SUPPORTING MATERIAL to

Chain Length Dependent Termination Rate Coefficients of Methyl Methacrylate (MMA) in the Gel Regime: Accessing $k_t^{i,i}$ using Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

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Surface Function of $k_t^{i,i}(x)$ for MMA at 80 ℃

$k_t^{i,i}(x)$ data was fit with a Fourier series bivariate polynomial surface function according to:

$$\log k_t^{i,i} = a + b\cos(x') + c\cos(y') + d\sin(x') + e\sin(y') + f\cos(2x') + g\cos(2y') + h\sin(2x') + i\sin(2y') + j\cos(x')\cos(y') + k\cos(x')\sin(y') + l\sin(x')\cos(y') + m\sin(x')\sin(y')$$

where *x'* is equal to the conversion (*x*) scaled from 0 to π, and *y'* is equal to *log i* scaled from 0 to π. The following numerical constants were used in the function

a = 7.552017301

b = 0.986723958

c = 1.05170365

d = -0.25827932

e = 0.344377396

f = -0.05650026

g = 0.061925297

h = -0.05985196

i = -0.14695416

j = -0.22194822

k = -0.72743255

l = -0.26547947

m = 0.250955657

Gel Effect Onset and the Overlap Concentration for VAc and MA

Analysis of the $k_t^{i,i}(x)$ data for methyl acrylate[1] (MA) and vinyl acetate[2] (VAc) polymerizations showed good agreement between c^* (theory) and $x_{\text{gel-onset}}$.

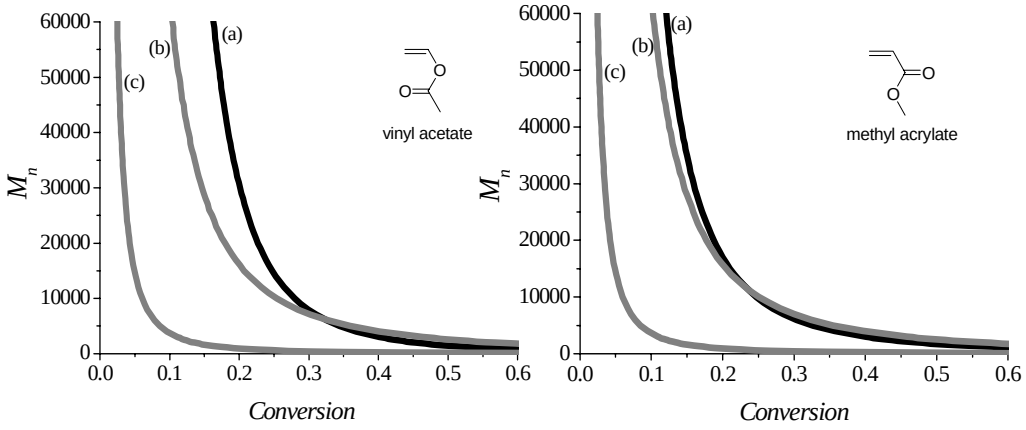

Figure S1. Gel onset conversion profiles for RAFT-mediated polymerizations of (A) vinyl acetate (VAc)[2] and (B) methyl acrylate (MA)[1]. Curve (a) represents $x_{\text{gel-onset}}$ determined from experimental data, (b) theoretical c^*_{max} calculated from eq 5a, and (c) theoretical c^*_{min} calculated from eq 5b. Parameters used to calculate c^*_{min} and c^*_{max} for VAc were $C_\infty = 8.9$[3], $l = 3.14$ Å[4], and $mw = 86.1$ g mol^{-1}.Parameters used to calculate c^*_{min} and c^*_{max} for MA were $C_\infty = 7.9$[4], $l = 3.40$ Å[4], and $mw = 86.1$ g mol^{-1}.

TERMINATION MODELS

Mahabadi and O'Driscoll Model:

The approach proposed by O'Driscoll and coworkers[5,6] is outlined in eq's S1a to S1e and describes one of the more complicated models for termination. This approach considers termination between two flexible polymers undergoing both translational diffusion (F_1 in eq S1b), and segmental diffusion (F_2 in eq S1c)[5], where k_β is Boltzmanns constant, N_{av} Avogadro's number, T the temperature (K), σ the capture radius, a_m the hydrodynamic radius of a monomeric unit, N_0 the number of monomeric units in a segment, η_0 the solvent viscosity, ζ_{sp} and ζ_0 the polymer segmental and segment friction coefficients, α_i the intramolecular linear expansion coefficient of an *i*-mer, and *i* and *j* the chain lengths of two terminating radicals. At infinite dilution F_1 is rate controlling, however, as conversions increase F_2 cancels out F_1 introducing segmental diffusion as the rate determining step. Beyond dilute solution regimes O'Driscoll proposed a critical or 'entangled' chain length (X_c, eq S1d) to account for onset of the gel effect above which $k_t^{i,i}$ is replaced by an 'entangled' rate coefficient $k_{te}^{i,i}$ (eq's S1d & S1e)[6]. Values of 7.33 and 0.136 were derived from the experimental data for K_c and α_0, respectively[6]. In the present article the following parameters were also used; σ=3.0 Å[5], N_0 =4.84[5], a_m= 5.0 Å[4], β=0.5[6], η_0 =0.0095 poise[5, 7], ζ_0/ζ_{sp}=5[5], and α_i was calculated using $\alpha_i=0.857 \cdot i^{0.0473}$ (at 298K)[5] and corrected with respect to temperature according to $\alpha_i \propto R_g^2$,[8, 9] where $\ln(R_g^2)=\kappa \cdot T$ and κ=100 K^{-1}.[4]

$$k_t^{i,j} = F_1(T,\zeta_0)\cdot F_2(\alpha_i,\alpha_j,i,j)$$

(S1a)

$$F_1(T,\zeta_0) = \frac{4\cdot 10^{-3} N_{av} k_B T \sigma}{3 a_m N_0 \eta_0 \left(\frac{\zeta_0}{\zeta_{sp}}\right)}$$

(S1b)

$$F_2(\alpha_i,\alpha_j,i,j) = (\alpha_i\alpha_j)^{-1.3}\left[1-\frac{0.37}{(\alpha_i\alpha_j)^{0.37}}\left\{1-4\sqrt{\frac{2N_0}{3\pi\alpha_i\alpha_j}(i\cdot j)^{-0.5}}\right\}\right]$$

(S1c)

$$if\ i > X_c,\ k_t^{i,i} = k_{te}^{i,i},\ X_c = \left(\frac{\phi_p}{K_c}\right)^{\beta}$$

(S1d)

$$k_{te}^{i,i} \equiv \alpha^2 k_t^{i,i}, \alpha = \frac{b}{\alpha_0 k_t^{i,i}}$$

(S1e)

Russell and Gilbert Model:

Gilbert et al approached termination in terms of the Smoluchowksi equation[10] which was originally developed to describe diffusion-controlled reactions in colloids; or more accurately colloidal aggregation. This approach is described in eq's S2a to S2d and combines the Smoluchowksi equation with an empirically derived chain length dependent self diffusion coefficient (eq S2b). In this approach *p* represents the probability of a radical pair possessing parallel spin, and D_i is the chain length dependent self diffusion coefficient for a *i*-mer[11-13]. To account for D_i (eq S2d), terms

for centre of mass diffusion (eq S2b) and reaction diffusion are introduced (eq S2c). Hence macromolecular diffusion is accounted for at low and intermediate conversions by translational diffusion until higher conversions where translational diffusion is negligible and reaction diffusion (eq S2d) becomes the only means by which diffusion may take place. A handful of different values for the scaling exponent u have been used in conjunction with this model, including a critical chain length concept[13] similar to the description introduced by O'Driscoll. In this study, however, we implemented the conversion dependent scaling exponent determined for PMMA by Griffiths et al, $u=0.664+2.02x$.[11] The following parameters were also introduced into this model: l = 1.54 Å,[14] σ was assumed equal to $2 \cdot l$,[13] p was taken as 0.25,[13] and D_{mon} was introduced and corrected for temperature using the empirical expression described in reference [11].

$$k_{\text{t}}^{i,j} = 4 \cdot \pi \cdot p \cdot \sigma \cdot \left(D_i + D_j \right) \cdot N_{\text{av}}$$

(S2a)

$$D^{\text{COM}}{}_i = D_{\text{mon}} i^{-u(x)}$$

(S2b)

$$D^{\text{RD}}{}_i = \frac{k_{\text{p}}[M]\, l^2}{6}$$

(S2c)

$$D_i = D^{\text{RD}}{}_i + D^{\text{COM}}{}_i$$

(S2d)

Ross and Laurence Model:

The Ross-Laurence correlation[15] described in eq's S3a to S3h has been consistently used in the literature to fit experimental data in studies involving both conventional FRP and LRP[16-18]. Popularity of this approach can no doubt be assigned to its simplicity and reasonable success rate. By examining experimental data Ross and Laurence correlated the onset of the gel effect to a critical free volume $V_F^{(gel)}$, either side of which $\langle k_t \rangle$ was described as scaling with free volume V_F according to a dilute solution expression (eq S3c) or gel regime expression (eq S4e). Parameters used with this model include T_g^P=392 K and T_g^M=143 K.[15]

$$\langle k_t \rangle = k_t^0 \cdot g_t$$

(S3a)

$$V_F < V_F^{(gel)}, g_t = g_t\left(V_F, T\right)^{(dilute)}$$

(S3b)

$$g_t\left(V_F, T\right)^{(dilute)} = 0.10575 \exp\left(17.15 \cdot V_F + 0.01715 \cdot T\right)$$

(S3c)

$$V_F \geq V_F^{(gel)}, g_t = g_t\left(V_F, T\right)^{(concentrated)}$$

(S3d)

$$g_t\left(V_F, T\right)^{(concentrated)} = 2.3 \cdot 10^{-6} \exp\left(75 \cdot V_F\right)$$

(S3e)

$$V_F^{(gel)} = 0.1856 - 2.965 \cdot 10^{-4} T$$

(S3f)

$$V_F = C^{\mathrm{M}} \cdot V_{\mathrm{F}}^{\mathrm{M}} + C^{P} \cdot V_{\mathrm{F}}^{\mathrm{P}}$$

(S3g)

$$V_{\mathrm{F}}^{\mathrm{M}} = 0.25 + 0.001 \cdot (T - T\mathrm{g}^{\mathrm{M}})$$

(S3h)

$$V_{\mathrm{F}}^{\mathrm{P}} = 0.25 + 4.8 \cdot 10^{-4} \cdot (T - T\mathrm{g}^{\mathrm{P}})$$

(S3j)

Peklak Model:

Peklak et al[19] recently approached this problem for the RAFT mediated polymerization of MMA and styrene by combining the two stage encounter-pair model described in eq S4a, the Smoluchowksi equation and eq's S2b, S2c & S2d similar to Gilbert and coworkers. The encounter pair model is commonly neglected from expressions involving the Smoluchowksi equation since the rate of chemical reaction k_t^0 is very rapid. Peklak et al., however, used a k_t^0 value of $9.8 \cdot 10^7 \exp(-2933/R \cdot T)$ that was taken from conventional FRP studies; a value much lower than traditional estimates of the diffusion-controlled termination rate coefficient of two 1-mers (eg $k_t^{1,1} \sim 1 \times 10^9$). In this approach D_{mon} was calculated according to the Vrenta-Dudas free volume theory[20-24] for small molecule diffusion according to eq's S4b & S4c and eq S3f, which assumes the ability of a molecule to diffuse depends on the amount of empty space. To account for chain length and conversion effects these authors also implemented *u* (eq S2b) as an adjustable parameter, leading to a best fit estimate of $u=0.664+1.616 \cdot x$. Other parameters used in conjunction with this model include $D_0=1.61 \cdot 10^{-7}$ $m^2 s^{-1}$, $E=3.26 \cdot 10^3$ J mol^{-1}, $K_{1M}/\gamma=8.15 \cdot 10^{-7}$ m^3 kg^{-1} K^{-1},

K_{1P}/γ=4.77·10^{-7}m^3 kg^{-1} K^{-1}, V_M^*8.70·10^{-4} m^3 kg^{-1}, V_P^*=7.57·10^{-4} m^3 kg^{-1}, ξ_{MP}=0.6, K_{2M} 143 K, K_{2P}=52.4 K, α_M=1, Tg^P=392 K, Tg^M =143 K, σ_M = 6.9·10^{-10} m,[19] and C^M and C^P represent the volume fraction of monomer and polymer, respectively.

$$\frac{1}{k_t^{i,i}} = \frac{1}{k_t^{0}} + \frac{1}{k_t^{i,i(\mathrm{diff})}} \tag{S4a}$$

$$D_{\mathrm{mon}} = D_0 \exp\left(-\frac{E}{RT} - \frac{\gamma\left(\Phi_M V_M + \Phi_P \xi_{MP} V_P\right)}{V_F} \right) \tag{S4b}$$

$$V_F^X = K_1^X \left[K_2^X + \alpha^X \left(T - Tg^X \right) \right] \tag{S4c}$$

Table S1. Time, conversion, molecular weight (M_n) and polydispersity (M_w/M_n) data for the cyanoisoprop-2-yl dithiobenzoate (CPDB) mediated bulk polymerization of methyl methacrylate (MMA) at 80°C using azobis (isobutyronitrile) (AIBN) as initiator. Concentrations of AIBN and CPDB were, experiment 1 [AIBN] 2.01 mM, [CPDB] = 0 mM; experiment 2 [AIBN] = 2.01 mM, [CPDB] = 2.13 mM.

Experiment	*Time* (min)	*Conversion*	M_n	M_w/M_n
1	20	0.06	509600	1.92
	49	0.17	296000	1.86
	75	0.27	346800	2.04
	99	0.42	157000	1.42
	135	0.99	962700	3.35
	155	0.99	782000	3.91
	175	0.99	721900	2.88
2	5.0	0.02	40500	1.41
	10	0.04	44400	1.49
	16	0.06	52000	1.44
	20	0.08	59400	1.40
	30	0.12	73400	1.35
	35	0.14	78700	1.39
	40	0.16	81700	1.39
	45	0.18	96700	1.31
	75	0.28	78900	1.42
	99	0.54	116600	1.42
	115	0.55	115500	1.63
	195	0.95	188000	1.58
	215	0.97	190100	1.59

Table S2. Time, conversion, molecular weight (M_n) and polydispersity (M_w/M_n) data for the cyanoisoprop-2-yl dithiobenzoate (CPDB) mediated bulk polymerization of methyl methacrylate (MMA) at 80°C using azobis (isobutyronitrile) (AIBN) as initiator. Concentrations of AIBN and CPDB were, experiment 3 [AIBN] 1.99 mM, [CPDB] = 4.98 mM; experiment 4 [AIBN] = 2.01 mM, [CPDB] = 9.93mM.

Experiment	*Time* (min)	*Conversion*	M_n	M_w/M_n
3	7.5	0.03	17200	1.56
	15	0.06	21900	1.48
	20	0.08	26000	1.40
	26	0.10	30200	1.37
	30	0.12	31800	1.37
	40	0.13	36500	1.22
	35	0.14	35600	1.34
	40	0.16	38600	1.32
	45	0.18	41900	1.30
	50	0.20	47500	1.28
	55	0.22	51200	1.28
	55	0.22	46500	1.20
	60	0.30	58300	1.17
	86	0.38	65900	1.19
	105	0.50	82200	1.18
	126	0.66	91000	1.18
4	7.5	0.04	8300	1.63
	15	0.06	10900	1.51
	20	0.09	13500	1.43
	25	0.11	16900	1.36
	32	0.12	20200	1.30
	35	0.14	22100	1.29
	40	0.16	25500	1.27
	45	0.17	28800	1.25
	50	0.19	33100	1.22
	60	0.24	34700	1.14
	85	0.32	41300	1.13
	105	0.41	43000	1.14
	125	0.46	64000	1.10

Table S3. Time, conversion, molecular weight (M_n) and polydispersity (M_w/M_n) data for the cyanoisoprop-2-yl dithiobenzoate (CPDB) mediated bulk polymerization of methyl methacrylate (MMA) at 80°C using azobis (isobutyronitrile) (AIBN) as initiator. Concentrations of AIBN and CPDB were, experiment 5 [AIBN] 2.28 mM, [CPDB] = 19.9 mM; experiment 6 [AIBN] = 8.83 mM, [CPDB] = 54.4 mM.

Experiment	*Time* (min)	*Conversion*	M_n	M_w/M_n
5	7.5	0.02	4000	1.42
	15	0.05	5100	1.40
	20	0.09	9000	1.23
	20	0.07	5700	1.43
	25	0.08	6400	1.41
	30	0.10	7300	1.37
	35	0.12	8100	1.30
	40	0.14	9200	1.31
	45	0.16	9800	1.30
	48	0.20	14400	1.15
	50	0.17	11000	1.27
	60	0.22	15100	1.15
	85	0.34	20000	1.12
	105	0.38	23200	1.10
	125	0.44	25100	1.10
	147	0.48	27000	1.09
	170	0.58	32900	1.07
	185	0.60	31200	1.08
	225	0.65	31700	1.10
6	20	0.09	2900	1.31
	28	0.13	4000	1.21
	37	0.18	6200	1.13
	52	0.23	7800	1.11
	68	0.30	10000	1.12
	87	0.38	12300	1.14
	97	0.42	13100	1.17
	103	0.43	13800	1.19
	130	0.53	16300	1.19
	290	0.89	23700	1.35
	310	0.89	24400	1.31

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