Supporting information for:

Gelation suppression in RAFT polymerization

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Since MMA and DM are structurally similar chemicals, ^{1}H NMR signals of their vinylic and allylic hydrogens are overlapped. However, the amount of two chemicals in the reaction mixture can be identified from their methoxy and methyleneoxy signals. Figure S1(a) shows the methoxy signal positions of pure MMA, methyleneoxy signal positions of pure DM, along with a series of DM and MMA mixtures. The results in Figure S1(b) validate the accuracy of NMR signals in distinguishing the two chemicals.

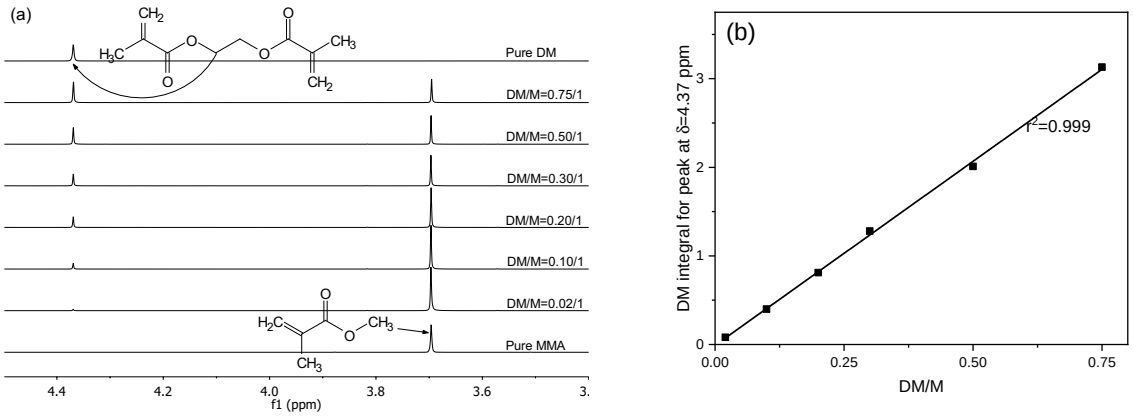

Figure S1: ^{1}H NMR spectra accuracy check for methoxy and methyleneoxy signals. (a) [DM]/[M]=X/1 denotes the spectra of X mole of DM over 1 mole of MMA. The integrated area of δ = 3.70 from MMA methoxy is fixed at 3. (b) The relative integrated area of δ = 4.37 from DM methyleneoxy in different DM and M mixtures.

Figure S2 shows a representative ^{1}H NMR spectra from the aliquot experiments. The methoxy and methyleneoxy signals for reacted M and DM species were shifted by approximately 0.15 ppm from their original monomeric positions. Accurate integration of the unreacted and reacted peaks was achieved through the peak deconvolution algorithm supplied with the MestreNova software.[S1] Each peak was split into several Gaussian peaks, optimized with least squares regression, for better curve fitting results. For instance, the unreacted methyleneoxy signals ("c-unreacted" in Figure S2) were split into three deconvoluted peaks, but the integrated area was the summation of all three peaks. Based on the integration of deconvoluted peaks, the conversion of methyl methacrylate (X_M) and ethylene glycol dimethacrylate (X_{DM}) were calculated as follows:

$$X_M = \frac{\int \delta 3.57}{\int \delta 3.57 + \int \delta 3.70} \tag{1}$$

$$X_{DM} = \frac{\int \delta 4.17}{\int \delta 4.17 + \int \delta 4.37} \tag{2}$$

The overall gel point in Figure 7 is determined as:

$$X = \frac{X_M + X_{DM} * [DM]/[M]}{1 + [DM]/[M]} \tag{3}$$

The dynamic light scattering (DLS) results indicate that the scaling behavior between hydrodynamic radius (R_h) and weight-average molecular weight (M_w) is relevant to [DM]/[M] but irrelevant to vinyl concentration. Figure S3 displays R_h with respect to M_w for the representative [DM]/[M] 0.5 entries. The summary of the slope and corresponding r^2 values is listed in Table S1.

Table S1: Summary of α and the corresponding r^2 of entries in Figure S3

Entry	DMM203	DMM303	DMM403
α	0.42	0.39	0.42
r^2	0.91	0.80	0.94

The numbers of data points shown in Figure 7 are listed in Table S2-S4. The calculation

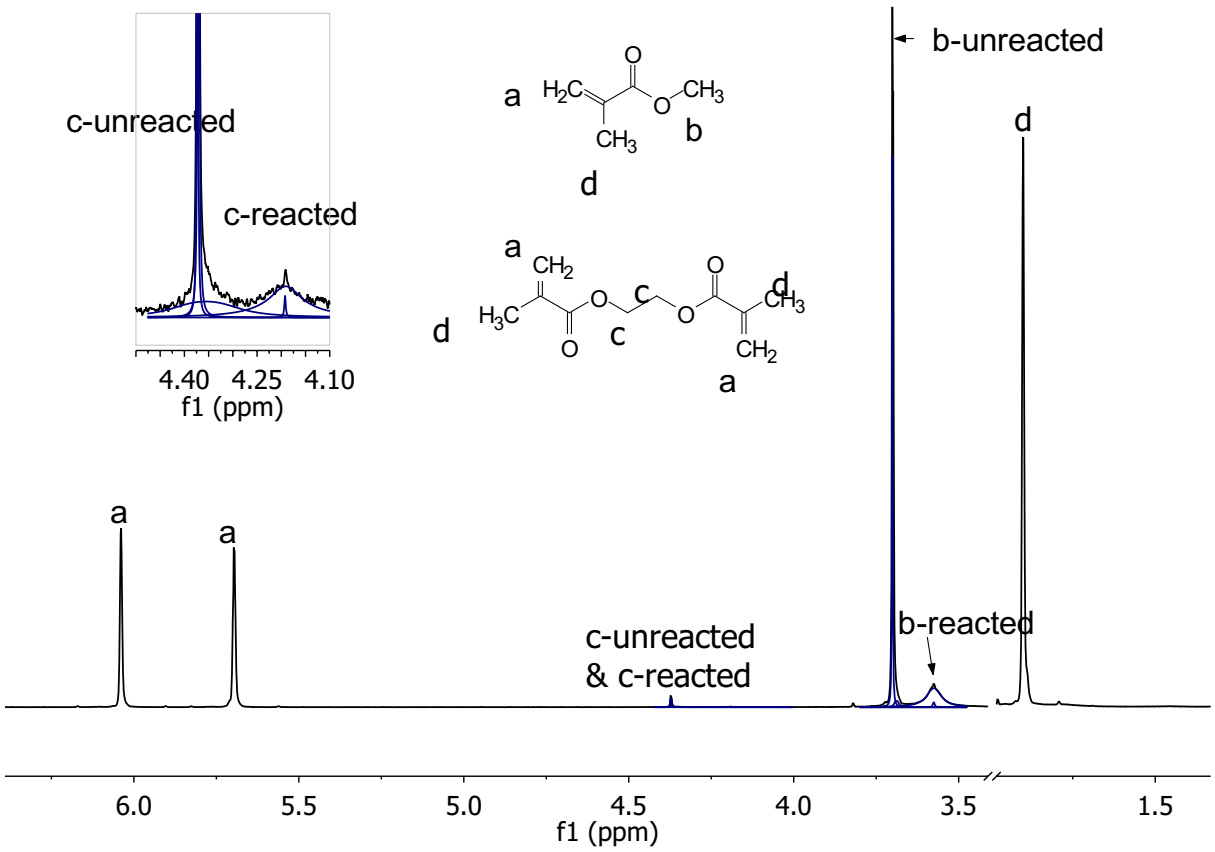

Figure S2: A representative NMR spectrum from DMM401. The inset provides an enlarged view of the methyleneoxy signals region for EGDMA. Methoxy and methyleneoxy peaks after deconvolution are shown in navy.

is based on Equation 8-10. To validate the efficacy of CT analysis, experimental conditions and results from Rosselgong *et al.* are used to compare the accuracy of CT prediction in Table S5.[S2] The calculated CT values are plugged in the linear regression equation $X_g^{CT} = 141.65 - 60 * log(CT)$ to obtain the predicted gel conversion by CT analysis (X_g^{CT}). A X_g^{CT} higher than 100% indicates that the entry does not reach the gel point since reaction conversion cannot go above 100%; whereas X_g^{CT} lower than 100% indicates the entry gels. The CT analysis successfully predicts the gelation behavior in Rosselgong's system with only 2 exceptions.

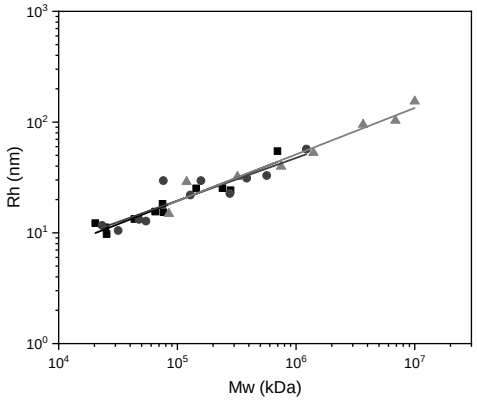

Figure S3: R_h of different vinyl concentrations for [DM]/[M] 0.5. Black, dark grey and light grey symbols are entries of DMM403, DMM303, and DMM203, respectively.

Table S2: RAFT and ATRP System parameters and gel points from literature and this work

Reference	Polymerization	Original sample code	Gel point /%	Overall monomer conc. /M	crosslinker functional-ity	$[C]/[PC]_{theo}$ [a]	η [b]	Crosslinking tendency	η reference
[S3]	RAFT	Batch synthesis of p(DVB)	68	2.19	2	2.53	1.01	5.50	[S4]
[S5]	RAFT	P6	75	1.01	2	100	1.46	69.44	[S6]
[S7]	RAFT	R102	11	0.15	2.6	208.00	1.00	126.46	[S8]
[S7]	RAFT	R105	8	0.15	2.6	208.00	1.00	126.46	[S8]
[S7]	RAFT	R202	18	0.10	2.6	208.00	1.00	83.20	[S8]
[S7]	RAFT	R205	20	0.10	2.6	208.00	1.00	83.20	[S8]
[S7]	RAFT	R302	24	0.07	2.6	208.00	1.00	63.23	[S8]
[S7]	RAFT	R305	26	0.07	2.6	208.00	1.00	63.23	[S8]
[S7]	RAFT	R402	45	0.10	2.6	208.00	1.00	49.92	[S8]
[S7]	RAFT	R405	40	0.10	2.6	208.00	1.00	49.29	[S8]
This work	RAFT	DMM301	33	2.84	2	20.00	0.88	64.55	This work
This work	RAFT	DMM302	8	2.49	2	199.80	0.88	565.34	This work
This work	RAFT	DMM303	7	2.18	2	499.40	0.88	1237.15	This work
This work	RAFT	DMM401	31	4.71	2	20.00	0.88	107.05	This work
This work	RAFT	DMM402	11	4.11	2	199.80	0.88	933.16	This work
This work	RAFT	DMM403	6	3.60	2	499.40	0.88	2043	This work
[S9]	ATRP	EGDMA0.02	81	2.89	2	2.00	0.80	7.22	[S10]
[S9]	ATRP	EGDMA0.05	57	2.87	2	5.00	0.80	17.94	[S10]
[S9]	ATRP	EGDMA0.1	28	2.84	2	10.00	0.80	35.54	[S10]
[S9]	ATRP	EGDMA0.2	16	2.79	2	20.00	0.80	69.76	[S10]
[S9]	ATRP	EGDMA0.5	5	2.64	2	50.00	0.80	165.25	[S10]
[S11]	ATRP	$MA_{8.5}EG_{5.0}$	44	9.49	2	5.00	1.10	42.5	[S12]
[S11]	ATRP	$MA_{6.0}EG_{5.0}$	51	6.68	2	5.00	1.10	30	[S12]
[S11]	ATRP	$MA_{2.5}EG_{5.0}$	73	2.76	2	5.00	1.10	12.5	[S12]
[S11]	ATRP	$MA_{8.5}EG_{1.1}$	100	8.72	2	1.10	1.10	8.69	[S12]
[S11]	ATRP	$MA_{6.0}EG_{1.1}$	97	6.15	2	1.10	1.10	6.13	[S12]
[S11]	ATRP	$MA_{8.5}EG_{1.5}$	79	8.80	2	1.50	1.10	11.94	[S12]
[S11]	ATRP	$MA_{6.0}EG_{1.5}$	87	6.20	2	1.50	1.10	8.43	[S12]

a $[C]/[PC]_{theo}$ = $[Crosslinker]/[CTA]$ for RAFT or $[C]/[PC]_{theo}$ = $[Crosslinker]/[Initiator]$ for ATRP. b η = $\frac{MW_{theo}}{MW_{exp}}$ see description of equation 9 for detail.

Table S3: RAFT and ATRP System parameters and gel points from literature-continuation of Table S2

Reference	Polymerization	Original sample code	Gel point /%	Overall monomer conc. /M	crosslinker function-ality	$[C]/[PC]_{theo}$ [a]	η [b]	Crosslinking tendency	η reference
S11	ATRP	$MA_{8.5}EG_{3.0}$	62	9.09	2	3.00	1.10	24.57	S12
S11	ATRP	$MA_{6.0}EG_{3.0}$	66	6.40	2	3.00	1.10	17.35	S12
S11	ATRP	$MA_{2.5}EG_{3.0}$	85	2.66	2	3.00	1.10	7.23	S12
S11	ATRP	$MA_{7.2}EG_{10}$	34	8.87	2	10.00	1.10	78.55	S12
S11	ATRP	$MA_{6.0}EG_{10}$	42	7.36	2	10.00	1.10	65.45	S12
S11	ATRP	$MA_{2.5}EG_{10}$	53	3.03	2	10.00	1.10	27.27	S12
S11	ATRP	$MA_{1.0}EG_{10}$	84	1.21	2	10.00	1.10	10.91	S12
S12	ATRP	GM-1.1	97	6.13	2	1.10	1.10	6.13	S12
S12	ATRP	GM-1.5	86	6.18	2	1.50	1.10	8.43	S12
S12	ATRP	GM-3.0	66	6.38	2	3.00	1.10	17.40	S12
S12	ATRP	GM-5.0	51	6.65	2	5.00	1.10	30.21	S12
S12	ATRP	GM-10.0	42	7.33	2	10.00	1.10	66.62	S12
S13	ATRP	Table 3 results	65	9.88	2	3.00	1.10	26.95	S12
S13	ATRP	Table 3 results	66	8.86	2	3.00	1.10	24.16	S12
S13	ATRP	Table 3 results	76	6.36	2	3.00	1.10	17.35	S12
S13	ATRP	Table 3 results	80	2.86	2	3.00	1.10	7.8	S12
S14	ATRP	2.2-2A	97	6.13	2	1.10	1.10	6.13	S12
S14	ATRP	2.2-3A	94	6.09	3	0.73	1.10	8.12	S12
S14	ATRP	2.2-4A	89	6.06	4	0.46	1.10	7.58	S12
S14	ATRP	2.2-5A	99	6.05	5	0.44	1.10	9.68	S12
S14	ATRP	3.0-2A	86	6.18	2	1.50	1.10	8.43	S12
S14	ATRP	3.0-3A	78	6.12	3	1.00	1.10	11.13	S12
S14	ATRP	3.0-4A	79	6.09	4	0.75	1.10	12.46	S12
S14	ATRP	3.0-5A	83	6.07	5	0.6	1.10	13.25	S12
S14	ATRP	4.0-2A	79	6.24	2	2.00	1.10	11.35	S12
S14	ATRP	4.0-3A	67	6.16	3	1.33	1.10	14.93	S12
S14	ATRP	4.0-4A	67	6.12	4	1.00	1.10	16.69	S12
S14	ATRP	4.0-5A	65	6.10	5	0.80	1.10	17.74	S12
S14	ATRP	4.0-6A	82	6.08	6	0.67	1.10	18.43	S12

a $[C]/[PC]_{theo} = [Crosslinker]/[CTA]$ for RAFT or $[C]/[PC]_{theo} = [Crosslinker]/[Initiator]$ for ATRP.
b $\eta = \frac{MW_{theo}}{MW_{exp}}$ see description of equation 9 for detail.

Table S4: RAFT and ATRP System parameters and gel points from literature-continuation of Table S3

Reference	Polymerization	Original sample code	Gel point /%	Overall monomer conc. /M	crosslinker function-ality	$[C]/[PC]_{theo}$ [a]	η [b]	Crosslinking tendency	η reference
[S14]	ATRP	10.0-2A	48	6.60	2	5.00	1.10	30.00	[S12]
[S14]	ATRP	10.0-3A	40	6.40	3	3.33	1.10	38.79	[S12]
[S14]	ATRP	10.0-4A	39	6.30	4	2.50	1.10	42.95	[S12]
[S14]	ATRP	10.0-5A	34	6.24	5	2.00	1.10	45.38	[S12]
[S14]	ATRP	10.0-6A	34	6.20	6	1.67	1.10	46.97	[S12]

a $[C]/[PC]_{theo}$ = $[Crosslinker]/[CTA]$ for RAFT or $[C]/[PC]_{theo}$ = $[Crosslinker]/[Initiator]$ for ATRP.
b $\eta = \frac{MW_{theo}}{MW_{exp}}$ see description of equation 9 for detail.

Table S5: CT analysis for methacrylic copolymer systems by RAFT and ATRP from Rosselgong *et al.*[S2]

Polymerization	Original sample code	MMA conc /wt%	conv. /%	Overall monomer conc. /M	$[C]/[PC]_{theo}$[b]	Crosslinking tendency[c]	X_g^{CT}[d] /%
ATRP	$PMMA_{50}$-$DSDMA_{1.0}$	10	97.6	0.89	1	0.99	141.9
ATRP	$PMMA_{50}$-$DSDMA_{3.0}$	10	96.7	0.93	3	3.08	112.3
ATRP	$PMMA_{50}$-$DSDMA_{5.0}$	10	96.9[a]	0.96	5	5.33	98.0
RAFT	$PMMA_{50}$-$DSDMA_{1.0}$	10	96.7	0.89	1	0.99	141.9
RAFT	$PMMA_{50}$-$DSDMA_{3.0}$	10	96.1	0.93	3	3.08	112.3
RAFT	$PMMA_{50}$-$DSDMA_{5.0}$	10	96.4	0.96	5	5.33	98.0[e]
ATRP	$PMMA_{50}$-$DSDMA_{1.25}$	30	99.1	2.73	1.25	3.79	107.0
ATRP	$PMMA_{50}$-$DSDMA_{1.5}$	30	98.9[a]	2.74	1.5	4.57	102.1[e]
RAFT	$PMMA_{50}$-$DSDMA_{1.5}$	30	98.7	2.74	1.5	4.57	102.1
RAFT	$PMMA_{50}$-$DSDMA_{1.6}$	30	98.5[a]	2.74	1.6	4.88	100.3
ATRP	$PMMA_{50}$-$DSDMA_{0.6}$	50	99.1	4.56	0.6	3.04	112.7
ATRP	$PMMA_{50}$-$DSDMA_{0.7}$	50	98.9	4.57	0.7	3.55	108.6
ATRP	$PMMA_{50}$-$DSDMA_{0.8}$	50	98.8	4.58	0.8	4.07	105.1
ATRP	$PMMA_{50}$-$DSDMA_{0.85}$	50	98.9	4.58	0.85	4.33	103.5
ATRP	$PMMA_{50}$-$DSDMA_{0.9}$	50	99.0	4.59	0.9	4.59	102.0
ATRP	$PMMA_{50}$-$DSDMA_{0.95}$	50	98.5[a]	4.59	0.95	4.85	100.5
RAFT	$PMMA_{50}$-$DSDMA_{0.6}$	50	96.2	4.56	0.6	3.04	112.7
RAFT	$PMMA_{50}$-$DSDMA_{0.7}$	50	96.5	4.57	0.7	3.55	108.6
RAFT	$PMMA_{50}$-$DSDMA_{0.8}$	50	97.3	4.58	0.8	4.07	105.1
RAFT	$PMMA_{50}$-$DSDMA_{0.85}$	50	96.1	4.58	0.85	4.33	103.5
RAFT	$PMMA_{50}$-$DSDMA_{0.9}$	50	96.6	4.59	0.9	4.59	102.0
RAFT	$PMMA_{50}$-$DSDMA_{0.95}$	50	96.1[a]	4.59	0.95	4.85	100.5

a Entries gelled.
b $[C]/[PC]_{theo} = [Crosslinker]/[CTA]$ for RAFT or $[C]/[PC]_{theo} = [Crosslinker]/[Initiator]$ for ATRP.
c η equals 0.9 according to Rosselgong *et al.*[S2]
d X_g^{CT} is the gel conversion predicted by linear regression in Figure 6, which $X_g^{CT} = 141.65 - 60 * log(CT)$.
e Entries fail to predict gelation by CT analysis.

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