

Supporting Information

Water Soluble Hyperbranched Polymers from Controlled Radical

Homopolymerization of PEG Diacrylate

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Table S1. Molecular weight of poly(PEGDA)s at different time points during the polymerization processes, monitored by GPC-RI detector.

Diacrylate	I:M	Time	Conv.	M _{n, RI}	M _{w, RI}	PDI
PEGDA ₅₇₅	1:2	1.5h	68%	2.7k	5.2k	1.9
		3.0h	88%	4.7k	15.7k	3.3
		4.5h	96%	85k	122.5k	14.5
	1:4	1.5h	59%	2.7k	4.2k	1.6
		3.0h	80%	4.7k	12.2k	2.6
		4.5h	89%	7.0k	38.1k	5.4
		6.0h	94%	11.2k	107.4k	9.6
	1:8	1.5h	39%	2.6k	3.7k	1.5
		3.0h	59%	4.4k	8.8k	2.0
		4.5h	72%	6.3k	16.9k	2.7
		6.0h	77%	8.4k	39.8k	4.8
PEGDA ₇₀₀	1:2	1.5h	47%	3.0k	4.1k	1.4
		3.0h	83%	4.8k	10.1k	2.1
		4.5h	91%	6.7k	22.9k	3.4
	1:4	1.5h	28%	2.8k	3.4k	1.2
		3.0h	68%	5.8k	11.9k	2.1
		4.5h	79%	7.6k	21.6k	2.8
		6.0h	93%	14.0k	89.2k	6.4
	1:8	1.5h	15%	2.7k	3.0k	1.1
		3.0h	47%	5.3k	9.0k	1.7
		4.5h	64%	7.3k	15.1k	2.1
		6.0h	71%	10.0k	32.3k	3.2

Table S2. Molecular weight of purified poly(PEGDA₅₇₅) 1:4 at different reaction time, monitored by GPC-RI detector. These polymers were also used for the phase transition study.

Polymer	Time	M _w (kg/mol) (M _w /M _n)	Branch ratio (%) of PEGDA unit)	Initiator content (%) of PEGDA unit)
poly(PEGDA ₅₇₅)	3.0h	39 (1.9)	40.7	29.7
1:4	4.5h	88 (2.9)	43.9	28.6
	6.0h	153 (5.6)	47.3	27.8

Determination of the polymer composition and branching ratio

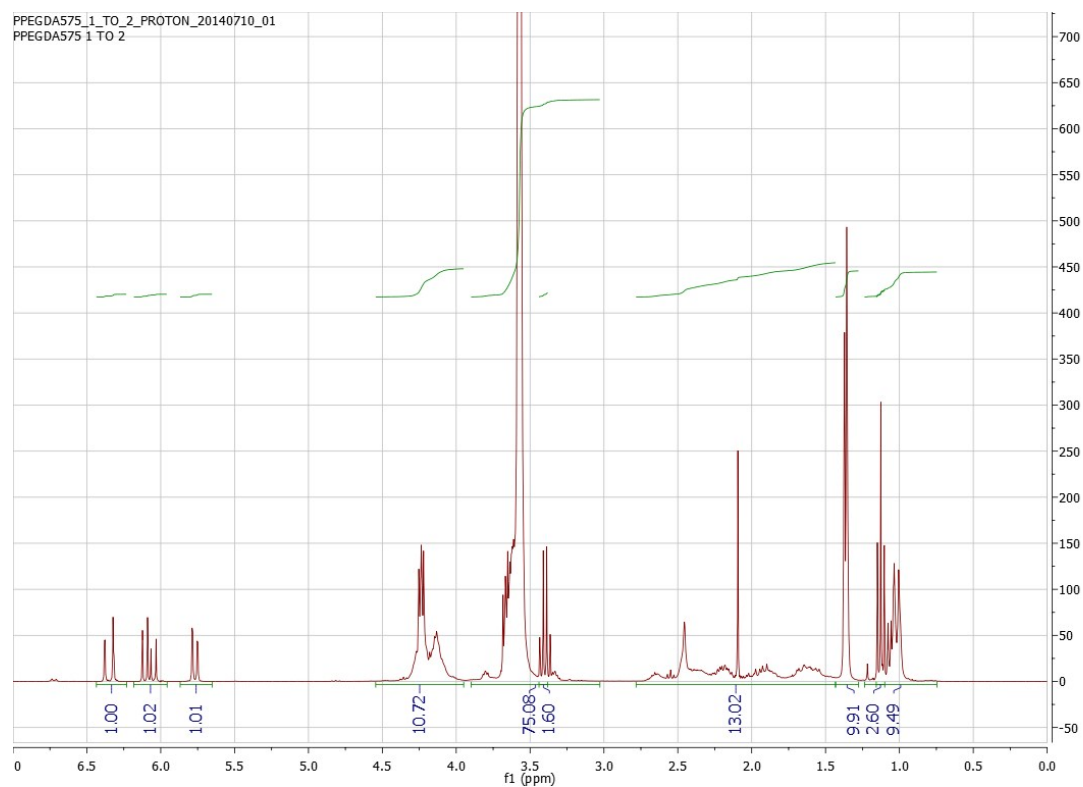
¹H-NMR analysis for the poly(PEGDA)s demonstrates the presence of a high amount of vinyl functional groups at characteristic peaks between 6.5 ppm and 5.7 ppm, as shown in Figure 3. The poly(PEGDA)s composition was determined by integrating a, d, d' and g peaks (Figure 3). Eq. S1 - S3 outline the calculations:

$$\text{Vinyl content (mol\%)} = \frac{a}{(d + d') / 4} \quad \text{S1}$$

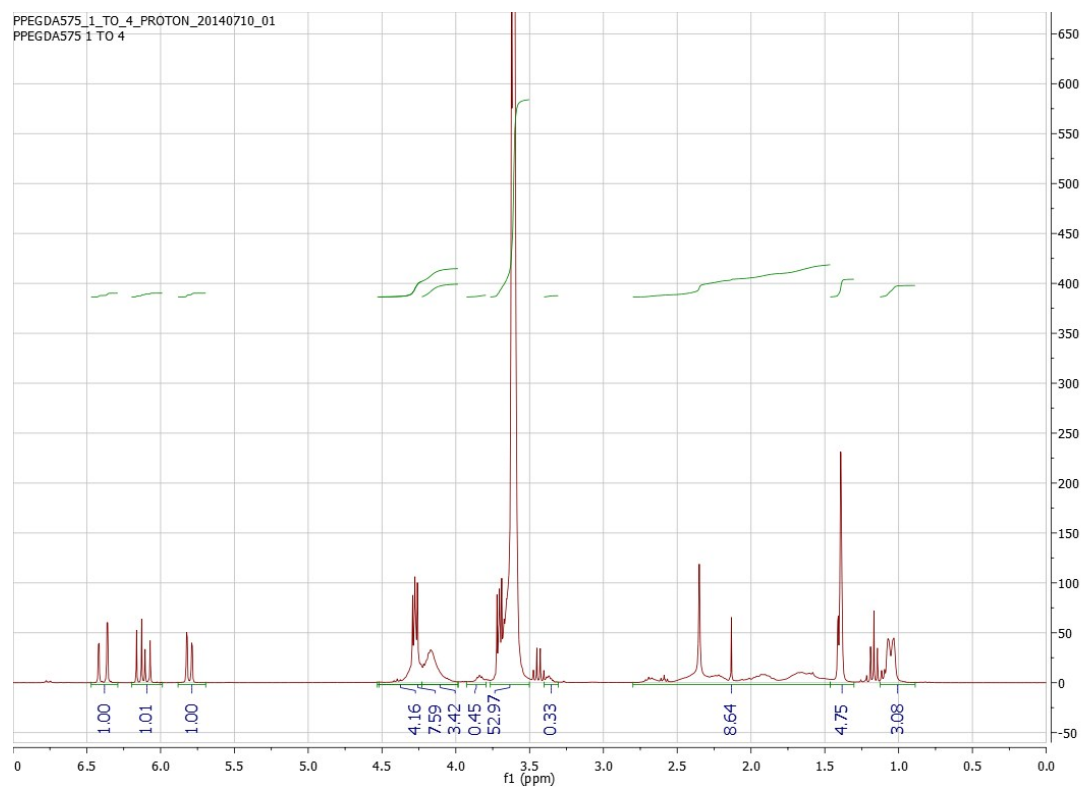
$$\text{Branch ratio (mol\%)} = 1 - \frac{a}{(d + d') / 4} \quad \text{S2}$$

$$\text{Initiator content (mol\%)} = \frac{g / 9}{(d + d') / 4} \quad \text{S3}$$

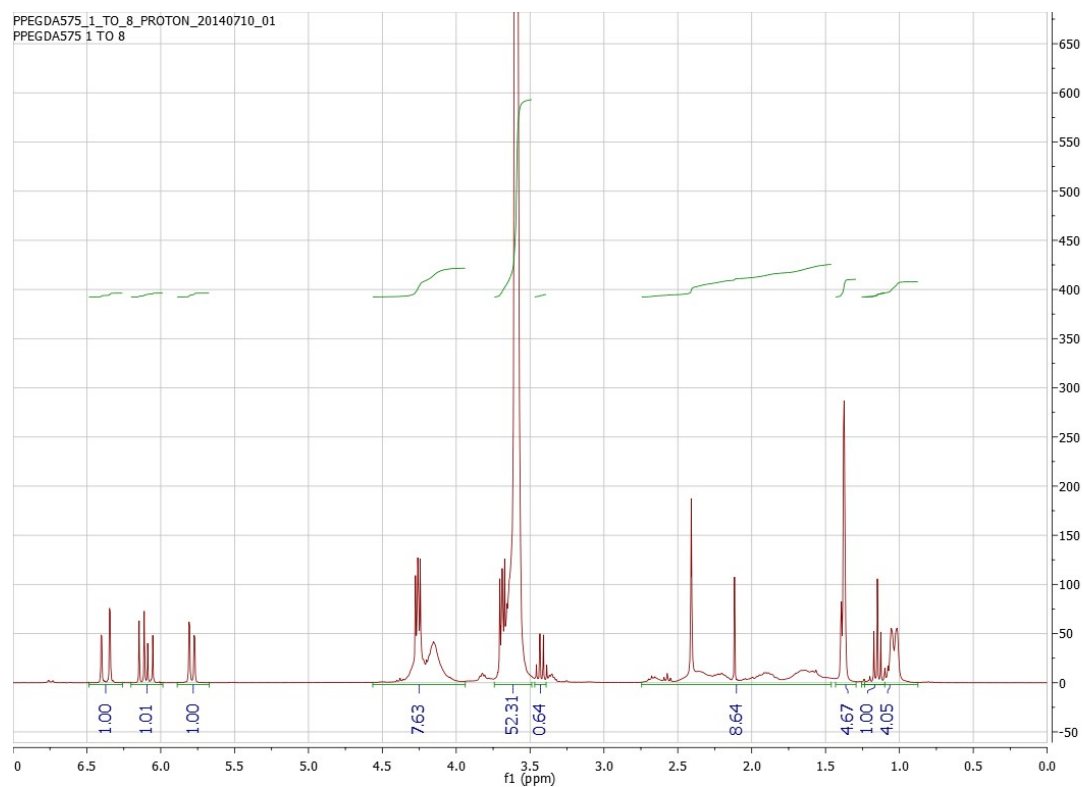
Peak integrations of poly(PEGDA₅₇₅) 1:2



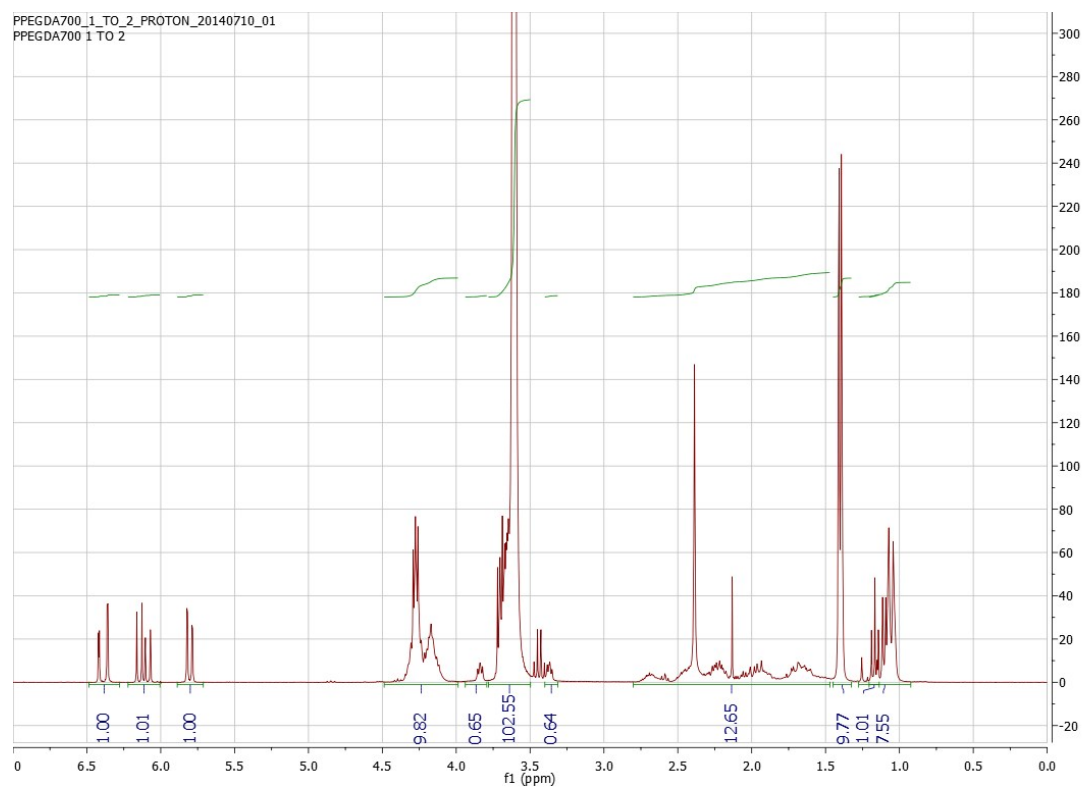
Peak integrations of poly(PEGDA₅₇₅) 1:4



Peak integrations of poly(PEGDA₅₇₅) 1:8

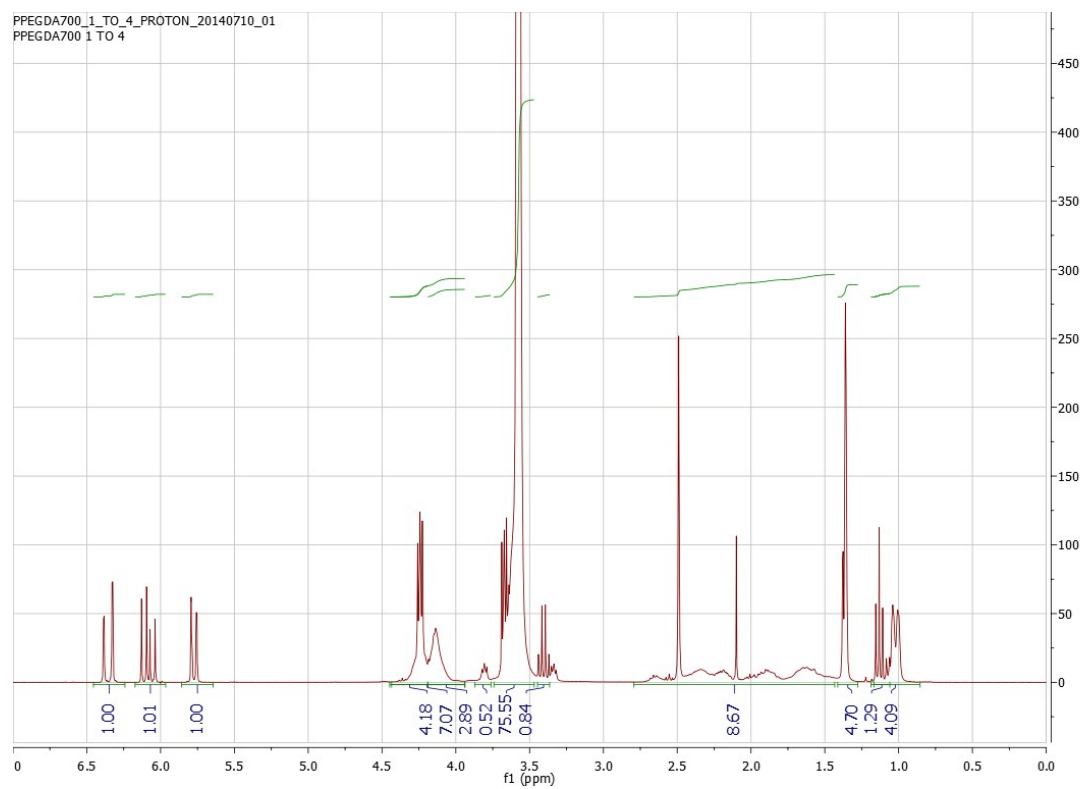


Peak integrations of poly(PEGDA₇₀₀) 1:2



Peak integrations of poly(PEGDA₇₀₀) 1:4

PPEGDA700_1_TO_4_PROTON_20140710_01
PPEGDA700 1 TO 4



Peak integrations of poly(PEGDA₇₀₀) 1:8

