H NMR analysis of **4** (Table 1) after purification. Residual vinylic signals can be seen from $\sim 5.5 - 6.25$ ppm.

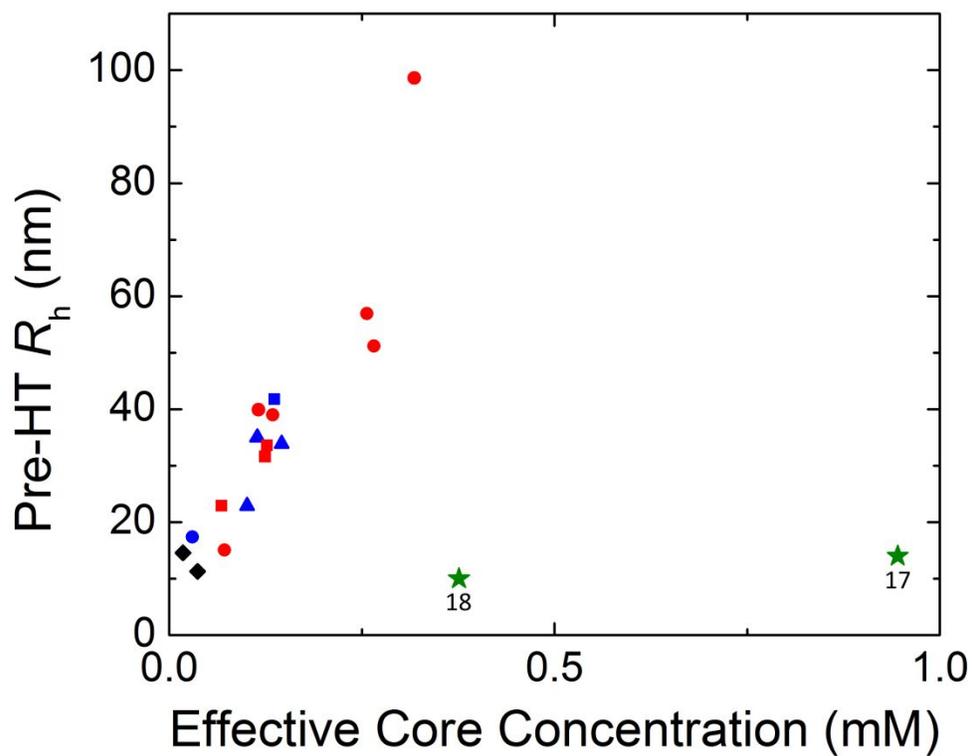


Figure S3. Comparison of R_h (Pre-HT) against the effective kinetic arm length. Symbols and numbers reference entries in **Table S1**. Samples **17** and **18** are control experiments that do not contain **DA-Xlink** and hence do not follow the same trend as samples 1-16.

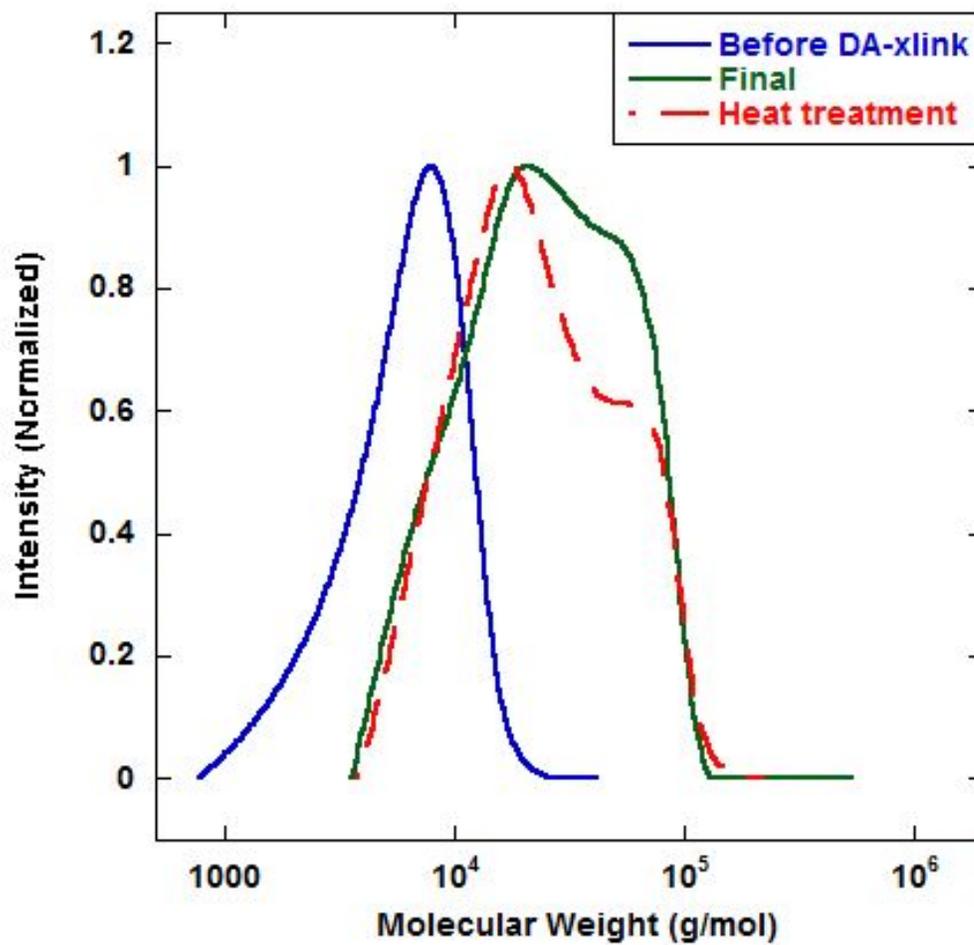


Figure S4. GPC analysis of Sample 1 referencing Table S1.

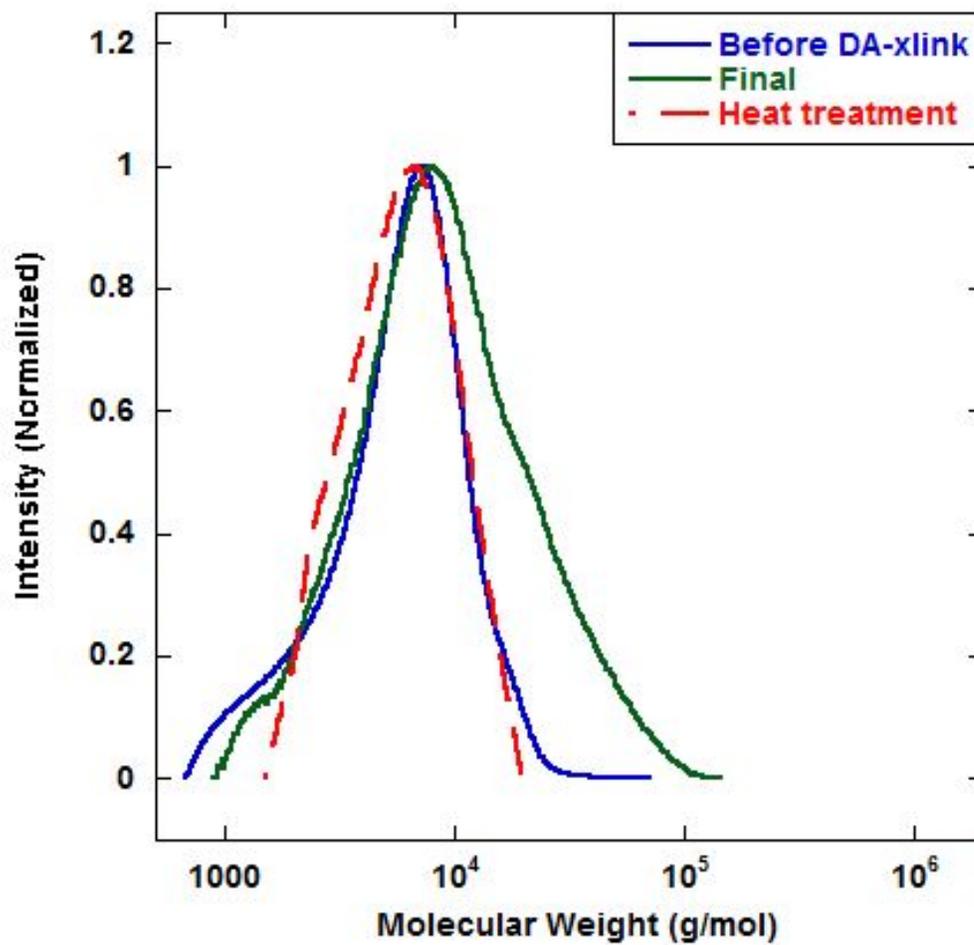


Figure S5. GPC analysis of Sample 2 referencing Table S1.

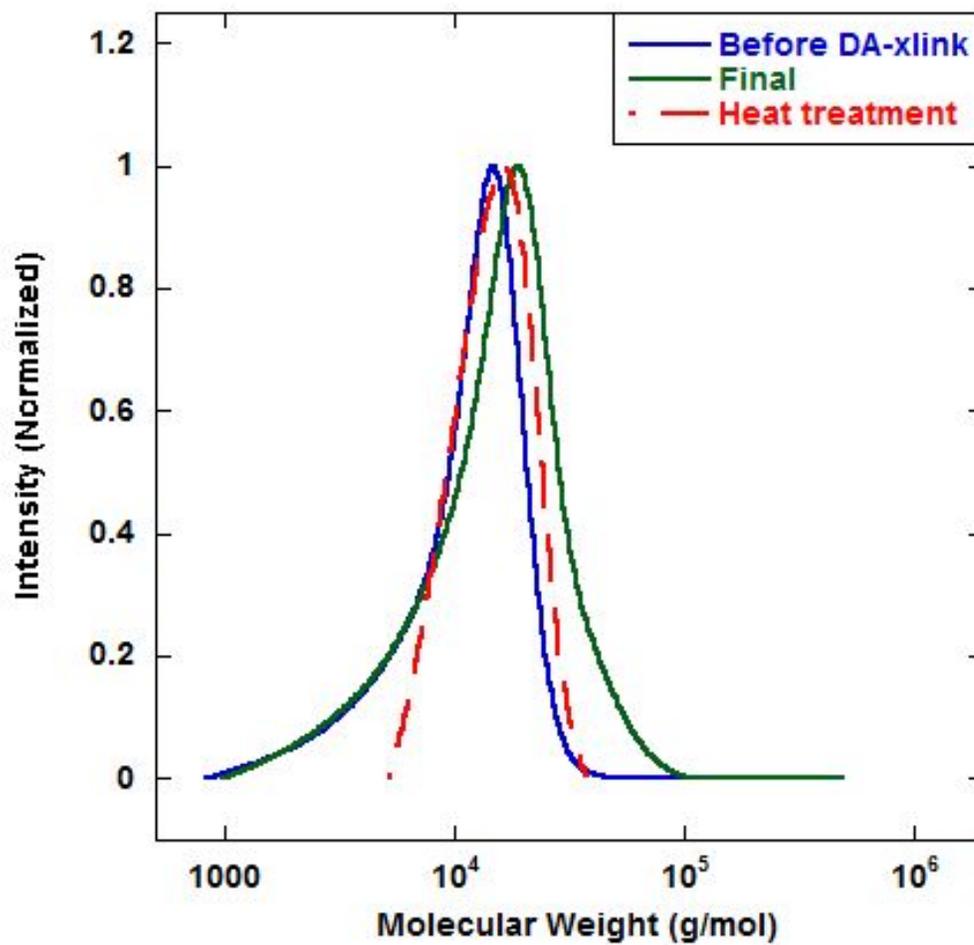


Figure S6. GPC analysis of Sample 3 referencing Table S1.

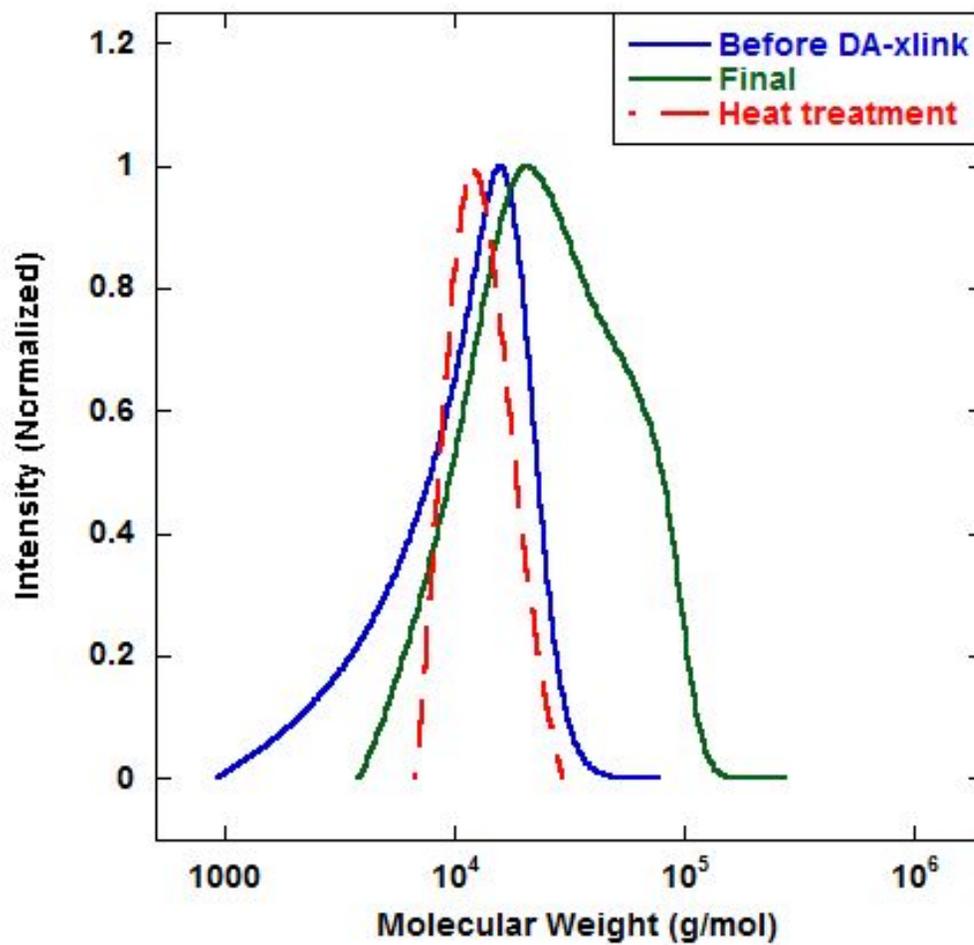


Figure S7. GPC analysis of Sample 4 referencing Table S1.

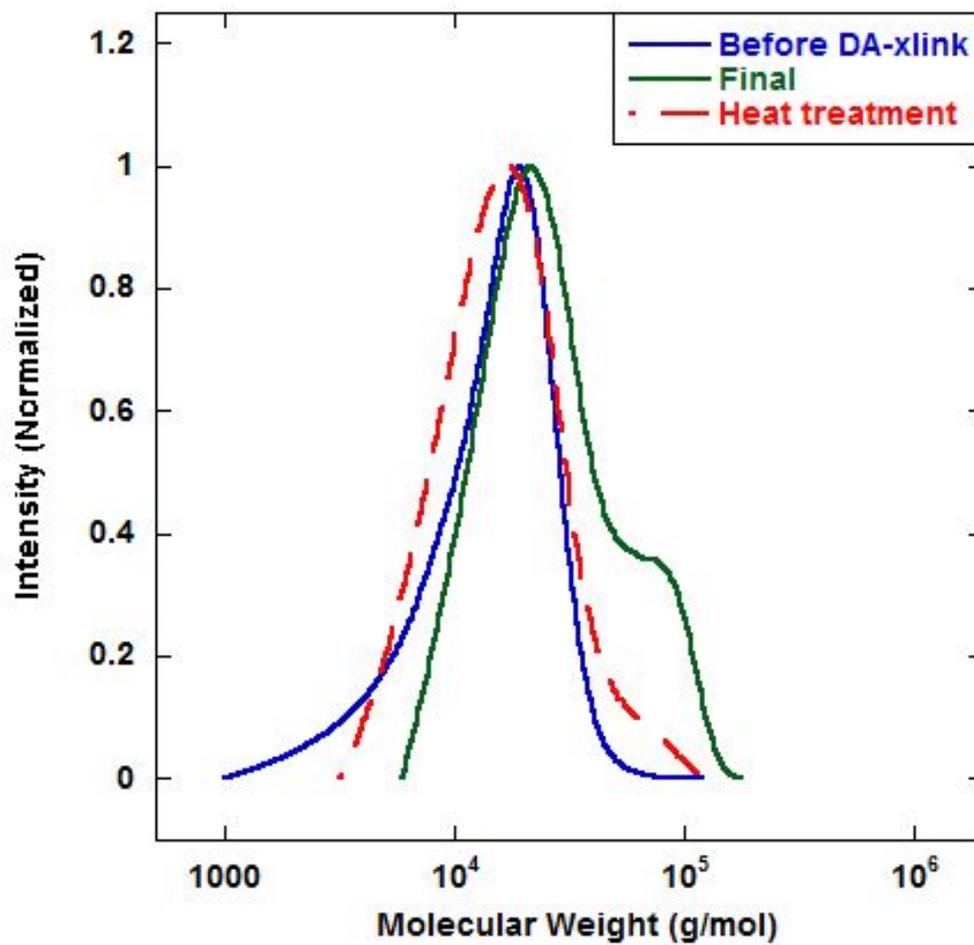


Figure S8. GPC analysis of Sample 5 referencing Table S1.

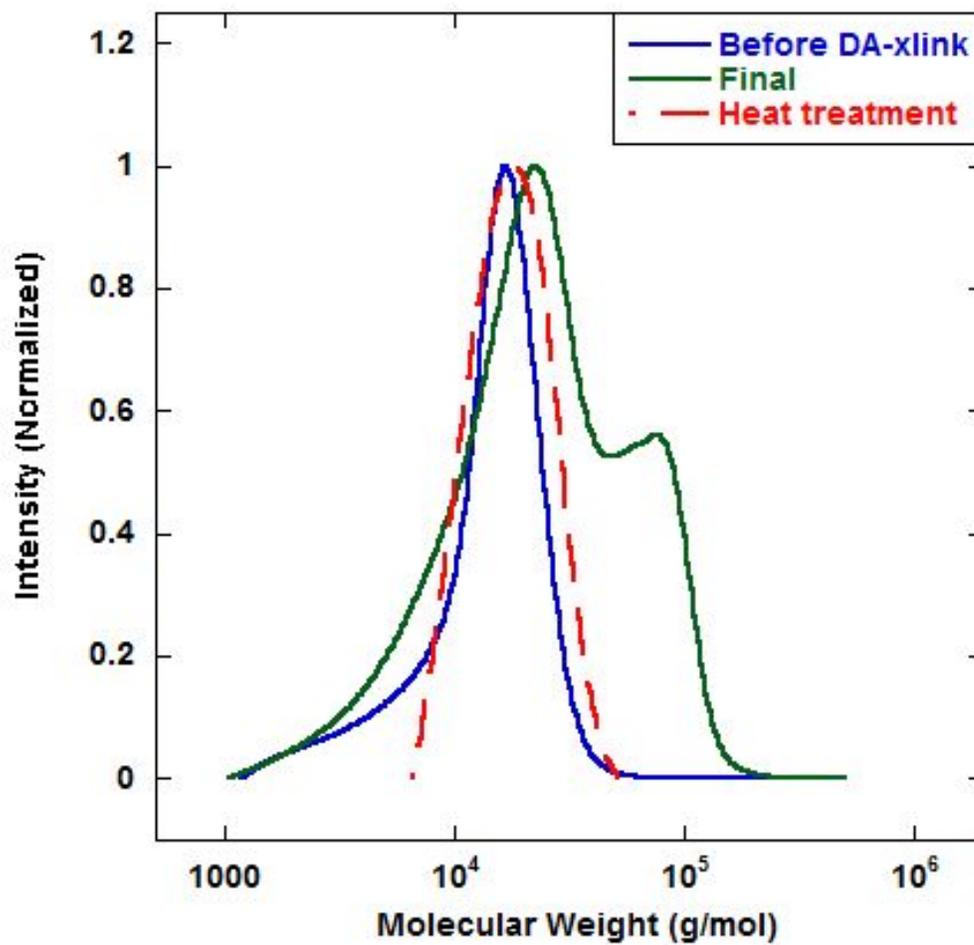


Figure S9. GPC analysis of Sample 6 referencing Table S1.

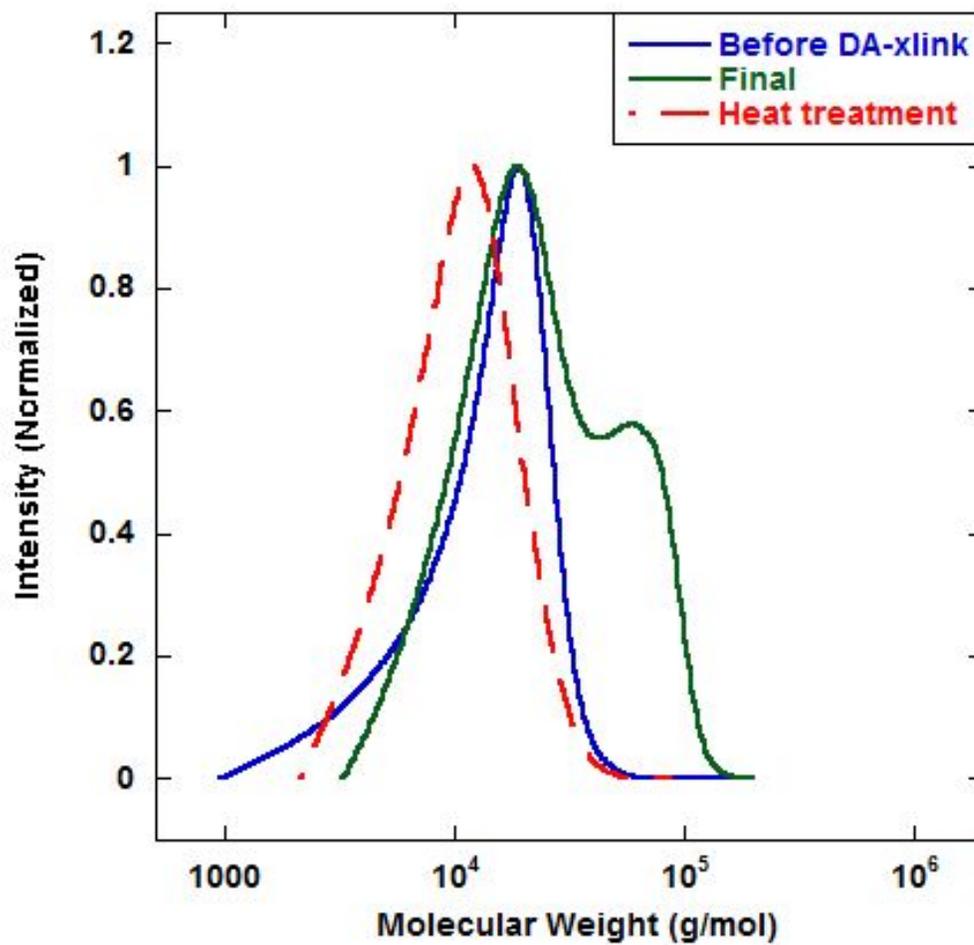


Figure S10. GPC analysis of Sample 7 referencing Table S1.

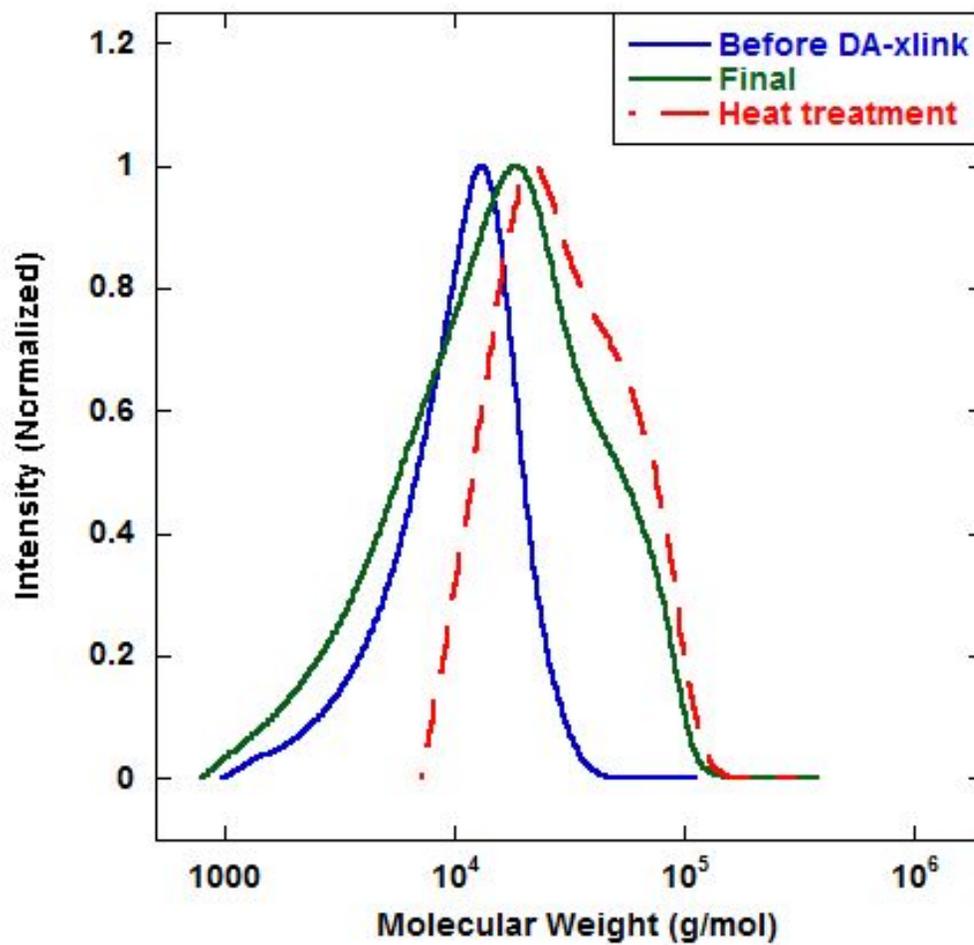


Figure S11. GPC analysis of Sample 8 referencing Table S1.

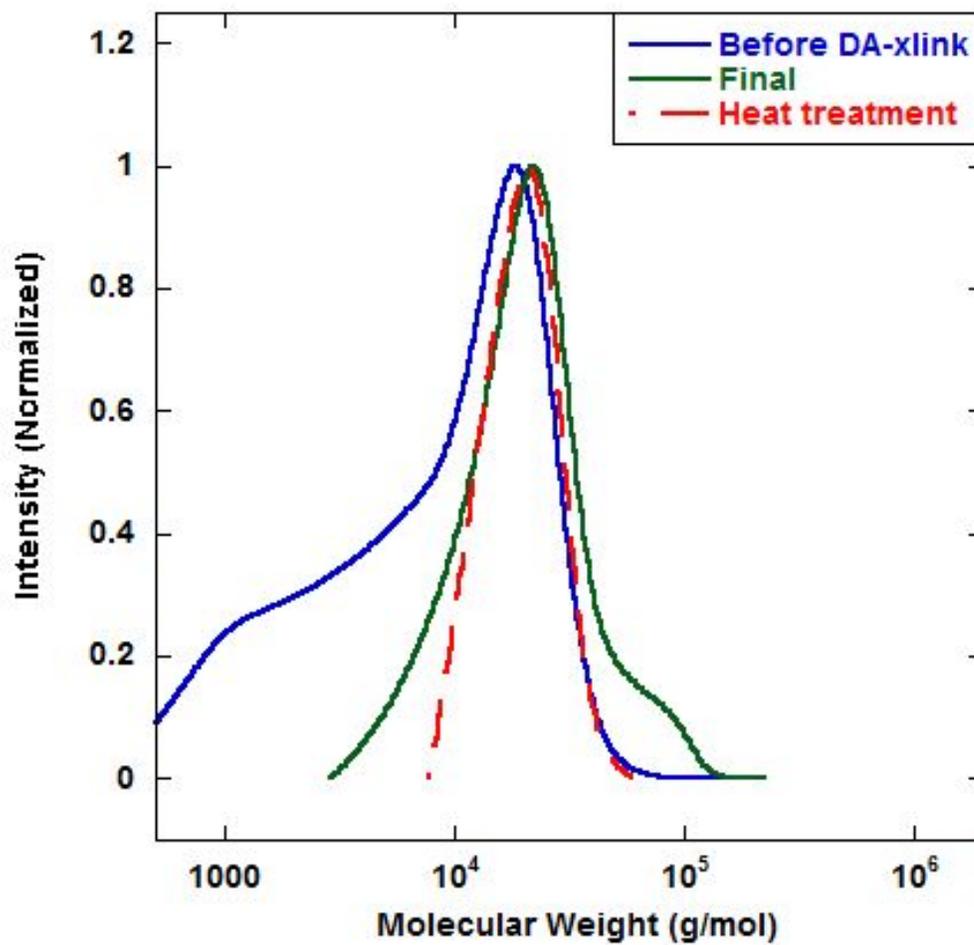


Figure S12. GPC analysis of Sample 9 referencing Table S1.

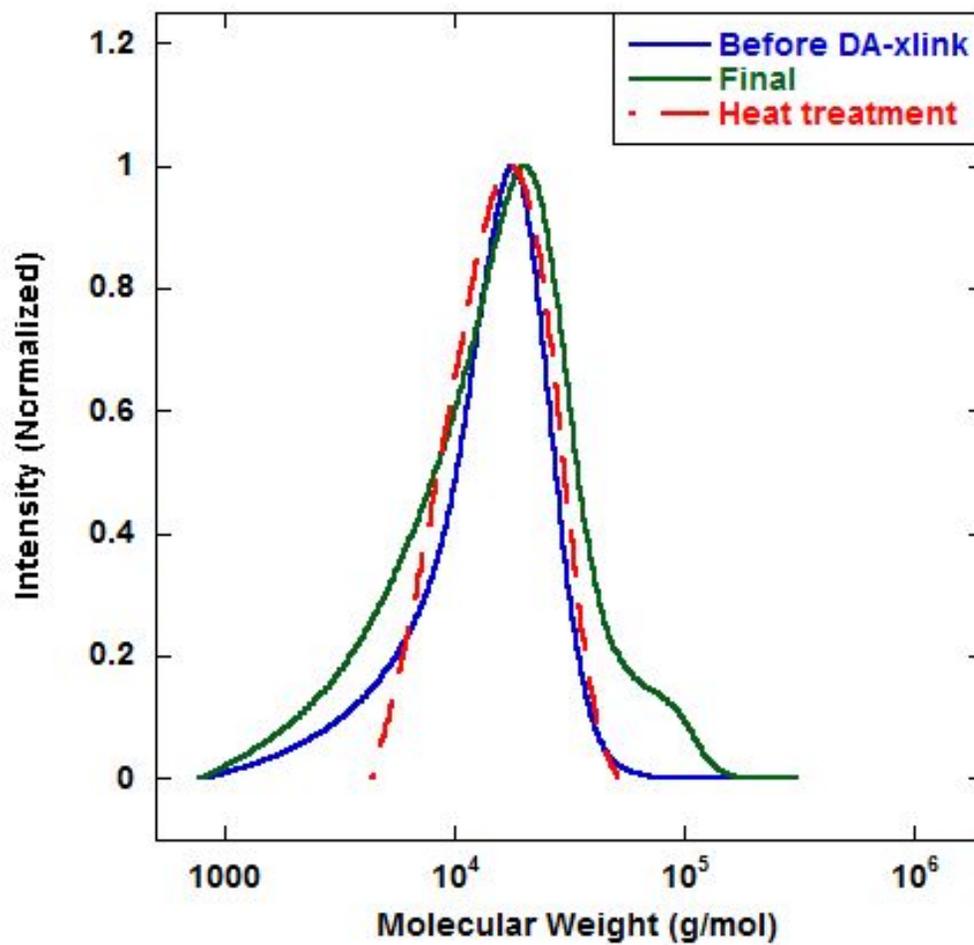


Figure S13. GPC analysis of Sample 10 referencing Table S1.

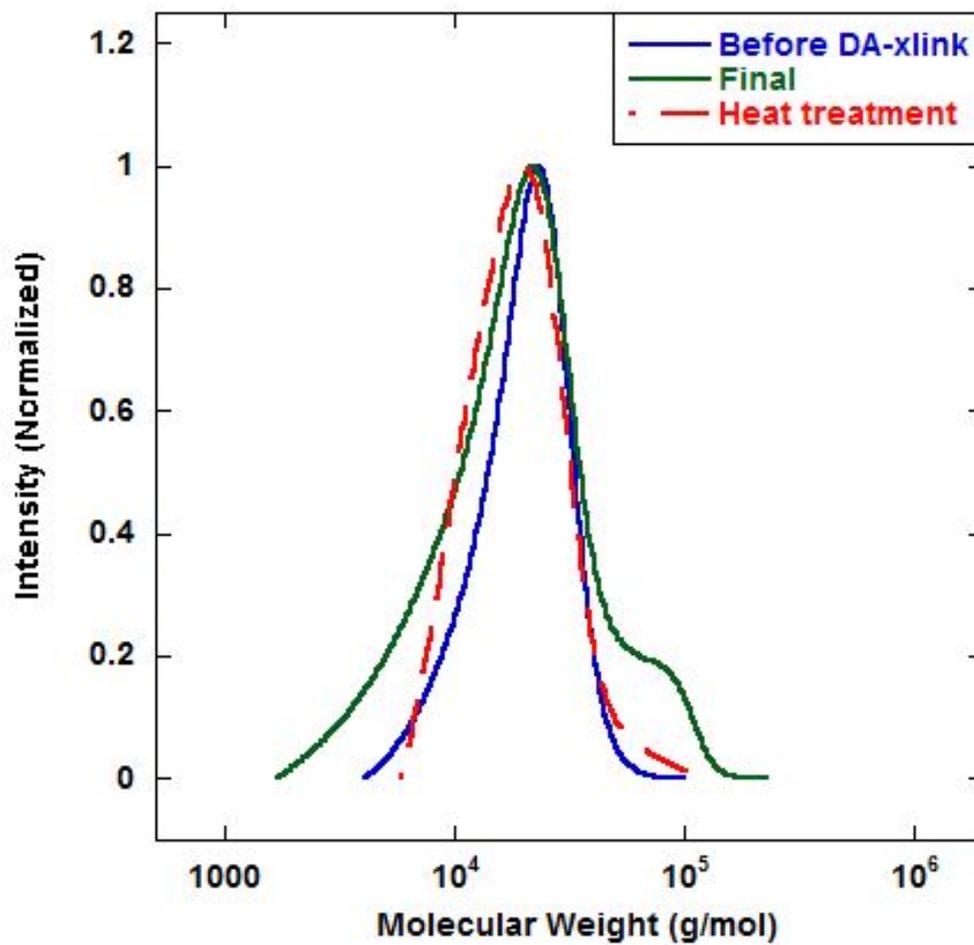


Figure S14. GPC analysis of Sample 11 referencing Table S1.

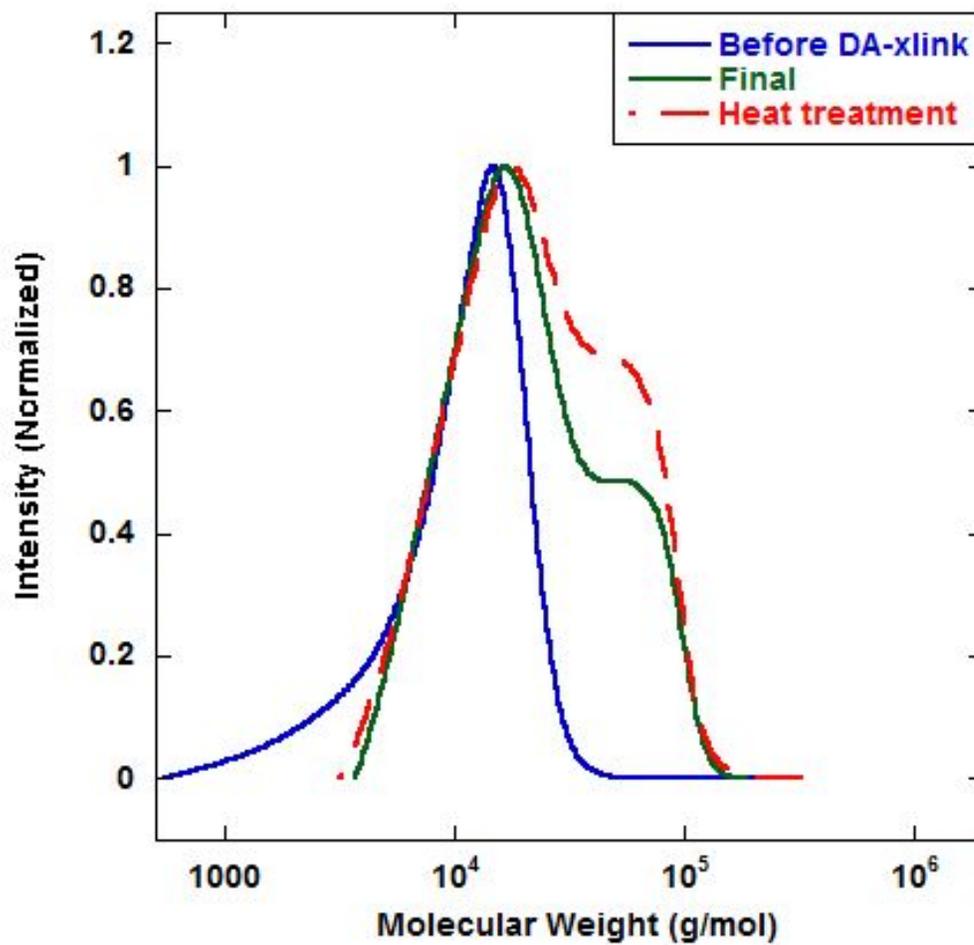


Figure S15. GPC analysis of Sample 12 referencing Table S1.

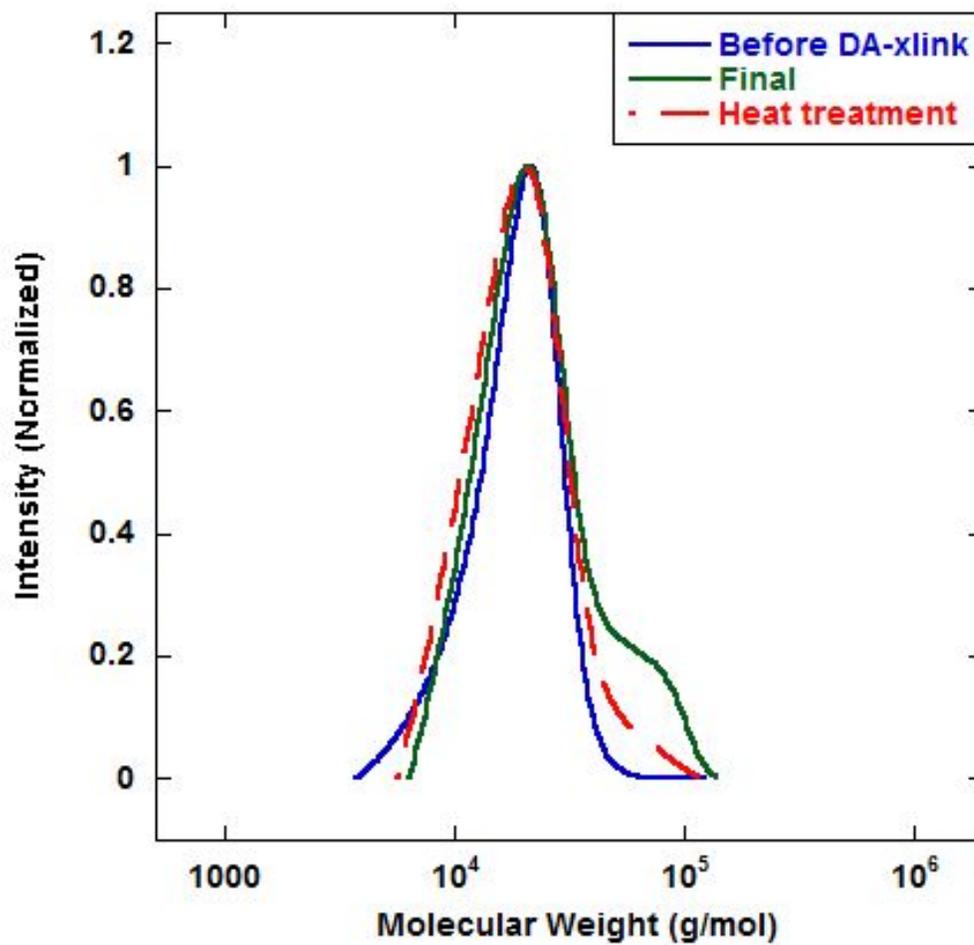


Figure S16. GPC analysis of Sample 13 referencing Table S1.

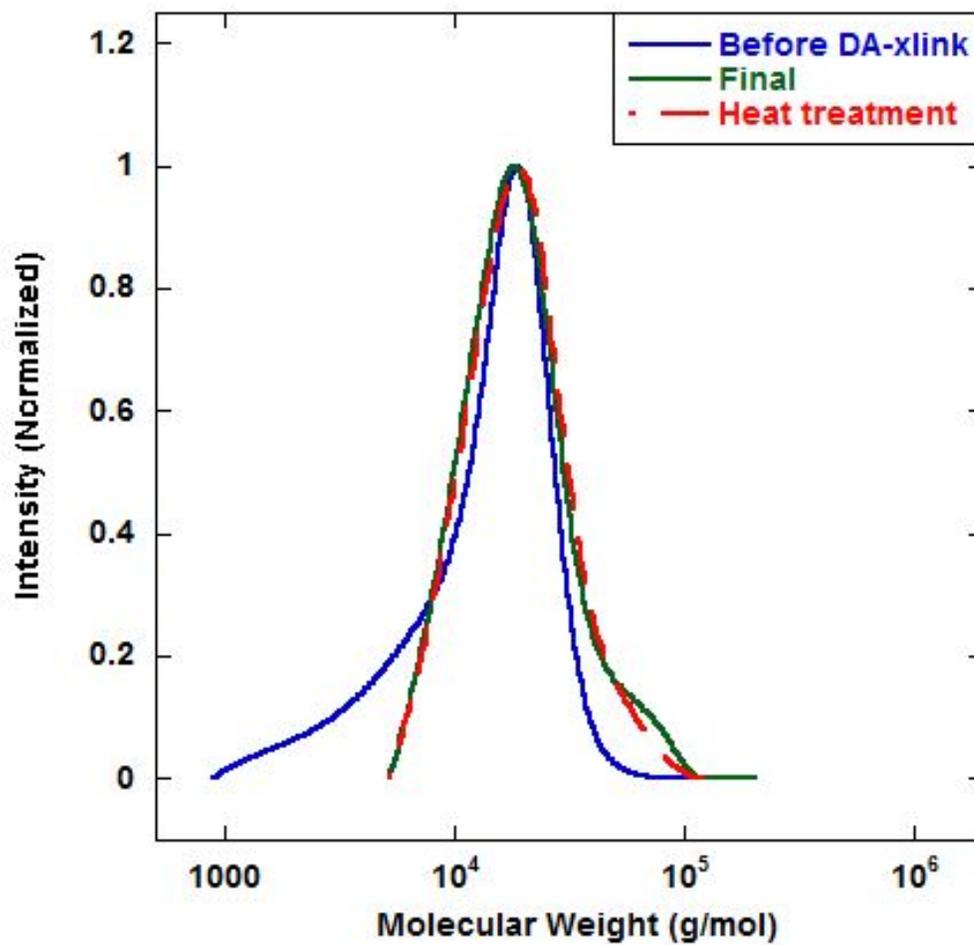


Figure S17. GPC analysis of Sample 14 referencing Table S1.

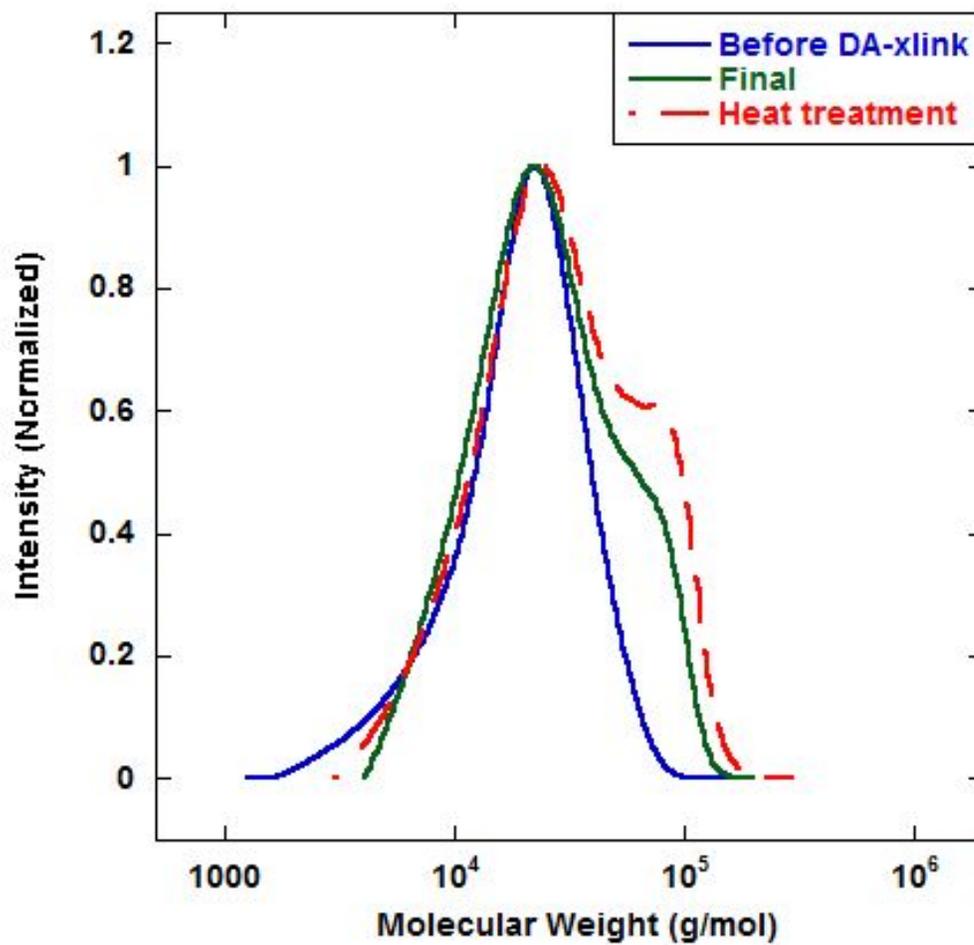


Figure S18. GPC analysis of Sample 15 referencing Table S1.

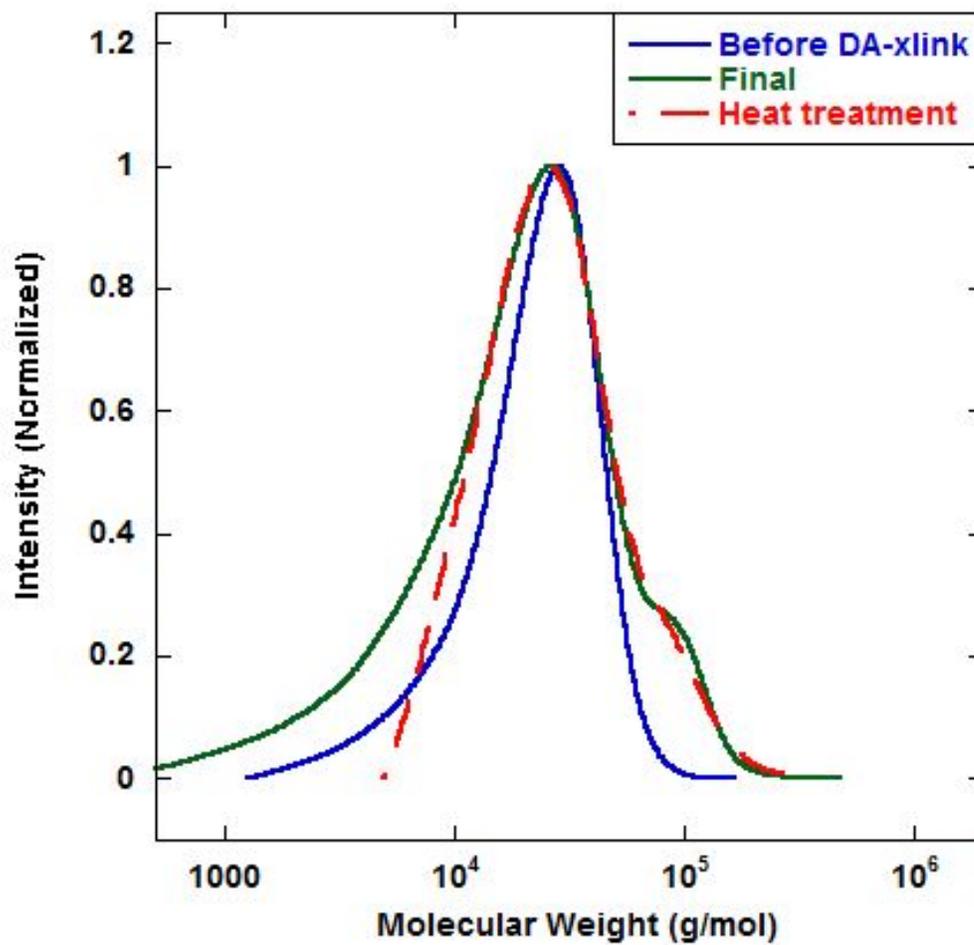


Figure S19. GPC analysis of Sample 16 referencing Table S1.