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Supporting Information

RAFT Agent Symmetry and the Effects on Photo-growth Behavior in Living Polymer Networks

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Experimental section

1.1 Materials

All commercial monomers and solvents were purchased from Sigma Aldrich, used as received unless otherwise noted. These include; N, N – dimethylacrylamide (DMAm), poly (ethylene glycol) diacrylate (PEGDA) (average Mn 250), Eosin Y (EY), and triethanolamine (TEtOHA). All monomers were filtered through basic alumina to remove inhibitors. 2-(Butylthiocarbonothioylthio) propanoic acid and Dibenzyl trithiocarbonate were purchased from Boron Molecular, and used as received. All the other reagents were used as received unless otherwise specified.

1.2 Characterization

Total monomer conversions of the prepared networks were measured based on the mass of the dry samples (after extensive washing and drying in the room temperature). The conversion of the newly incorporated monomers after post-synthesis transformations process were also measured based on the mass of the dry samples after extensive washing of networks in different solvents (such as DMSO, MeCN and tetrahydrofuran (THF)) for a minimum of 24 h.

Swelling ratios of networks were measured in fully swollen state at room temperature: swelling ratio defined as Ww/ W_D, where Ww is the weight of a sample swollen in DMSO; W_D is the weight of sample in the dry state.

Mass increase percentage was determined by the following equation

$$mass\ increase\ (\%) = \frac{W_{D\ daughter\ gel} - W_{D\ parent\ gels}}{W_{D\ parent\ gels}} \times 100$$

1.3 Procedure for Production of Asymmetrical Parent RAFT Networks, eg. B-50-90

A typical experiment of a parent RAFT network formation was set up as follow: a glass vial was filled with DMAm (8.6 µL, 83.9 µmol), PEGDA 250 (170.1 µL, 755.1 µmol), BTPA (4.0 mg, 16.8 µmol), EY (29.0 µL, 167.8×10^{-3} µmol) from a 4 mg/mL stock solution, TEtOHA (50.3 mg, 335.6 µmol), and DMSO (91.4 µL, 50 wt% monomers). The polymerization was carried under a green LED light (532 nm, 0.7 mW/cm^2) for 3 hours. After polymerization the solid network was removed from the vial and washed in DMSO, MeCN, and THF to remove EY/TEtOHA and any unreacted monomers. This process was also used to make networks with differing ratios of [DMAm]: [PEGDA] and various concentrations of BTPA.

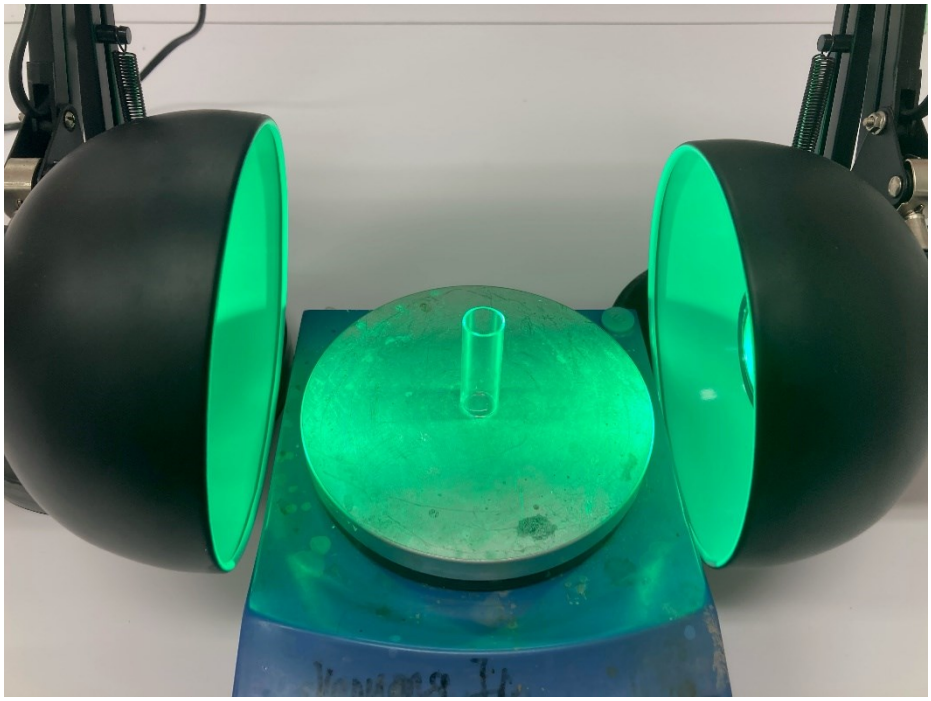

Figure 1. Image of the typical photo-polymerisation setup with green LED lamps.

Table S1. Amounts of each component in the equivalently named asymmetric RAFT sample.

Sample Name	BTPA	DMAm	PEGDA	EY	TEtOHA	DMSO
B-50-90	5 mg	10.4 mg	236.0 mg	29.0 µL	62.6 mg	125.7 µL
B-50-80	5 mg	20.8 mg	209.7 mg	29.0 µL	62.6 mg	117.8 µL
B-50-70	5 mg	31.2 mg	132.3 mg	29.0 µL	62.6 mg	109.9 µL
B-50-60	5 mg	41.6 mg	157.3 mg	29.0 µL	62.6 mg	101.9 µL

B-50-50	5 mg	52.0 mg	131.1 mg	29.0 µL	62.6 mg	94.0 µL
B-50-40	5 mg	62.4 mg	104.9 mg	29.0 µL	62.6 mg	86.1 µL
B-50-30	5 mg	72.8 mg	78.7 mg	29.0 µL	62.6 mg	78.2 µL
B-50-20	5 mg	83.2 mg	52.4 mg	29.0 µL	62.6 mg	70.3 µL
B-50-10	5 mg	93.6 mg	26.2 mg	29.0 µL	62.6 mg	62.4 µL
B-100-90	3 mg	12.5 mg	283.1 mg	14.5 µL	37.6 mg	149.3 µL
B-100-80	3 mg	24.9 mg	251.7 mg	14.5 µL	37.6 mg	139.8 µL
B-100-70	3 mg	37.6 mg	220.2 mg	14.5 µL	37.6 mg	130.3µL
B-100-60	3 mg	49.9 mg	188.8 mg	14.5 µL	37.6 mg	120.8 µL
B-100-50	3 mg	62.4 mg	157.3 mg	14.5 µL	37.6 mg	111.3 µL
B-100-40	3 mg	74.8 mg	125.8 mg	14.5 µL	37.6 mg	101.8µL
B-100-30	3 mg	87.3 mg	94.4 mg	14.5 µL	37.6 mg	92.4 µL
B-100-20	3 mg	99.8 mg	62.9 mg	14.5 µL	37.6 mg	82.9 µL
B-100-10	3 mg	112.3 mg	31.5 mg	14.5 µL	37.6 mg	73.4 µL
B-200-90	2 mg	16.6 mg	377.5 mg	7.3 µL	25.0 mg	198.1 µL
B-200-80	2 mg	33.3 mg	335.6 mg	7.3 µL	25.0 mg	185.4 µL
B-200-70	2 mg	49.9 mg	293.6 mg	7.3 µL	25.0 mg	172.8 µL
B-200-60	2 mg	66.5 mg	251.7 mg	7.3 µL	25.0 mg	160.1 µL
B-200-50	2 mg	83.2 mg	209.7 mg	7.3 µL	25.0 mg	147.5 µL
B-200-40	2 mg	99.8 mg	167.8 mg	7.3 µL	25.0 mg	134.8 µL
B-200-30	2 mg	116.4 mg	125.8 mg	7.3 µL	25.0 mg	122.1 µL
B-200-20	2 mg	133.1 mg	83.9 mg	7.3 µL	25.0 mg	109.5 µL
B-200-10	2 mg	149.7 mg	41.9 mg	7.3 µL	25.0 mg	96.8 µL

1.4 Procedure for Production of Symmetrical Parent RAFT Networks, eg. D-50-90

A typical experiment of a parent RAFT network formation was set up as follow: a glass vial was filled with DMAm (8.9 µL, 86.1 µmol), PEGDA 250 (174.5 µL, 774.6 µmol), DBTTC (5.0 mg, 17.2 µmol), EY (29.8 µL, 172.1×10^{-3} µmol) from a 4 mg/mL stock solution, TEtOHA (51.6 mg, 344.3 µmol), and DMSO (94.2 µL, 50 wt% monomers). The polymerization was carried under a green LED light (532 nm, 0.7 mW/cm^2) for 3 hours. After polymerization the solid network was removed from the vial and washed in DMSO, MeCN, and THF to remove EY/TEtOHA and any unreacted monomers. This process was also used

to make networks with differing ratios of [DMAm]: [PEGDA] and various concentrations of DBTTC.

Table S2. Amounts of each component in the equivalently named symmetric RAFT sample.

Sample Name	DBTTC	DMAm	PEGDA	EY	TEtOHA	DMSO
D-50-90	5 mg	8.5 mg	194.0 mg	29.8 µL	51.4 mg	103.8 µL
D-50-80	5 mg	17.1 mg	175.4 mg	29.8 µL	51.4 mg	97.33 µL
D-50-70	5 mg	25.6 mg	150.9 mg	29.8 µL	51.4 mg	90.7 µL
D-50-60	5 mg	34.2 mg	129.3 mg	29.8 µL	51.4 mg	84.2 µL
D-50-50	5 mg	42.7 mg	107.8 mg	29.8 µL	51.4 mg	77.7 µL
D-50-40	5 mg	51.3 mg	86.2 mg	29.8 µL	51.4 mg	71.2 µL
D-50-30	5 mg	59.8 mg	64.7 mg	29.8 µL	51.4 mg	64.7 µL
D-50-20	5 mg	68.4 mg	43.1 mg	29.8 µL	51.4 mg	58.2 µL
D-50-10	5 mg	76.9 mg	21.6 mg	29.8 µL	51.4 mg	47.0 µL
D-100-90	3 mg	10.3 mg	232.8 mg	14.9 µL	30.9 mg	123.0 µL
D-100-80	3 mg	20.5 mg	206.9 mg	14.9 µL	30.9 mg	115.2 µL
D-100-70	3 mg	30.8 mg	181.0 mg	14.9 µL	30.9 mg	107.4 µL
D-100-60	3 mg	41.0 mg	155.2 mg	14.9 µL	30.9 mg	99.6 µL
D-100-50	3 mg	51.3 mg	129.3 mg	14.9 µL	30.9 mg	91.8 µL
D-100-40	3 mg	61.5 mg	103.4 mg	14.9 µL	30.9 mg	84.0 µL
D-100-30	3 mg	71.8 mg	77.6 mg	14.9 µL	30.9 mg	76.2 µL
D-100-20	3 mg	82.0 mg	51.7 mg	14.9 µL	30.9 mg	68.4 µL
D-100-10	3 mg	79.8 mg	19.4 mg	14.9 µL	30.9 mg	45.8 µL
D-200-90	1.5 mg	10.3 mg	232.8 mg	8.9 µL	15.5 mg	122.3 µL
D-200-80	1.5 mg	20.5 mg	206.9 mg	8.9 µL	15.5 mg	114.5 µL
D-200-70	1.5 mg	30.8 mg	181.0 mg	8.9 µL	15.5 mg	106.6 µL
D-200-60	1.5 mg	41.0 mg	155.2 mg	8.9 µL	15.5 mg	98.8 µL
D-200-50	1.5 mg	51.3 mg	129.3 mg	8.9 µL	15.5 mg	91.0 µL
D-200-40	1.5 mg	61.5 mg	103.4 mg	8.9 µL	15.5 mg	83.2 µL
D-200-30	1.5 mg	71.8 mg	77.6 mg	8.9 µL	15.5 mg	75.4 µL
D-200-20	1.5 mg	82.0 mg	51.7 mg	8.9 µL	15.5 mg	67.6 µL
D-200-10	1.5 mg	92.3 mg	25.9 mg	8.9 µL	15.5 mg	59.8 µL

1.5 General Procedure for Post-Production Growth of Parent RAFT Networks

For photo-growth the growth solution was targeted as 200 DP monomer relative to the initial amount of RAFT agent included in the parent RAFT network, assumed none lost during washing, drying, or other procedures.

A typical photo-growth for a parent network was carried out as follows for a D-50-X gel: a growth medium containing DMAm (341.8 mg, 3.45 mmol), DMSO (341.8 μL), TEtOHA (51.4 mg, 0.34 mmol), and EY (29.8 μL, 172.1×10^{-3} μmol) from a 4 mg/mL stock solution was prepared. The parent network (D-50-X) was then soaked in this solution for 48 hours, before being irradiated under a green LED light (6 h). After photo-growth reaction, the subsequent daughter RAFT network (D-50-X-G) was removed from the light source, and was extensively washed in DMSO, THF and MeCN to remove ZnTPP and unreacted monomers.

Table S3. Growth media components and corresponding amounts.

Sample Name	DMAm	DMSO	EY	TEtOHA
B-50-X-G	415.8 mg	415.8 μL	29.0 μL	62.6 mg
B-100-X-G	249.5 mg	249.5 μL	14.5 μL	37.6 mg
B-200-X-G	166.3 mg	166.3 μL	7.3 μL	25.0 mg
D-50-X-G	341.8 mg	341.8 μL	29.8 μL	51.4 mg
D-100-X-G	205.1 mg	205.1 μL	14.9 μL	30.9 mg
D-200-X-G	102.5 mg	102.5 μL	8.9 μL	15.5 mg

Table S4. Results for asymmetric BTPA daughter gels. [a] Suffix –G added to network name to denote grown sample. [b] Conversion was calculated using the difference in dry mass between parent and daughter networks over the mass of monomer in the growth medium. [c] Mass increase measured as the difference in dry mass between parent and daughter networks. This value is tied to conversion within each set, but it is important to remember that each concentration of RAFT has a different amount of monomer in the growth solution. [d] Swelling ratio was calculated by the swollen mass (W_W) over the dry mass (W_D) of the network.

Daughter Sample [a]	**Conversion [b] (%)**	**Mass Difference [c] (mg)**	**Actual number units inserted**	**Swelling Ratio [d]**
B-50-90-G	56.4	234.1	113	1.02
B-50-80-G	51.8	215.0	104	1.06
B-50-70-G	53.3	221.2	107	1.10
B-50-60-G	52.1	216.4	104	1.19
B-50-50-G	51.0	211.9	102	1.24
B-50-40-G	56.9	236.2	114	1.32

B-50-30-G	63.7	264.2	127	1.40
B-50-20-G	61.8	256.4	124	1.51
B-50-10-G	65.4	271.3	131	1.61
B-100-90-G	68.5	170.6	137	1.01
B-100-80-G	70.3	175.0	141	1.18
B-100-70-G	67.6	168.3	135	1.21
B-100-60-G	70.0	174.2	140	1.27
B-100-50-G	69.2	172.3	138	1.36
B-100-40-G	67.0	166.9	134	1.49
B-100-30-G	65.9	164.1	132	1.57
B-100-20-G	68.5	170.5	137	1.64
B-100-10-G	70.5	175.4	141	1.72
B-200-90-G	82.6	137.1	165	1.22
B-200-80-G	76.1	126.3	152	1.24
B-200-70-G	78.7	130.6	157	1.27
B-200-60-G	82.4	136.7	165	1.39
B-200-50-G	77.7	128.9	155	1.47
B-200-40-G	80.3	133.2	161	1.55
B-200-30-G	83.0	137.7	166	1.69
B-200-20-G	85.1	141.3	170	1.83
B-200-10-G	81.7	135.6	163	1.97

Table S5. Results for symmetric DBTTC daughter gels. [a] Suffix –G added to network name to denote grown sample. [b] Conversion was calculated using the difference in dry mass between parent and daughter networks over the mass of monomer in the growth medium. [c] Mass increase measured as the difference in dry mass between parent and daughter networks. This value is tied to conversion within each set, but it is important to remember that each concentration of RAFT has a different amount of monomer in the growth solution. [d] Swelling ratio was calculated by the swollen mass (W_W) over the dry mass (W_D) of the network.

Daughter Sample [a]	**Conversion [c] (%)**	**Mass Difference [d] (mg)**	**Actual number units inserted**	**Swelling Ratio [e]**
D-50-90-G	76.7	261.5	153	5.04
D-50-80-G	83.4	284.4	167	4.77
D-50-70-G	81.0	276.2	162	4.18
D-50-60-G	67.0	228.6	134	4.09
D-50-50-G	55.5	189.1	111	3.91
D-50-40-G	42.6	145.4	85	3.84
D-50-30-G	37.3	127.0	75	3.98
D-50-20-G	33.3	113.7	67	4.22
D-50-10-G	28.8	98.4	58	4.25
D-100-90-G	73.2	149.3	146	2.8
D-100-80-G	90.8	185.2	182	2.64

D-100-70-G	89.6	182.8	179	2.42
D-100-60-G	70.8	144.3	142	2.32
D-100-50-G	56.8	115.9	114	2.55
D-100-40-G	42.6	86.8	85	2.73
D-100-30-G	38.0	77.5	76	2.90
D-100-20-G	27.4	55.9	55	3.23
D-100-10-G	28.0	57.2	56	3.31
D-200-90-G	74.8	76.3	150	2.04
D-200-80-G	72.3	73.7	145	2.02
D-200-70-G	77.5	79.1	155	1.91
D-200-60-G	65.8	67.2	132	2.36
D-200-50-G	64.9	66.2	130	2.41
D-200-40-G	58.2	59.4	116	2.51
D-200-30-G	47.8	48.8	96	2.87
D-200-20-G	41.6	42.4	83	3.01
D-200-10-G	33.0	33.6	66	3.25