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Accessory Publication

The Mechanism of Diffusion-Controlled Termination in Semi-Dilute and Concentrated Polymer Solutions: Linear, 4-Arm and 6-Arm Star Polystyrene Matrices

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Table S1. Reaction conditions used for the polymerization of styrene (STY) initiated with 1,1- azobis (cyclohexanecarbonitrile) (VAZO-88) at 90 °C, in the presence of monofunctional RAFT agent *cumyl phenyldithioacetate* (CPDA), 4-arm-star RAFT agent *pentaerythritoltetrakis(3-(s-benzyltrithiocarbonyl)propionate*) (4-BTTC), and 6-arm-star RAFT agent *dipentaerythritolhexakis(3-(s-benzyltrithiocarbonyl)propionate*) (6-BTTC).

Expt	T ℃	Monomer	RAFT Agent	$[RAFT]_0$ (mM)	$[VAZO\text{-}88]_0$ (mM)
1	90	STY	CPDA	9.98	11.0
2	90	STY	CPDA	25.0	6.41
3	90	STY	CPDA	49.8	12.4
4	90	STY	CPDA	94.3	41.6
5	90	STY	4-BTTC	9.98	4.92
6	90	STY	4-BTTC	25.1	12.5
7	90	STY	4-BTTC	50.0	25.0
8	90	STY	4-BTTC	100	49.7
9	90	STY	6-BTTC	24.6	12.3
10	90	STY	6-BTTC	48.6	24.3
11	90	STY	6-BTTC	98.6	49.2
12	90	STY	6-BTTC	198.2	99.0

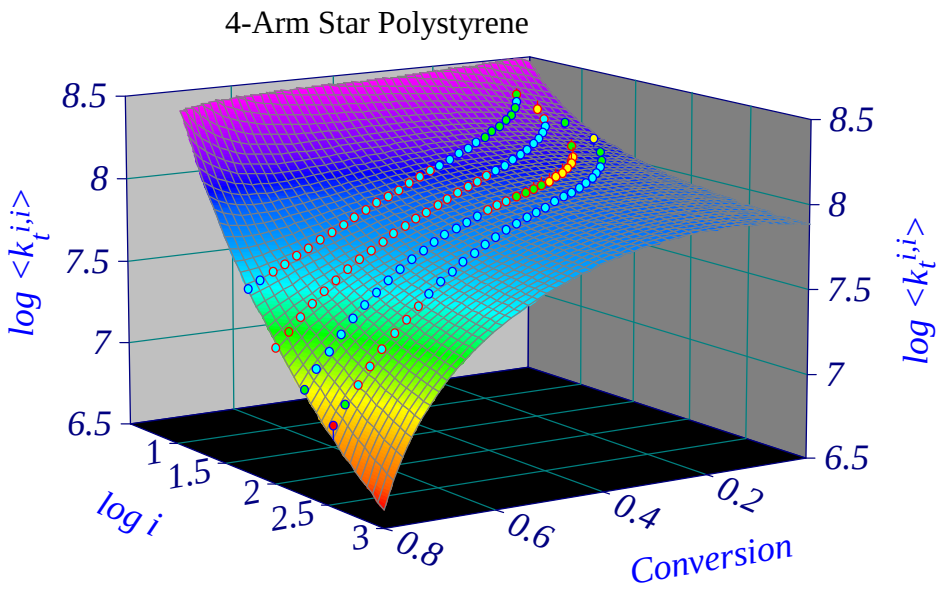

Figure S1. Three dimensional plot of the termination rate coefficients, k_t's, for RAFT-mediated styrene (STY) polymerized in bulk and in the presence of the 4-arm star RAFT agent *pentaerythritoltetrakis(3-(s-benzyltrithiocarbonyl)propionate)* (4-BTTC), initiated with 1,1- azobis (cyclohexanecarbonitrile) (VAZO88) at 90 °C. The data was fit with a surface plot using TableCurve 3D software ($r^2 > 0.99$). Drop lines indicate some minor deviation from the surface fit function.

Figure S2. Three dimensional plot of the termination rate coefficients, kt's, for the RAFT-mediated bulk polymerisation of styrene (STY) in the presence of the 6-arm star RAFT agent dipentaerythritol hexakis(3-(s-benzyltrithiocarbonyl)propionate) (6-BTTC) with 1,1- azobis (cyclohexanecarbonitrile) (VAZO88) as initiator at 90 °C. The data was fit with a surface plot using TableCurve 3D software ($r2 > 0.99$). Drop lines indicate some minor deviation from the surface fit function.

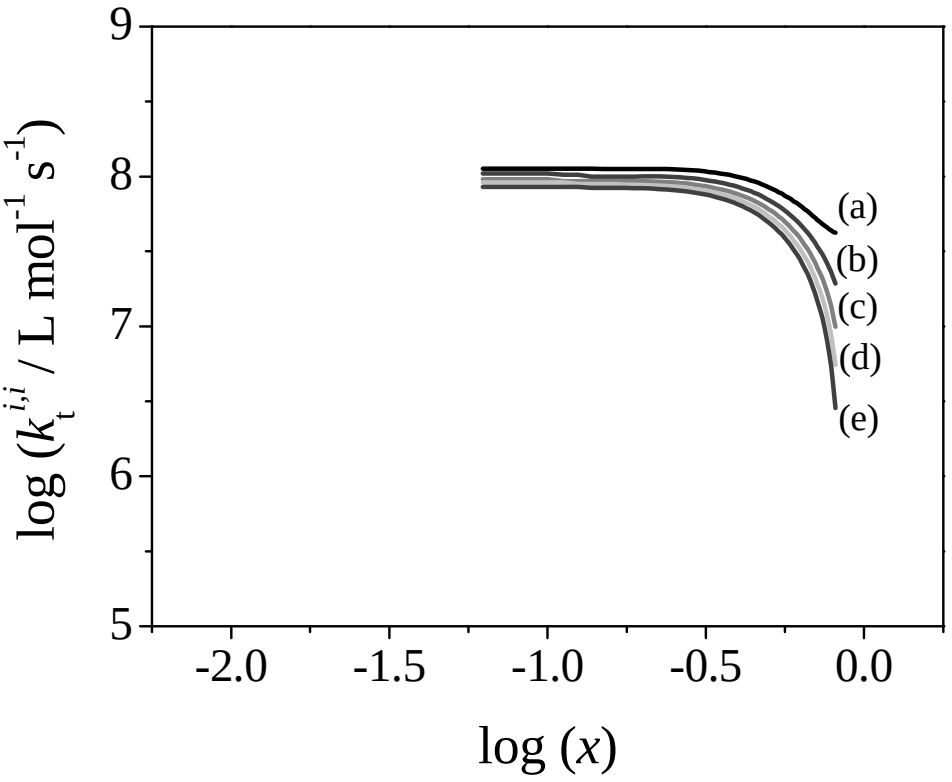

Figure 3. log-log plot of the chain length and conversion dependent termination rate coefficient, $k_t^{i,i}(x)$, vs conversion, x, extracted from the 3-dimensional log $k_t^{i,i}(x)$ vs log i vs x surface profile for the RAFT-mediated polymerization of styrene (STY, 8.15 M) at 90°C using 4-arm star RAFT agent pentaerythritoltetrakis(3-(s-benzyltrithiocarbonyl)propionate) (4-BTTC), initiated with 1,1- azobis (cyclohexanecarbonitrile) (VAZO88) at 90 °C.

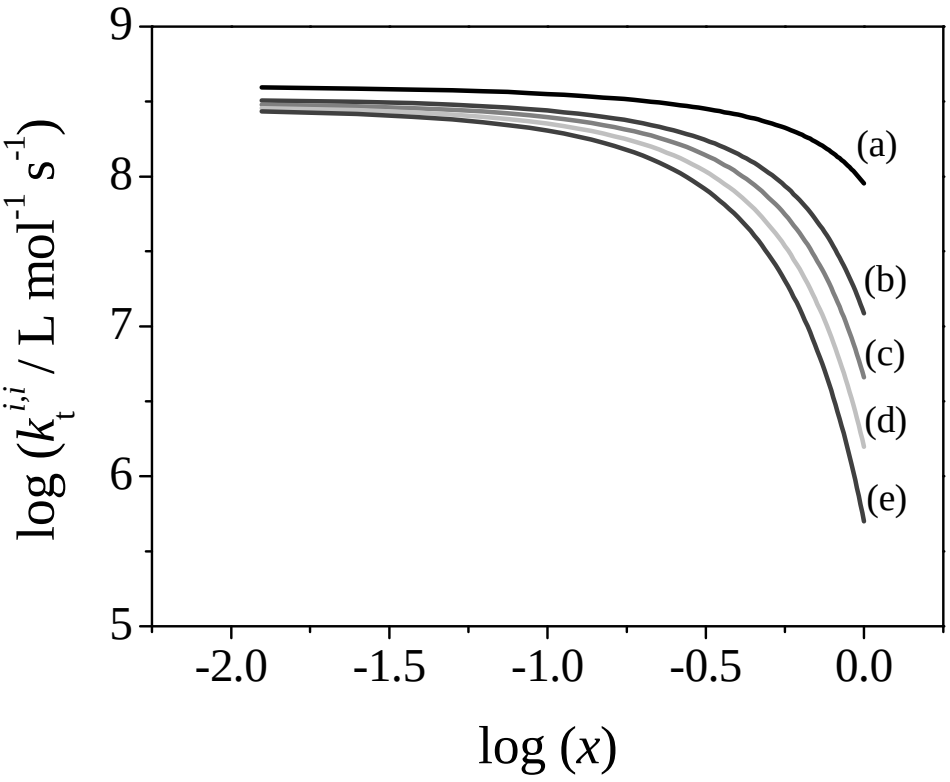

Figure 4. log-log plot of the chain length and conversion dependent termination rate coefficient, $k_t^{i,i}(x)$, vs conversion, x, extracted from the 3-dimensional log $k_t^{i,i}(x)$ vs log i vs x surface profile for the RAFT-mediated polymerization of styrene (STY, 8.15 M) using the 6-arm star RAFT agent dipentaerythritol hexakis(3-(s-benzyltrithiocarbonyl)propionate) (6-BTTC) with 1,1- azobis (cyclohexanecarbonitrile) (VAZO88) as initiator at 90 °C