

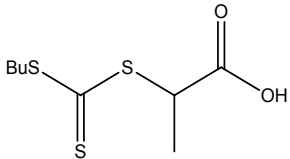
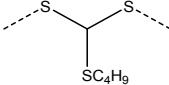
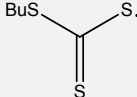
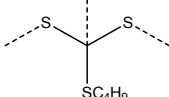
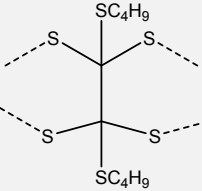

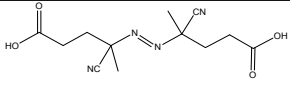
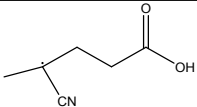
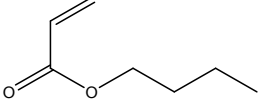
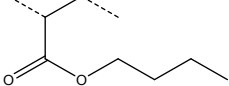
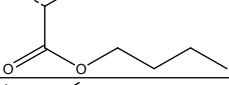
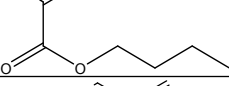


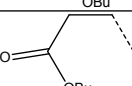
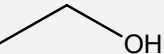
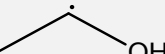
SUPPORTING INFORMATION

Determining the effect of side reactions on product distributions in RAFT polymerization by MALDI-TOF MS

Antonio Veloso, Wendy García, Amaia Agirre, Nicholas Ballard, Fernando Ruipérez, José C. de la Cal & José M. Asua[†]

POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta R&D Ctr, Avda. Tolosa-72, Donostia-San Sebastián 20018, Spain

Table 1S. Molecular structure of the reagents used in the RAFT reaction and the possible formed radicals. The molecular formula and exact mass of each ion is shown.

Reagent	Name	Structure	Ion	Molecular formula	<i>m/z</i> (Da)
RAFT agent	TTCA-4			C ₅ H ₁₀ S ₃ (2-arm stars)	165.99
				C ₅ H ₉ S ₃	164.99
				C ₅ H ₉ S ₃ (3-arm stars)	164.99
				C ₁₀ H ₁₈ S ₆ (4-arm stars)	329.97
				C ₃ H ₅ O ₂ (R)	73.03
Initiator	V-501			C ₆ H ₈ NO ₂ (I)	126.06
Monomer	BA			C ₇ H ₁₂ O ₂	128.08
				C ₇ H ₁₃ O ₂	129.09
				C ₇ H ₁₁ O ₂	127.07
				*C ₈ H ₁₃ O ₂	141.09
				*C ₆ H ₁₁ O ₂	115.08
				*C ₇ H ₁₃ O ₂	129.09
Solvent	Ethanol			C ₂ H ₅ O	45.03

*Generated after backbiting and β scission^{22, 57}

Table 2S. Proposed pBA structures for spectral peaks in order to verify all the explained species. The same MALDI-TOF analysis was performed using KTFA cationization agent. As expected, all the series were related to the previous assigned series from S1 to S5, but in this case there were related to potassium adducts. In this table, it can be seen both end-groups for each polymer series, the number of BA units, the detected adducts, theoretical m/z values ($(m/z)_{cal}$), the experimentally obtained values ($(m/z)_{exp}$) and the error between theoretical and experimental values in Daltons. Most of the calculated errors are acceptable, having a value lower than 0.2 Da.

Label (series)	Z group	BA units	R group	Adduct	$(m/z)_{cal}$	$(m/z)_{exp}$	Error (Da)
S1	C ₅ H ₉ S ₃	13	R	Na	1926.093	1925.990	-0.103
		18			2566.521	2566.394	-0.127
S2	H	14	R	Na	1890.198	1890.105	-0.093
		19			2530.607	2530.503	-0.104
S3	C ₅ H ₉ S ₃	13	R	Na ₂ -H	1948.075	1947.970	-0.105
		18			2588.481	2588.374	-0.107
S4	H	14	R	Na ₂ -H	1912.180	1912.084	-0.096
		19			2552.596	2552.475	-0.121
S5	C ₈ H ₁₃ O ₂	13	R	Na	1902.198	1902.101	-0.097
		18			2542.617	<i>Low int.</i>	-
S6 (S1+K)	C ₅ H ₉ S ₃	13	R	K	1942.067	1942.000	-0.067
		18			2582.486	2582.434	-0.052
S7 (S2+K)	H	14	R	K	1906.172	1906.117	-0.055
		19			2546.591	2546.534	-0.057
S8 (S3+Na+K-H)	C ₅ H ₉ S ₃	13	R	Na+K-H	1964.049	1963.981	-0.068
		18			2604.468	2604.380	-0.088
S9 (S4+Na+K-H)	H	14	R	Na+K-H	1928.154	1927.065	-1.089
		19			2568.573	2567.434	-1.139
S10 (S5+K)	C ₈ H ₁₃ O ₂	13	R	K	1918.172	1918.125	-0.047
		18			2558.590	<i>Low int.</i>	-

R is the leaving group (C₃H₅O₂) of the RAFT agent and (C₈H₁₃O₂) is the end-group from the backbiting and β -scission reaction. "*Low int.*" is written because the exact mass value of the spectral peak has low intensity.

Mathematical model

In order to understand the origin of the multiple species and their relative abundance, a mathematical model that solves the differential equations for the material balances for all species including the end-groups was constructed.

The material balances for initiator [I] and monomer [M] concentrations are given by

$$\frac{d[I]}{dt} = -k_d[I] \quad (1)$$

$$\frac{d[M]}{dt} = -k_p[M] \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_y P_s] - k_{p3}[M] \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_y P_{3,s}] - k_{fm}[M] \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_y P_s]$$

(2)

Where k_d is the rate coefficient for decomposition of the initiator; k_p and k_{p3} are the rate coefficients for propagation of secondary and tertiary radicals respectively; k_{fm} is the rate coefficient for chain transfer to monomer; and $[X_y P_s]$ and $[X_y P_{3,s}]$ are secondary and tertiary radical respectively with s butyl acrylate molecules in the chain and end group X_y where $y=1,2,3,4$ for initiator, R group, solvent derived radicals and the small radicals formed in one of the pathways of β scission shown in Scheme 1 respectively. The material balances for the initiator radicals $[I]$, radicals from the RAFT R group $[R]$, solvent radicals $[S]$, for secondary and tertiary radicals with end groups X_y , $[X_y P_n]$ and $[X_y P_{3,n}]$, and for RAFT intermediate radicals with chain ends X_y and X_z on either arm, $[X_y P_n RAFT P_m X_z]$, are given by

$$\begin{aligned} \frac{d[I]}{dt} &= 2fk_d[I] - k_p[M][I] - k_a[I] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_s RAFT] + \frac{1}{2}k_f \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_s RAFT P_0 X_1] - k_t[I] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_s] \end{aligned} \quad (3)$$

$$\frac{d[R]}{dt} = -k_p[M][R] - k_a[R] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_s RAFT] + \frac{1}{2}k_f \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_s RAFT P_0 X_2] - k_t[R] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_s] \quad (4)$$

$$\begin{aligned} \frac{d[S]}{dt} &= k_{ctf_s}[S] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_s] - k_p[M][S] - k_a[S] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_s RAFT] + \frac{1}{2}k_f \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_s RAFT P_0 X_1] \\ &\quad - k_t[S] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_s] \end{aligned} \quad (5)$$

$$\begin{aligned}
& \frac{d[X_y P_n]}{dt} \\
&= k_p[M][X_y P_{n-1}] - k_p[M][X_y P_n] - k_a[X_y P_n] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_s RAFT] + \frac{1}{2} k_f \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_y P_n RAFT P_s X_z] \\
& k_t[X_y P_n] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_s] - k_{t23}[X_y P_n] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_{3^{\circ},s}] - k_{bb}[X_y P_n][n \geq 3] + k_{p3}[M] \\
& [X_y P_{3^{\circ},n-1}] - k_{ct}[X_y P_n][S] + \frac{1}{2} k_{\beta}[X_y P_{3^{\circ},n+3}] - k_{pMM}[X_y P_n] \sum_{s=0}^{\infty} [HP_s MM] \\
& (6)
\end{aligned}$$

$$\begin{aligned}
& \frac{d[X_y P_{3^{\circ},n}]}{dt} \\
&= k_{bb}[X_y P_n][n \geq 3] - k_{p3}[M][X_y P_{3^{\circ},n}] - k_{\beta}[X_y P_{3^{\circ},n}] + k_{pMM} \sum_{s=0}^{\infty} [X_y P_{n-s}] [HP_s MM] - k_{t23}[X_y P_{3^{\circ},n}] \sum_{s=0}^{\infty} \\
& - k_{t3}[X_y P_{3^{\circ},n}] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_z P_{3^{\circ},s}] \\
& (7)
\end{aligned}$$

$$\frac{d[X_y P_n RAFT P_m X_z]}{dt} = k_a[X_y P_n][X_z P_m RAFT] + k_a[X_z P_m][X_y P_n RAFT] - \frac{1}{2} k_f[X_y P_n RAFT P_m X_z] \quad (8)$$

Where k_a is the rate coefficient for addition of a growing radical to the RAFT agent; k_f is the rate coefficient for fragmentation of the RAFT intermediate radical; k_t , k_{t23} and k_{t3} are the rate coefficients for termination of the between secondary radicals, between secondary and tertiary radicals and between tertiary radicals respectively; k_{bb} is the rate coefficient for intramolecular transfer to polymer; k_{ct} is the rate coefficient for chain transfer to solvent; k_{β} is the rate coefficient for β scission of the tertiary radicals; k_{pMM} is the rate coefficient for propagation of the macromonomer terminated species; f is the initiator efficiency; f_s is the fraction of solvent radicals that will undergo propagation; $[X_y P_n MM]$ are macromonomer terminated species with n butyl acrylate units in the polymer chain and end group X_y ; and $[X_y P_n RAFT]$ are dormant RAFT species with n butyl acrylate units in the polymer chain and end group X_y . Propagation of radical $[X_y P_n]$ to macromonomer $[X_y P_s MM]$ results in a midchain radical with two end groups. Since this reaction is rare and impacts very little on the product distribution but adds significant complication to the tracking of end groups and expands greatly the number of equations to be solved its effect was not accounted for in the model. The intramolecular transfer reaction was assumed to react via a six membered ring state and therefore the products of the β scission of the resulting midchain radical were assumed to be those shown in Scheme 1 based on the experimental observations shown herein. The subsequent β scission reaction is assumed to proceed by the two pathways shown in Scheme 1 at an equal rate. In addition, no additional rate coefficients are introduced to account for the initial RAFT equilibrium shown in Scheme 1. Although the initial RAFT equilibrium is important when considering reaction kinetics, particularly at early times, at long reaction times and high conversion as studied herein there will be little observable effect of the initial RAFT equilibrium process and therefore this assumption should have little impact on the results.

The value for the backbiting rate coefficient was adjusted depending on the experimental conditions in accordance with known effects of hydrogen bonding solvents and reversible deactivation on this reaction. Hutchinson and co-workers^{41, 42} have demonstrated that in the presence of butanol as solvent a reduction in the backbiting rate coefficient by a factor of

approximately 3 compared to bulk polymerization was observed. Therefore reactions conducted in ethanol were simulated with the rate coefficient for backbiting lowered by a fraction of 3. Similarly it is known that reactions conducted under reversible deactivation reduce the amount of products arising from the backbiting reaction. From previous work using a trithiocarbonate RAFT agent at 80 °C at similar relative concentration of RAFT agent to monomer as the reactions described here, the rate of backbiting was reduced by a factor of 1.5⁴⁴ and therefore this reduction was applied to all simulations conducted in this work.

The material balances for RAFT dormant species are given by

$$\frac{d[X_yP_nRAFT]}{dt} = -k_a[X_yP_nRAFT] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_zP_s] + \frac{1}{2}k_f \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_yP_nRAFTP_sX_z] \quad (9)$$

Finally, the material balances for hydrogen terminated chains $[X_yP_nH]$ arising from chain transfer to solvent, and macromonomers are given by

$$\frac{d[X_yP_nH]}{dt} = k_{ct}[X_yP_n][S] + k_{fm}[X_yP_n][M] \quad (10)$$

$$\frac{d[X_yP_nMM]}{dt} = \frac{1}{2}k_{\beta}[X_yP_{3^{\circ},n+2}] - k_{pMM}[X_yP_nMM] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_zP_s] \quad (11)$$

In the absence of migration of the midchain radical the rate of formation of oligomeric macromonomer is given by

$$\frac{d[HP_3MM]}{dt} = \frac{1}{2}k_{\beta} \sum_{s=3}^{\infty} \sum_{z=1,2,3} [X_zP_{3^{\circ},s}] - k_{pMM}[HP_3MM] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_zP_s] \quad (12)$$

The effect of the RAFT equilibrium on the tertiary radicals is ignored because inclusion results in a substantial increase in the number of equations to be solved and has little effect on the result if it is assumed that equilibrium between the active and dormant species is rapid⁵⁸. The rate coefficients for formation and fragmentation of the intermediate RAFT radicals were estimated based on low temperature EPR studies of butyl acrylate polymerization in the presence of trithiocarbonate RAFT agents at low temperature⁵⁹. It should be noted that if it is assumed that k_a is on the order of 10⁶ or higher and the rate of fragmentation is fast such that intermediate radicals have negligible effect on the polymerization there is virtually no effect of the rate coefficients on product distributions. The former assumption is justified by the low polydispersity index of the produced polymers and the latter by the lack of observation of any products arising from termination of the intermediate radicals in the MALDI spectra.

Analysis of effect of chain transfer on living fraction

The rate of formation of dead chains due to transfer to monomer $[C_{mon}]$ is given by

$$\frac{d[C_{mon}]}{dt} = k_{fm}[M][P\cdot] \quad (13)$$

Where $[P\cdot]$ is the propagating radical concentration. The material balance for the monomer is given by

$$\frac{d[M]}{dt} = -k_p[M][P\cdot] - k_{p3}[M][P_3\cdot] - k_{fm}[M][P\cdot] \quad (14)$$

Taking the ratio of these two gives

$$\frac{d[C_{mon}]}{d[M]} = -\frac{k_{fm}[P\cdot]}{k_p[P\cdot] + k_{p3}[P_3\cdot] + k_{fm}[P\cdot]} \quad (15)$$

Under steady state conditions the tertiary radical concentration, $[P_3\cdot]$, is given by

$$[P_3\cdot] = \frac{k_{bb}[P\cdot]}{k_\beta + k_{p3}[M]} \quad (16)$$

And combining with Equation B.3 gives

$$\frac{d[C_{mon}]}{d[M]} = -\frac{k_{fm}}{k_p + \frac{k_{p3}k_{bb}}{k_\beta + k_{p3}[M]} + k_{fm}} \quad (17)$$

Which when integrated and assuming $k_p \gg k_{fm}$ gives

$$[C_{mon}] = -\frac{k_{fm}}{k_p^2} \left(k_{bb} \ln \frac{(k_{p3}k_{bb} + k_p k_\beta + k_p k_{p3}[M]_0)}{(k_{p3}k_{bb} + k_p k_\beta + k_p k_{p3}(1-X)[M]_0)} - k_p X[M]_0 \right) \quad (18)$$

If no chain transfer to polymer is assumed (*i.e.* $k_{bb} = 0$) then the following is obtained

$$[C_{mon}] = \frac{k_{fm}}{k_p} [M]_0 X \quad (19)$$

Similarly the rate of formation of dead chains due to transfer to solvent $[C_s]$ is given by

$$\frac{d[C_s]}{dt} = k_{ct}[S][P] \quad (20)$$

assuming a constant solvent concentration. Taking the ratio of this and the material balance of the monomer gives

$$\frac{d[C_s]}{d[M]} = - \frac{k_{ct}[S][P]}{k_p[P][M] + k_{p3}[P_3][M] + k_{fm}[P][M]} \quad (21)$$

Assuming the steady state condition for tertiary radicals (Equation B.4) this gives

$$\frac{d[C_s]}{d[M]} = - \frac{k_{ct}[S]}{[M] \left(k_p + \frac{k_{p3}k_{bb}}{k_\beta + k_{p3}[M]} + k_{fm} \right)} \quad (22)$$

Which when integrated and assuming $k_p \gg k_{fm}$ gives

$$[C_s] = -k_{ct}[S] \left(\frac{k_{p3}k_{bb} \ln \left(\frac{k_p k_\beta + k_p k_{p3}(1-X)[M]_0 + k_{p3}k_{bb}}{k_p k_\beta + k_p k_{p3}[M]_0 + k_{p3}k_{bb}} \right) + k_p k_\beta \ln \left(\frac{[M]}{[M]_0} \right) (1-X)}{k_p^2 k_\beta + k_p k_{p3} k_{bb}} \right) \quad (23)$$

This equation can be simplified by substituting the rate coefficients for various ratios such that

$$C_{ct} = \frac{k_{ct}}{k_p} \quad (24)$$

$$K_{p3} = \frac{k_{p3}}{k_\beta} \quad (25)$$

$$K_{bb} = \frac{k_{bb}}{k_p} \quad (26)$$

Such that

$$[C_s] = - \frac{K_{ct}[S]}{1 + K_{p3}K_{bb}} \left(K_{p3}K_{bb} \ln \left(1 - \frac{K_{p3}[M]_0 X}{1 + K_{p3}[M]_0 + K_{p3}K_{bb}} \right) + \ln \left(\frac{[M]}{[M]_0} \right) (1-X) \right) \quad (27)$$

On the assumption that $K_{p3} \gg 1$ (propagation from the tertiary center is greater than the rate of scission) and $K_{bb} \ll [M]_0$ then this leads to a result which identical to that when no chain transfer to polymer is assumed (*i.e.* $k_{bb} = 0$) such that

$$[C_s] = -C_{ct}[S] \ln(1 - X) \quad (28)$$

Finally, the rate of formation of chains formed by β scission, $[C_\beta]$, is given by

$$\frac{d[C_\beta]}{dt} = k_\beta [P_3] \quad (29)$$

Assuming the steady state condition for tertiary radicals (Equation B.4) and dividing by the material balance for monomer gives

$$\frac{d[C_\beta]}{d[M]} = - \frac{k_\beta \frac{k_{bb}}{k_\beta + k_{p3}[M]}}{k_p[M] + k_{p3}[M] \frac{k_{bb}}{k_\beta + k_{p3}[M]} + k_{fm}[M]} \quad (30)$$

Assuming negligible effect of transfer to monomer this leads to

$$\frac{d[C_\beta]}{d[M]} = - \frac{k_\beta k_{bb}}{[M](k_p k_\beta + k_{p3} k_p [M] + k_{p3} k_{bb})} \quad (31)$$

Which when integrated gives

$$[C_\beta] = -k_\beta k_{bb} \left(\frac{\ln(1 - X) + \ln \left(\frac{k_p k_\beta + k_{p3} k_p [M]_0 + k_{p3} k_{bb}}{k_p k_\beta + k_{p3} k_p (1 - X) [M]_0 + k_{p3} k_{bb}} \right)}{k_p k_\beta + k_{p3} k_{bb}} \right) \quad (32)$$

Substituting equations 25 and 26 leads to

$$[C_\beta] = \frac{K_{bb}}{1 + K_{p3} K_{bb}} \left(-\ln(1 - X) + \ln \left(1 - \frac{K_{p3} [M]_0 X}{1 + K_{p3} [M]_0 + K_{p3} K_{bb}} \right) \right) \quad (33)$$

Which can be further reduced to give

$$[C_\beta] = \frac{K_{bb}}{1 + K_{p3}K_{bb}} \ln \left(1 + \frac{1 + K_{p3}K_{bb}}{1 + K_{p3}[M]_0 + K_{p3}K_{bb}(1 - X)} X \right) \quad (34)$$

Table 3S. Rate constants as well as the references for their values.

Parameter	Value	Ref
k_d (s ⁻¹) (AMBN)	$1.3 \times 10^{15} \exp(-128930/RT)$	Suppliers data sheet
k_d (s ⁻¹) (ACVA)	$4.0 \times 10^{15} \exp(-130000/RT)$	60
k_p (M ⁻¹ s ⁻¹)	$2.2 \times 10^7 \exp(-17900/RT)$	61
k_t (M ⁻¹ s ⁻¹)	$(1-0.1) \times 3.9 \times 10^9 \exp(-8400/RT)$	62
k_{t3} (M ⁻¹ s ⁻¹)	$(1-0.9) \times 5.3 \times 10^9 \exp(-19600/RT)$	62
k_{t23} (M ⁻¹ s ⁻¹)	$(1-0.7) \times (k_t k_{t3})^{1/2}$	62
k_{bb} (s ⁻¹)	$4.84 \times 10^7 \exp(-31700/RT)^*$	63,44
k_{p3} (M ⁻¹ s ⁻¹)	$1.5 \times 10^6 \exp(-28900/RT)$	63
k_{ct} (M ⁻¹ s ⁻¹)(ethanol)	$4.28 \times 10^{-4} k_p$	64
k_β (s ⁻¹)	$1.5 \times 10^9 \exp(-63900/RT)$	62
k_{fm} (M ⁻¹ s ⁻¹)	$2.9 \times 10^5 \exp(-32600/RT)$	65
k_a (M ⁻¹ s ⁻¹)	5×10^6	This work
k_f (s ⁻¹)	5×10^5	This work

* Note that this value was reduced by a factor of 1.5 for all reactions due to the effect of reversible deactivation⁴⁴ and by a further factor of 3 due to the effect of hydrogen bonding^{41,42} as detailed in the description of the model and its assumptions above.

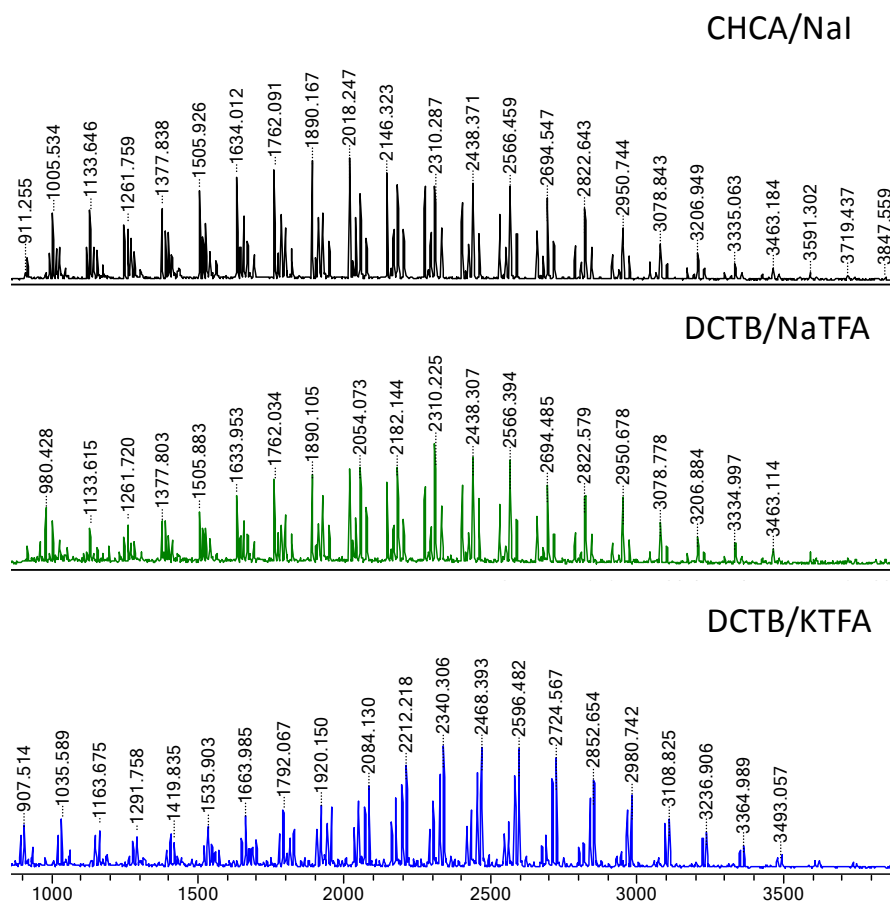


Figure 1S. MALDI-TOF mass spectra of pBA synthesized in ethanol solution using different matrices and cationization agents: CHCA/NaI, DCTB/NaTFA, and DCTB/KTFA.

Effect of solvent

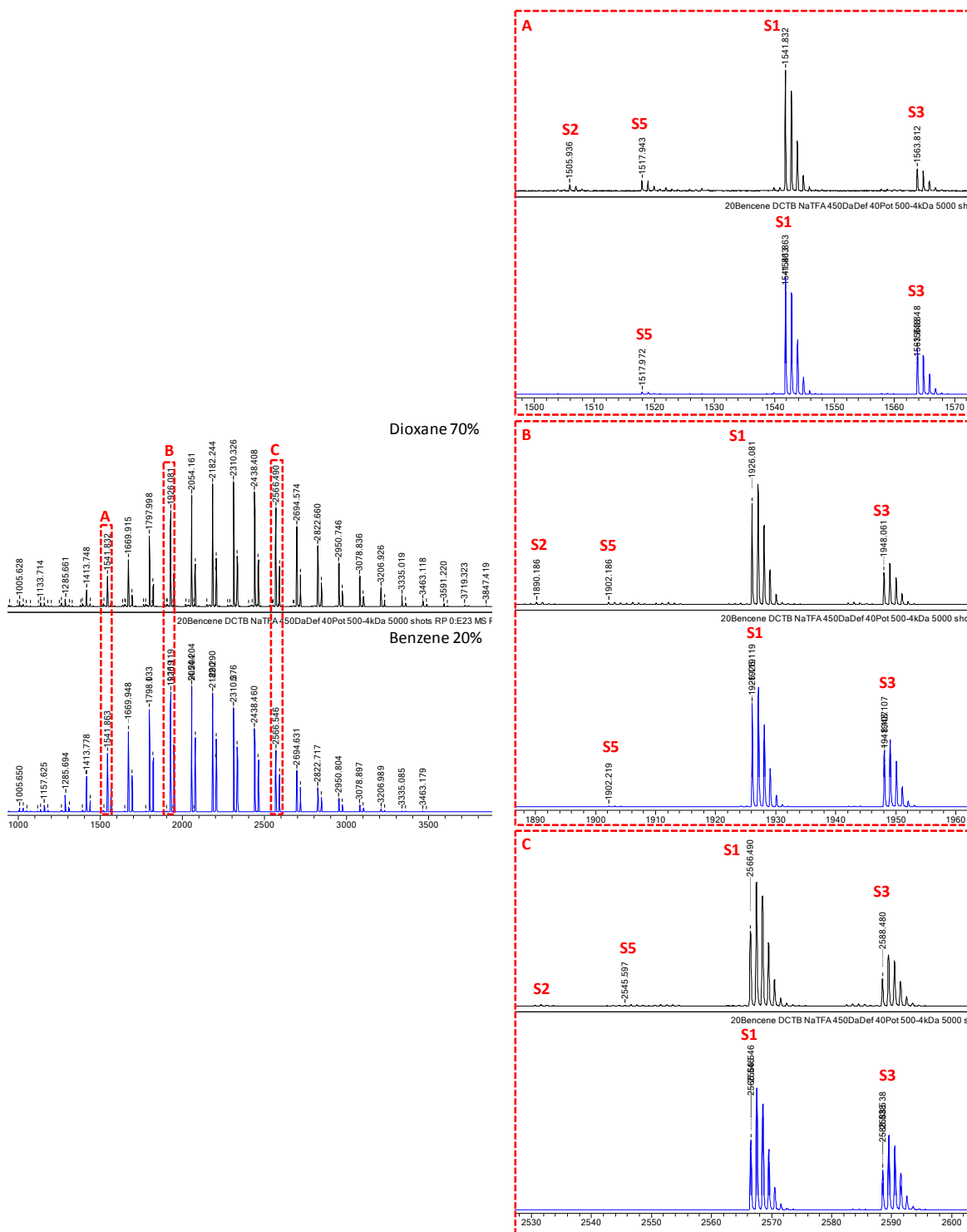


Figure 2S. MALDI-TOF mass spectra of pBA reaction using different solvents: Dioxane 70% (black) and benzene 20% (blue). Complete spectra in 1-4 kDa mass range (left). Enlargements in different mass ranges (right): (A) 1500-1580 Da, (B) 1880-1960 Da, and (C) 2520-2600 Da. Different series detected: S1, S2, S3 and S5 are assigned. All the samples were dissolved in THF at a concentration 20 g L^{-1} . DCTB and NaTFA were used as matrix/salt system.

Table 4S. Number and weight-average molar masses (\bar{M}_n , \bar{M}_w), dispersity (\mathfrak{D}) and polymerization degree (DP_n) obtained by MALDI-TOF MS and SEC/MALS techniques together with the theoretical values for the pBA synthesized in: ethanol solution (98% conversion), bulk (99% conversion), dioxane 70% solution (99% conversion) and benzene 20% solution (93% conversion).

pBA	Label	\bar{M}_n (g mol ⁻¹)	\bar{M}_w (g mol ⁻¹)	\mathfrak{D}	DP_n
In ethanol solution	Theoretical	2102	-	-	15
	SEC/MALS	2900	3000	1.025	21
	MALDI	2393	2509	1.048	17
In bulk	Theoretical	2140	-	-	17
	SEC/MALS	2400	2500	1.013	19
	MALDI	2279	2349	1.031	18
In dioxane 70% solution	Theoretical	2140	-	-	17
	SEC/MALS	2463	2500	1.015	19
	MALDI	2421	2500	1.033	19
In benzene 20% solution	Theoretical	2025	-	-	16
	SEC/MALS	2270	2300	1.013	18
	MALDI	2145	2216	1.033	17

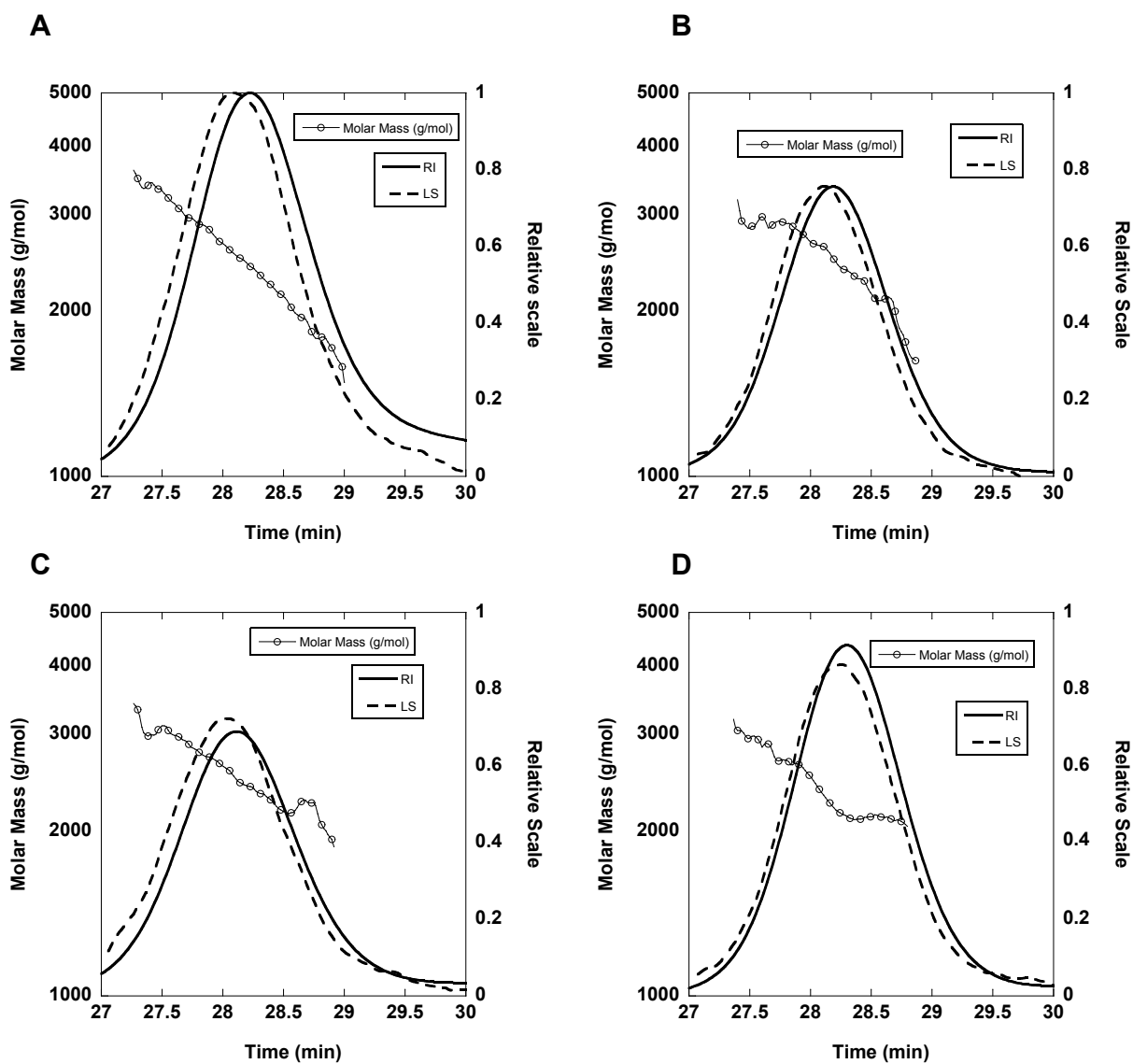


Figure 3S. SEC/MALS chromatograms for RAFT pBA synthesized in: (A) ethanol solution, (B) bulk, (C) dioxane 70% solution, and (D) benzene 20% solution.

References

- 1 K. Matyjaszewski, Y. Nakagawa, C. Jasieczek, *Macromolecules*, 1998, **31**, 1535-1541.
- 2 C. J. Hawker, *Acc. Chem. Res.*, 1997, **30**, 373-382.
- 3 J. Chiefari, Y. Chong, F. Ercole, J. Krstina, J. Jeffery, T. Le, R.; Mayadunne, G. Meijs, C. Moad, G. Moad, E. Rizzardo, S. Thang, *Macromolecules*, 1998, **31**, 5559-5562.
- 4 G. Moad, J. Chiefari, Y. Chong, J. Krstina, R. Mayadunne, A. Postma, E. Rizzardo, S. Thang, *Polymer International*, 2000, **49**, 993-1001.
- 5 M. Dietrich, M. Glassner, T. Gruending, C. Schmid, J. Falkenhagen, C. Barner-Kowollik, *Polymer Chemistry*, 2010, **1**, 634-644.
- 6 K. Matyjaszewski, *Macromolecules* 2012, **45**, 4015-4039.
- 7 E. Rizzardo, D. H. Solomon, *Australian Journal of Chemistry*, 2012, **65**, 945-969.
- 8 D. Keddie, G. Moad, E. Rizzardo, S. Thang, *Macromolecules*, 2012, **45**, 5321-5342.
- 9 C. Barner-Kowollik, *Handbook of RAFT Polymerization*. WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim ed.; 2008; p 5 – 49.
- 10 G. Gody, T. Maschmeyer, P.B. Zetterlund, S. Perrier, *Nat. Commun*, 2013, **4**, 2505-2514.
- 11 P.B. Zetterlund, G. Gody, S. Perrier, *Macrom. Theory and Simul.*, 2014, **23**, 331-339.
- 12 K. Matyjaszewski, *Controlled and Living Radical Polymerizations: Progress in ATRP, NMP and RAFT*. first edition ed.; *American Chemical Society*, 2000.
- 13 S. Perrier, C. Barner-Kowollik, J. F. Quinn, P. Vana, T. P. Davis, *Macromolecules* 2002, **35**, 8300-8306.
- 14 A. Ah Toy, P. Vana, T. P. Davis, C. Barner-Kowollik, *Macromolecules*, 2004, **37**, 744-751.
- 15 G. Moad, E. Rizzardo, S. H. Thang, *Polymer*, 2008, **49**, 1079-1131.
- 16 C. Plessis, G. Arzamendi, J. R. Leiza, H. A. S. Schoonbrood, D. Charmot, J. M. Asua, *Macromolecules*, 2000, **33**, 5041-5047.
- 17 A. N. Nikitin, R. A. Hutchinson, G. A. Kalfas, J. R. Richards, C. Bruni, *Macromolecular Theory and Simulations*, 2009, **18**, 247-258.
- 18 C. Plessis, G. Arzamendi, J. R. Leiza, H. A. S. Schoonbrood, D. Charmot, J.M. Asua, *Macromolecules*, 2000, **33**, 5041-5047.
- 19 R. X. E. Willemsse, A. M. van Herk, E. Panchenko, T. Junkers, M. Buback, *Macromolecules*, 2005, **38**, 5098-5103.
- 20 T. Junkers, C. Barner-Kowollik, *J Pol Sci Part A: Polymer Chemistry*, 2008, **46**, 7585-7605.
- 21 C. Schilli, M. G. Lanzendörfer, A.H.E. Müller, *Macromolecules*, 2002, **35**, 6819-6827.
- 22 F. D'Agosto, R. Hughes, M. Charreyre, C. Pichot, R. Gilbert, *Macromolecules*, 2003, **36**, 621-629.
- 23 J. Loiseau, N. Doerr, J. Suau, J. Egraz, M. Llauro, C. Ladaviere, *Macromolecules*, 2003, **36**, 3066-3077.
- 24 A. Favier, C. Ladaviere, M. Charreyre, C. Pichot, *Macromolecules*, 2004, **37**, 2026-2034.
- 25 J.T. Lai, D. Filla, R. Shea, *Macromolecules*, 2002, **35**, 6754-6756.
- 26 R. Venkatesh, B. Staal, B. Klumperman, M. Monteiro, *Macromolecules*, 2004, **37**, 7906-7917.
- 27 H. Chirowodza, P. Hartmann, H. Pasch, *Macromolecular Chemistry and Physics*, 2012, **213**, 847-857.
- 28 M. Jacquin, P. Muller, G. Lizarraga, C. Bauer, H. Cottet, O. Théodoly, *Macromolecules*, 2007, **40**, 2672-2682.
- 29 A. Krieg, C. Pietsch, A. Baungaertel, M.D. Hager, C.R. Becer, U.S. Schubert, *Polymer Chemistry*, 2010, **1**, 1669-1676.
- 30 X. Zhang, F. Boisson, O. Colombani, C. Chassenieux, B. Charleux, *Macromolecules*, 2014, **47**, 51-60.
- 31 C. Ferguson, R. Hughes, D. Nguyen, B. Pham, R.; Gilbert, A. Serelis, C. Such, B. Hawket, *Macromolecules*, 2005, **38**, 2191-2204.
- 32 S. Podzimeck, *Light Scattering, Size Exclusion Chromatography and Asymmetric Flow Field Fractionation: Powerful Tools for the Characterization of Polymers, Proteins and Nanoparticles*. Wiley, Canada ed.; 2011.
- 33 M. Frisch, al, e. *Gaussian 09*, Revision A.1; 2009.
- 34 Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.
- 35 W.; Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.
- 36 R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.
- 37 R. Arakawa, S. Egami, S. Okuno, *Journal of Mass Spectrometry*, 2006, **41**, 549-550.
- 38 X. Jiang, P. Schoenmakers, J. van Dongen, X. Lou, V. Lima, J. Brokken-Zijp, *Analytical Chemistry*, 2003, **75**, 5517-5524.
- 39 J. Vandenbergh, T. Junkers, *Macromolecules*, 2012, **45**, 6850-6856.
- 40 J. Vandenbergh, T. Junkers, *Macromolecules*, 2013, **46**, 3324-3331.
- 41 K. Liang, R. A. Hutchinson, J. Barth, S. Samrock, M. Buback, *Macromolecules*, 2011, **44**, 5843-5845.
- 42 K. Liang and R. A. Hutchinson, *Macromolecular Rapid Communications*, 2011, **32**, 1090-1095.
- 43 W. Wang, A.N. Nikitin, R. A. Hutchinson, *Macromolecular Rapid Communications*, 2009, **30**, 2022-2027.
- 44 N. Ballard, S. Rusconi, E. Akhmatskaya, D. Sokolovski, J. C. de la Cal, J. M. Asua, *Macromolecules*, 2014, **47**, 6580-6590.
- 45 M. Bednarek, T. Biedron, P. Kubisa, *Macromol Chem and Phys*, 2000, **201**, 58-66.
- 46 L. Charles, *Mass Spectrometry Reviews*, 2014, **33**, 523-543.
- 47 A. Postma, T. P. Davis, G. Li, G. Moad, M. S. O'Shea, *Macromolecules*, 2006, **39**, 5307-5318.
- 48 A. H. Soeriyadi, C. Boyer, F. Nyström, P. B. Zetterlund, M. R. Whittaker, *JACS*, 2011, **133**, 11128-11131.
- 49 A. Anastasaki, C. Waldron, P. Wilson, C. Boyer, P. B. Zetterlund, M. R. Whittaker, D. Haddleton, *ACS Macro Letters*, 2013, **2**, 896-900.
- 50 G. Gody, T. Maschmeyer, P.B. Zetterlund, S. Perrier, *Macromolecules*, 2014, **47**, 3451-3460.
- 51 G. Gody, T. Maschmeyer, P.B. Zetterlund, S. Perrier, *Macromolecules*, 2014, **47**, 639-649.

- 52 J. Vandenberg, T. Junkers, *Macromolecules*, 2014, **47**, 5051-5059.
- 53 J. Brandrup, E.H. Immergut, *Polymer Handbook*. 4th ed.; Wiley-Interscience: New York, 1999.
- 54 J. Loiseau, N. Doërr, J. M. Suau, J. B. Egraz, M. F. Llauro, C. Ladavière, *Macromolecules*, 2003, **36**, 3066-3077.
- 55 M. Gaborieau, S. P. S. Koo, P. Castignolles, T. Junkers, C. Barner-Kowollik, *Macromolecules*, 2010, **43**, 5492-5495.
- 56 N. Ballard, J. C. de la Cal, J. M. Asua, *Macromolecules*, 2015, **48**, 987-993.
- 57 S. P. S. Koo, T. Junkers, C. Barner-Kowollik, *Macromolecules*, 2008, **42**, 62-69.
- 58 J.P.A. Heuts, T.P. Davis, *Macromolecular Rapid Communications*, 1998, **19**, 371-375.
- 59 W. Meiser, M. Buback, A. Sidoruk, *Macromol Chem and Phys*, 2013, **214**, 2108-2114.
- 60 T. Cheikhalard, L. Tighzert, J.P. Pascault, *Die Angewandte Makromolekulare Chemie*, 1998, **256**, 49-59.
- 61 J.M. Asua, S. Beuermann, M. Buback, P. Castignolles, B. Charleux, R.G.; Gilbert, R.A. Hutchinson, J.R. Leiza, A.N. Nikitin, J.P. Vairon, A.M. van Herk, *Macromol Chem and Phys*, 2004, **205**, 2151 - 2160.
- 62 A. N. Nikitin, R. A. Hutchinson, W. Wang, G. A. Kalfas, J. R. Richards, C. Bruni, *Macromolecular Reaction Engineering*, 2010, **4**, 691 - 706.
- 63 A.N. Nikitin, R.A. Hutchinson, M. Buback, P. Hesse, *Macromolecules*, 2007, **40**, 8631-8641.
- 64 U.S. Nandi, M. Singh, P.V.T. Raghuram, *Die Makromolekulare Chemie*, 1982, **183**, 1467 - 1472.
- 65 S. Maeder, R. G. Gilbert, *Macromolecules*, 1998, **31**, 4410-4418.