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.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Name</th>
<th>Structure</th>
<th>Ion</th>
<th>Molecular formula</th>
<th>m/z (Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RAFT agent</td>
<td>TTCA-4</td>
<td><img src="#" alt="Structure" /></td>
<td>C₆H₁₀S₃ (2-arm stars)</td>
<td>C₆H₁₀S₃</td>
<td>165.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C₅H₉S₃</td>
<td></td>
<td>164.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C₅H₉S₃ (3-arm stars)</td>
<td></td>
<td>164.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C₁₀H₁₈S₆ (4-arm stars)</td>
<td></td>
<td>329.97</td>
</tr>
<tr>
<td>Initiator</td>
<td>V-501</td>
<td><img src="#" alt="Structure" /></td>
<td>C₃H₅O₂ (R)</td>
<td></td>
<td>73.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C₆H₈NO₂ (I)</td>
<td></td>
<td>126.06</td>
</tr>
<tr>
<td>Monomer</td>
<td>BA</td>
<td><img src="#" alt="Structure" /></td>
<td>C₇H₁₂O₂</td>
<td></td>
<td>128.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C₇H₁₃O₂</td>
<td></td>
<td>129.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C₇H₁₁O₂</td>
<td></td>
<td>127.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>*C₈H₁₃O₂</td>
<td></td>
<td>141.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>*C₆H₁₁O₂</td>
<td></td>
<td>115.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>*C₇H₁₃O₂</td>
<td></td>
<td>129.09</td>
</tr>
<tr>
<td>Solvent</td>
<td>Ethanol</td>
<td><img src="#" alt="Structure" /></td>
<td>C₂H₅O</td>
<td></td>
<td>45.03</td>
</tr>
</tbody>
</table>

*Generated after backbiting and β scission"22,17"
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.

<table>
<thead>
<tr>
<th>Label (series)</th>
<th>Z group</th>
<th>BA units</th>
<th>R group</th>
<th>Adduct</th>
<th>$(m/z)_{cal}$</th>
<th>$(m/z)_{exp}$</th>
<th>Error (Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>C$_5$H$_9$S$_3$</td>
<td>13</td>
<td>R</td>
<td>Na</td>
<td>1926.093</td>
<td>1925.990</td>
<td>-0.103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td></td>
<td></td>
<td>2566.521</td>
<td>2566.394</td>
<td>-0.127</td>
</tr>
<tr>
<td>S2</td>
<td>H</td>
<td>14</td>
<td>R</td>
<td>Na</td>
<td>1890.198</td>
<td>1890.105</td>
<td>-0.093</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19</td>
<td></td>
<td></td>
<td>2530.607</td>
<td>2530.503</td>
<td>-0.104</td>
</tr>
<tr>
<td>S3</td>
<td>C$_5$H$_9$S$_3$</td>
<td>13</td>
<td>R</td>
<td>Na$_2$-H</td>
<td>1948.075</td>
<td>1947.970</td>
<td>-0.105</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td></td>
<td></td>
<td>2588.481</td>
<td>2588.374</td>
<td>-0.107</td>
</tr>
<tr>
<td>S4</td>
<td>H</td>
<td>14</td>
<td>R</td>
<td>Na$_2$-H</td>
<td>1912.180</td>
<td>1912.084</td>
<td>-0.096</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19</td>
<td></td>
<td></td>
<td>2552.596</td>
<td>2552.475</td>
<td>-0.121</td>
</tr>
<tr>
<td>S5</td>
<td>C$<em>8$H$</em>{13}$O$_2$</td>
<td>13</td>
<td>R</td>
<td>Na</td>
<td>1902.198</td>
<td>1902.101</td>
<td>-0.097</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td></td>
<td></td>
<td>2542.617</td>
<td>Low int.</td>
<td>-</td>
</tr>
<tr>
<td>S6 (S1+K)</td>
<td>C$_5$H$_9$S$_3$</td>
<td>13</td>
<td>R</td>
<td>K</td>
<td>1942.067</td>
<td>1942.000</td>
<td>-0.067</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td></td>
<td></td>
<td>2582.486</td>
<td>2582.434</td>
<td>-0.052</td>
</tr>
<tr>
<td>S7 (S2+K)</td>
<td>H</td>
<td>14</td>
<td>R</td>
<td>K</td>
<td>1906.172</td>
<td>1906.117</td>
<td>-0.055</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19</td>
<td></td>
<td></td>
<td>2546.591</td>
<td>2546.534</td>
<td>-0.057</td>
</tr>
<tr>
<td>S8 (S3+Na+K-H)</td>
<td>C$_5$H$_9$S$_3$</td>
<td>13</td>
<td>R</td>
<td>Na+K-H</td>
<td>1964.049</td>
<td>1963.981</td>
<td>-0.068</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td></td>
<td></td>
<td>2604.468</td>
<td>2604.380</td>
<td>-0.088</td>
</tr>
<tr>
<td>S9 (S4+Na+K-H)</td>
<td>H</td>
<td>14</td>
<td>R</td>
<td>Na+K-H</td>
<td>1928.154</td>
<td>1927.065</td>
<td>-1.089</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19</td>
<td></td>
<td></td>
<td>2568.573</td>
<td>2567.434</td>
<td>-1.139</td>
</tr>
<tr>
<td>S10 (S5+K)</td>
<td>C$<em>8$H$</em>{13}$O$_2$</td>
<td>13</td>
<td>R</td>
<td>K</td>
<td>1918.172</td>
<td>1918.125</td>
<td>-0.047</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18</td>
<td></td>
<td></td>
<td>2558.590</td>
<td>Low int.</td>
<td>-</td>
</tr>
</tbody>
</table>

R is the leaving group (C$_3$H$_5$O$_2$) of the RAFT agent and (C$_8$H$_{13}$O$_2$) 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

\[
\frac{d[I]}{dt} = -k_d[I]
\]

(1)

\[
\frac{d[M]}{dt} = -k_p[M] \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_s] - k_{p3}[M] \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_{3s}] - k_{fM}[M] \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_s]
\]

(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 \([X_yP_s]\) and \([X_yP_{3s}]\) 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 \(\beta\) 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 \(X_y\) \([X_yP_s]\) and \([X_yP_{3s}]\), and for RAFT intermediate radicals with chain ends \(X_y\) and \(X_o\) on either arm, \([X_yP_{nRAFT}P_{m}X_z]\), are given by

\[
\frac{d[I]}{dt} = 2fk_d[I] - k_p[M][I] - k_a[I] \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_sRAFT] + \frac{1}{2}k_f \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_sRAFTP_0X_1] - k_t[I] \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_s]
\]

(3)

\[
\frac{d[R]}{dt} = -k_p[M][R] - k_a[R] \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_sRAFT] + \frac{1}{2}k_f \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_sRAFTP_0X_2] - k_t[R] \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_s]
\]

(4)

\[
\frac{d[S]}{dt} = k_c k_f [S] \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_s] - k_p[M][S] - k_a[S] \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_sRAFT] + \frac{1}{2}k_f \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_sRAFTP] + \sum_{s=0}^{\infty} \sum_{y=1,2,3} [X_yP_s]
\]

(5)
\[
\frac{d[X_\gamma P_n^\gamma]}{dt} = k_p[M][X_\gamma P_{n-1}^\gamma] - k_p[M][X_\gamma P_n^\gamma] - k_{ct}[X_\gamma P_n^\gamma] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_s P_s RAFT] + \frac{1}{2} k_f \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_s P_n RAFT P_s X_z] \\

k_t[X_\gamma P_n^\gamma] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_s P_s] - k_{t23}[X_\gamma P_n^\gamma] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_s P_{3^\pm_s}] - k_{bb}[X_\gamma P_n^\gamma][n \geq 3] + k_p[M] \\

[X_\gamma P_{3^\pm_s}^\gamma - 1] - k_{ct}[X_\gamma P_n^\gamma][S] + \frac{1}{2} k_p[X_\gamma P_{3^\pm_s}^\gamma + 3] - k_{pMM}[X_\gamma P_n^\gamma] \sum_{s=0}^{\infty} [HP_s MM] \\

(6)
\]

\[
\frac{d[X_\gamma P_{3^\pm_s}^\gamma]}{dt} = k_{bb}[X_\gamma P_n^\gamma][n \geq 3] - k_p[M][X_\gamma P_{3^\pm_s}^\gamma] - k_p[X_\gamma P_{3^\pm_s}^\gamma] + k_{pMM} \sum_{s=0}^{\infty} [X_s P_n^\gamma] [HP_s MM] - k_{t23}[X_\gamma P_{3^\pm_s}^\gamma] \sum_{s=0}^{\infty} [X_s P_{3^\pm_s}^\gamma] \\

- k_{ct}[X_\gamma P_{3^\pm_s}^\gamma] \sum_{s=0}^{\infty} \sum_{z=1,2,3} [X_s P_{3^\pm_s}] \\

(7)
\]

\[
\frac{d[X_\gamma P_n^\gamma RAFT P_m X_z]}{dt} = k_a[X_\gamma P_n^\gamma][X_z P_m RAFT] + k_a[X_z P_m][X_\gamma P_n^\gamma RAFT] - \frac{1}{2} k_f[X_\gamma P_n^\gamma RAFT P_m X_z] \\

(8)
\]

Where \( k_\gamma \) is the rate coefficient for addition of a growing radical to the RAFT agent; \( k_t \) 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; \( k_\gamma \) is the rate coefficient for chain transfer to solvent; \( k_\beta \) is the rate coefficient for \( \beta \) scission of the tertiary radicals; \( k_{prop} \) 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; \( [X_s P_{MM}] \) are macromonomer terminated species with \( n \) butyl acrylate units in the polymer chain and end group \( X_p \); and \( [X_\gamma P_n^\gamma RAFT] \) are dormant RAFT species with \( n \) butyl acrylate units in the polymer chain and end group \( X_p \). Propagation of radical \( [X_\gamma P_n^\gamma] \) to macromonomer \( [X_s P_{MM}] \) 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 \( \beta \) scission of the resulting midchain radical were assumed to be those shown in Scheme 1 based on the experimental observations shown herein. The subsequent \( \beta \) 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\textsuperscript{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 1.5 and therefore this reduction was applied to all simulations conducted in this work.

The material balances for RAFT dormant species are given by

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

(9)

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

\[
\frac{d[X_yP_nH]}{dt} = k_{ct}[X_yP_n][S] + k_{fm}[X_yP_n][M]
\]

(10)

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

(11)

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

\[
\frac{d[HP_3MM]}{dt} = \frac{1}{2}k_\beta \sum_{s=3z=1,2,3}^\infty [X_zP_s] - k_{pMM}[HP_3MM] \sum_{s=0z=1,2,3}^\infty [X_zP_s]
\]

(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 rapid. 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 temperature. It should be noted that if it is assumed that \(k_a\) is on the order of \(10^6\) 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

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

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

\[
\frac{d[M]}{dt} = -k_p[M][P] - k_{p3}[M][P^3] - k_{fm}[M][P]
\]  
(14)

Taking the ratio of these two gives

\[
\frac{d[C_{mon}]}{d[M]} = -\frac{k_{fm}[P]}{k_p[P] + k_{p3}[P^3] + k_{fm}[P]}
\]  
(15)

Under steady state conditions the tertiary radical concentration, \([P^3]\), is given by

\[
[P^3] = \frac{k_{bb}[P]}{k_\beta + k_{p3}[M]}
\]  
(16)

And combining with Equation B.3 gives

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

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

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

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

\[
[C_{mon}] = \frac{k_{fm}}{k_p}[M]_0X
\]  
(19)
Similarly the rate of formation of dead chains due to transfer to solvent \([C_s]\) is given by

\[
\frac{d[C_s]}{dt} = k_{ct}[S][P]
\]  

(20)

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

\[
\frac{d[C_s]}{d[M]} = \frac{k_{ct}[S][P]}{k_p[M][p] + k_{p3}[M] + k_{fm}[P][M]}
\]  

(21)

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

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

(22)

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

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

(23)

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

\[
C_{ct} = \frac{k_{ct}}{k_p}
\]  

(24)

\[
K_{p3} = \frac{k_{p3}}{k_{\beta}}
\]  

(25)

\[
K_{bb} = \frac{k_{bb}}{k_p}
\]  

(26)

Such that

\[
[C_s] = -\frac{K_{ct}[S]}{1 + K_{p3}K_{bb}}\left(K_{p3}K_{bb}ln\left(1 - \frac{K_{p3}[M]_0X}{1 + K_{p3}[M]_0 + K_{p3}K_{bb}}\right) + ln(1 - X)\right)
\]  

(27)
On the assumption that $K_{p3} > 1$ (propagation from the tertiary center is greater than the rate of scission) and $K_{bb} << [M]_0$ 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

$$[C_3] = -C_c[S] \ln(1 - X) \quad (28)$$

Finally, the rate of formation of chains formed by $\beta$ 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

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

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

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

Substituting equations 25 and 26 leads to

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

Which can be further reduced to give
\[ [C_\beta] = \frac{K_{bb}}{1 + K_{p3}K_{bb}} \ln \left( 1 + \frac{1 + K_{p3}K_{bb}}{1 + K_{p3}[M]_0 + K_{p3}K_{bb}1 - X} \right) \] (34)
Table 3S. Rate constants as well as the references for their values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_d$ (s$^{-1}$) (AMBN)</td>
<td>$1.3 \times 10^{15}\exp(-128930/RT)$</td>
<td>Suppliers data sheet</td>
</tr>
<tr>
<td>$k_d$ (s$^{-1}$) (ACVA)</td>
<td>$4.0 \times 10^{15}\exp(-130000/RT)$</td>
<td>60</td>
</tr>
<tr>
<td>$k_p$ (M$^{-1}$s$^{-1}$)</td>
<td>$2.2 \times 10^{7}\exp(-17900/RT)$</td>
<td>61</td>
</tr>
<tr>
<td>$k_f$ (M$^{-1}$s$^{-1}$)</td>
<td>$1.0 \times 3.9 \times 10^{2}\exp(-8400/RT)$</td>
<td>62</td>
</tr>
<tr>
<td>$k_{t3}$ (M$^{-1}$s$^{-1}$)</td>
<td>$(1.0-0.9) \times 5.3 \times 10^{8}\exp(-19600/RT)$</td>
<td>62</td>
</tr>
<tr>
<td>$k_{t23}$ (s$^{-1}$)</td>
<td>$4.84 \times 10^{7}\exp(-31700/RT)$</td>
<td>63,44</td>
</tr>
<tr>
<td>$k_{p3}$ (M$^{-1}$s$^{-1}$)</td>
<td>$1.5 \times 10^{8}\exp(-28900/RT)$</td>
<td>63</td>
</tr>
<tr>
<td>$k_{ct}$ (M$^{-1}$s$^{-1}$) (ethanol)</td>
<td>$4.28 \times 10^{-4} k_p$</td>
<td>64</td>
</tr>
<tr>
<td>$k_{ct}$ (s$^{-1}$)</td>
<td>$1.5 \times 10^{6}\exp(-63900/RT)$</td>
<td>62</td>
</tr>
<tr>
<td>$k_{fm}$ (M$^{-1}$s$^{-1}$)</td>
<td>$2.9 \times 10^{5}\exp(-32600/RT)$</td>
<td>65</td>
</tr>
<tr>
<td>$k_f$ (s$^{-1}$)</td>
<td>$5 \times 10^{6}$</td>
<td>This work</td>
</tr>
<tr>
<td>$k_f$ (s$^{-1}$)</td>
<td>$5 \times 10^{5}$</td>
<td>This work</td>
</tr>
</tbody>
</table>

* Note that this value was reduced by a factor of 1.5 for all reactions due to the effect of reversible deactivation $^{44}$ 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 15. 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 ($M_n$, $M_w$), dispersity ($\bar{D}$) 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).

<table>
<thead>
<tr>
<th>pBA</th>
<th>Label</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>$\bar{D}$</th>
<th>$DP_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>In ethanol solution</td>
<td>Theoretical</td>
<td>2102</td>
<td>-</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>SEC/MALS</td>
<td>2900</td>
<td>3000</td>
<td>1.025</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>MALDI</td>
<td>2393</td>
<td>2509</td>
<td>1.048</td>
<td>17</td>
</tr>
<tr>
<td>In bulk</td>
<td>Theoretical</td>
<td>2140</td>
<td>-</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>SEC/MALS</td>
<td>2400</td>
<td>2500</td>
<td>1.013</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>MALDI</td>
<td>2279</td>
<td>2349</td>
<td>1.031</td>
<td>18</td>
</tr>
<tr>
<td>In dioxane 70% solution</td>
<td>Theoretical</td>
<td>2140</td>
<td>-</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>SEC/MALS</td>
<td>2463</td>
<td>2500</td>
<td>1.015</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>MALDI</td>
<td>2421</td>
<td>2500</td>
<td>1.033</td>
<td>19</td>
</tr>
<tr>
<td>In benzene 20% solution</td>
<td>Theoretical</td>
<td>2025</td>
<td>-</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>SEC/MALS</td>
<td>2270</td>
<td>2300</td>
<td>1.013</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>MALDI</td>
<td>2145</td>
<td>2216</td>
<td>1.033</td>
<td>17</td>
</tr>
</tbody>
</table>
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
33. M. Frisch, al. e. Gaussian 09, Revision A.1; 2009.