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 $k_t/k_p^2 = 0.047$.

conversion	f_{PBr}	fitted conversion	fitted f_{PBr}	point of closest approach	distance to model curve
0.22	1.00	0.00	0.99	(0.22, 0.99)	0.010
0.34	1.00	0.00	0.98	(0.34, 0.98)	0.017
0.77	0.91	0.90	0.94	(0.78, 0.94)	0.031
0.83	0.89	0.94	0.92	(0.84, 0.93)	0.038
0.999[a]	0.88	0.95	0.72	(0.97, 0.86)	0.035

[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,

$$\widehat{conv} = 1 - e^{\frac{60 \times 0.09}{4.61} \cdot \frac{f_{PBr}}{a}}$$

In each equation, a is the parameter to be fitted and represents the value of k_p/k_t^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:

$$r^2 \approx \frac{(\Delta y)^2}{1 + \left(\frac{\Delta y}{\Delta x}\right)^2}$$

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 $\sqrt{\frac{1}{1+\left(\frac{\Delta y}{\Delta x}\right)^2}}$.

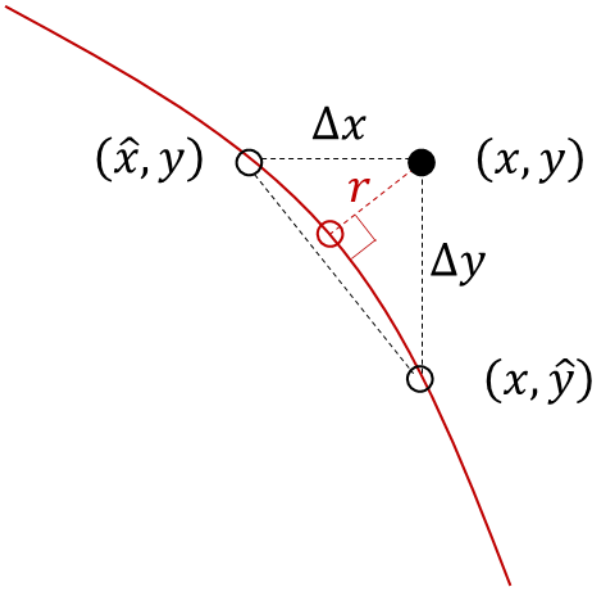

Figure S1. Relationship between distance between experimental data point and model curve, *r*, and distances between experimental and fitted data points, Δx and Δy.

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

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

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 **Δy** is the vector of residuals

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

The new value of *a* was obtained by adding Δ*a* to the previous value until the difference between iterations was less than 1×10^{-5}. This procedure gave a best estimate for *a* of 0.0468 s·mol·L^{-1}.

The standard error in *a* can be estimated from

$$se_a = \sqrt{\frac{(\mathbf{J^T W J})^{-1} \Delta \mathbf{y^T W} \Delta \mathbf{y}}{n-1}}$$

where n is the number of observations (5 in this case).

The standard error in a 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 ± 0.0133. The probability that the true value of k_t/k_p^2 falls in this range is approximately 70%.

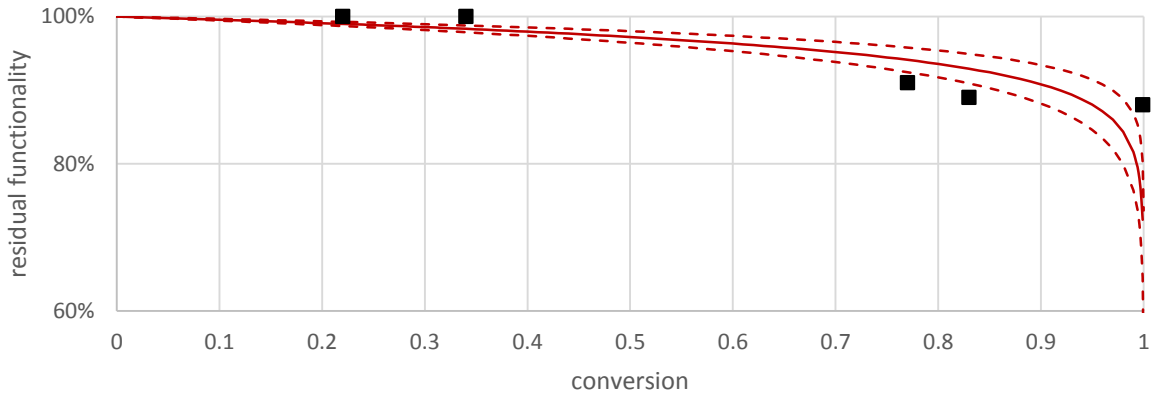

Figure S2. Curve of best fit (solid line) to experimental residual functionality and conversion data from reference 1, Fig. 8b, with curves corresponding to best estimate of k_t/k_p^2 plus or minus the standard error (dashed lines).

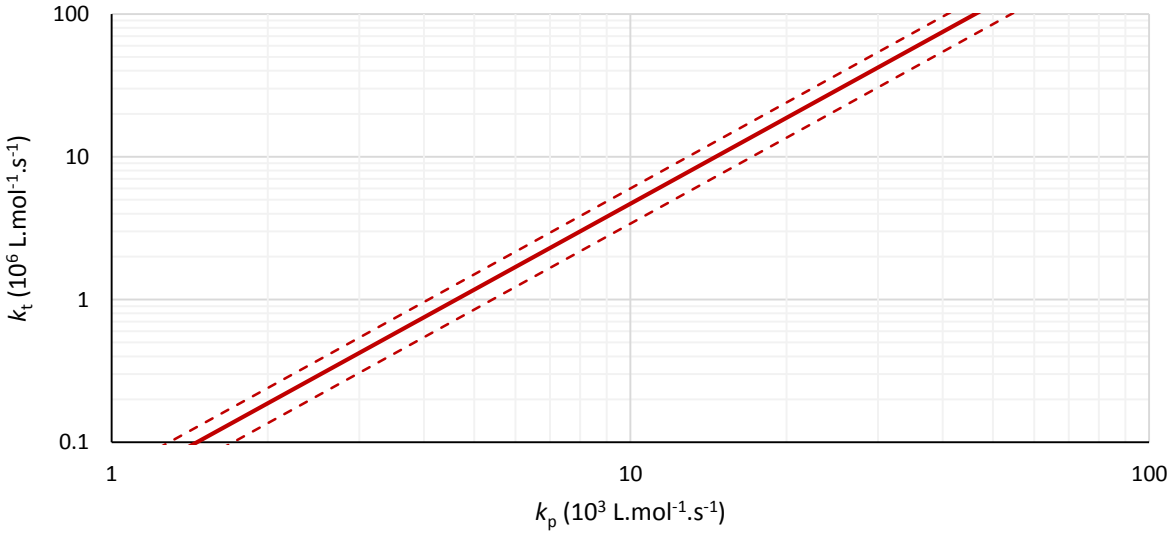

Figure S3. Values of k_p and k_t which are consistent with the experimental data shown in Figure S2. Solid line indicates values of k_p and k_t which satisfy k_t/k_p^2 = 0.0468. Dashed lines correspond to k_t/k_p^2 = 0.0468 ± 0.0133 (best estimate ± 1 standard error). The probability that the true values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