Electronic Supplementary Information for ‘Comment on “Aqueous SET-LRP catalyzed with in situ generated Cu(0) demonstrates surface mediated activation and bimolecular termination” by S. Samanta et al., Polym. Chem. 2015, 6, 2084’

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Details of non-linear least squares fitting procedure.

Conversion and residual functionality \( f_{PBr} \) data were read from Fig. 8b of reference 1, and are shown in Table S1.

Table S1. Conversion and residual functionality \( f_{PBr} \) data from Fig. 8b of reference 1, and results of NLLS fitting assuming error in both variables with \( k_t/k_p^2 = 0.047 \).

<table>
<thead>
<tr>
<th>conversion</th>
<th>( f_{PBr} )</th>
<th>fitted conversion</th>
<th>fitted ( f_{PBr} )</th>
<th>point of closest approach</th>
<th>distance to model curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.22</td>
<td>1.00</td>
<td>0.00</td>
<td>0.99</td>
<td>(0.22, 0.99)</td>
<td>0.10</td>
</tr>
<tr>
<td>0.34</td>
<td>1.00</td>
<td>0.00</td>
<td>0.98</td>
<td>(0.34, 0.98)</td>
<td>0.017</td>
</tr>
<tr>
<td>0.77</td>
<td>0.91</td>
<td>0.90</td>
<td>0.94</td>
<td>(0.78, 0.94)</td>
<td>0.031</td>
</tr>
<tr>
<td>0.83</td>
<td>0.89</td>
<td>0.94</td>
<td>0.92</td>
<td>(0.84, 0.93)</td>
<td>0.038</td>
</tr>
<tr>
<td>0.999(^a)</td>
<td>0.88</td>
<td>0.95</td>
<td>0.72</td>
<td>(0.97, 0.86)</td>
<td>0.035</td>
</tr>
</tbody>
</table>

\(^a\) A value of 0.999 was used to represent 100% conversion.

The data were fitted to the following single-parameter model:

\[
\hat{f}_{PBr} = \frac{4.61}{60 \times 0.09} \times a \ln(1 - conv)
\]

Equivalently,

\[
c\hat{n}v = 1 - e^{-\frac{60 \times 0.09 \times f_{PBr}}{a}}
\]

In each equation, \( a \) is the parameter to be fitted and represents the value of \( k_t/k_p^2 \). Using these equations, fitted values of conversion and \( f_{PBr} \) can be obtained from experimental values of \( f_{PBr} \) and conversion, respectively.

The fitting procedure is carried out with the aim of minimizing the sum of squared residuals, \( \sum r^2 \), assuming an error of similar magnitude in both variables. The distance, \( r \), between the model curve and a data point \((x,y)\) (Figure S1) is approximately given by:

\[
r^2 \approx \frac{(\Delta y)^2}{1 + (\Delta y/\Delta x)^2}
\]

This is equivalent to carrying out a conventional non-linear least squared fit, assuming negligible error in conversion, with the residuals weighted by a factor of

\[
\sqrt{\frac{1}{1 + (\Delta y/\Delta x)^2}}.
\]
Fitting was carried out by an iterative procedure, in which an initial estimate of $a$ was used to generate a new estimate by solving the matrix equation

$$
\Delta a = (J^T W)^{-1} J^T W \Delta y
$$

Where $J$ is the Jacobian matrix whose elements are given by

$$
J_i = \left( \frac{\partial \hat{f}_{PBR}}{\partial a} \right)_i
$$

$W$ is the weight matrix

$$
W_{ii} = \frac{1}{1 + \left( \frac{\Delta y}{\Delta x} \right)_i^2}
$$

$$
W_{ij} = 0 \ (i \neq j)
$$

and $\Delta y$ is the vector of residuals

$$
\Delta y_i = f_{PBR,i} - \hat{f}_{PBR,i}
$$

The new value of $a$ was obtained by adding $\Delta a$ to the previous value until the difference between iterations was less than $1 \times 10^{-5}$. This procedure gave a best estimate for $a$ of $0.0468 \text{ s} \cdot \text{mol} \cdot \text{L}^{-1}$.

The standard error in $a$ can be estimated from
where $n$ is the number of observations (5 in this case).

The standard error in $\alpha$ was thus estimated at 0.0133 s·mol·L$^{-1}$. Figure S2 shows the curve of best fit ($k_p/k_t^2 = 0.0468$) together with the curves corresponding to $k_p/k_t^2 = 0.0468 \pm 0.0133$. The probability that the true value of $k_t/k_p^2$ falls in this range is approximately 70%.

**Figure S2.** Curve of best fit (solid line) to experimental residual functionality and conversion data from reference 1, Fig. 8b, with curves corresponding to best estimate of $k_t/k_p^2$ plus or minus the standard error (dashed lines).

**Figure S3.** Values of $k_p$ and $k_t$ which are consistent with the experimental data shown in Figure S2. Solid line indicates values of $k_p$ and $k_t$ which satisfy $k_t/k_p^2 = 0.0468$. Dashed lines correspond to $k_t/k_p^2 = 0.0468 \pm 0.0133$ (best estimate $\pm$ 1 standard error). The probability that the true values of $k_p$ and $k_t$ fall between the dashed lines is approximately 70%.