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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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In a recent paper, Samanta et al. investigated the kinetics of the SET-LRP polymerization of oligoethylene oxide methyl ether acrylate (OEOMEA) in aqueous solution, and proposed that bimolecular termination in this reaction is suppressed due to adsorption of the propagating radicals on the surface of the catalyst. A key piece of evidence for this claim was the observation that the high residual chain end functionality of the polymer could not be explained using reasonable values of $k_p$. The measured values of chain end functionality, and the predictions of a simple model using $k_t$ of $1 \times 10^8$ L·mol$^{-1}$·s$^{-1}$ and $k_o$ of $1 \times 10^4$, $3 \times 10^4$ and $5 \times 10^4$ L·mol$^{-1}$·s$^{-1}$ were displayed separately in ref. 1, but are superimposed here (Fig. 1a). In ref. 1 it is implied that none of the $k_o$ values considered explain the observed residual chain end functionality at 100% conversion, as the highest $k_p$ considered gives only about 68% residual functionality at 100% conversion. In fact, the model used breaks down at 100% conversion for all values of $k_o$ and $k_t$, giving a residual functionality of $\approx 0$. Furthermore, if the residual functionality measured at intermediate conversions is taken into account, it is evident from Fig. 1 that a $k_o$ of $5 \times 10^4$ L·mol$^{-1}$·s$^{-1}$ fits the data reasonably well.

The model used to predict the residual functionality assumes that dead polymer is produced at a constant rate:

$$[\text{dead polymer}]_t = k_t[P^*]^2 \cdot t$$

(1)

This assumes that $k_t$ is independent of chain length and the radical concentration is constant throughout the reaction. The reaction is first order in monomer concentration, such that conversion increases with time according to equation 2.

$$\text{conv} = 1 - e^{-k_{app} \cdot t}$$

(2)

In this equation, $k_{app}$ is the apparent rate constant of propagation, equal to 4.61 min$^{-1}$, or 0.0768 s$^{-1}$, at 0°C. The radical concentration, $[P^*]$, is given by equation 3.

$$[P^*] = \frac{k_{app}}{k_p}$$

(3)

Finally, the residual chain end functionality, $f_{PB}$, is given by equation 4 ([I]$_0$ is the initiator concentration at time 0, equal to 0.09 M):

$$f_{PB} = 1 - \frac{[\text{dead polymer}]_t}{[I]_0}$$

(4)

Combining these equations gives $f_{PB}$ as a function of conversion:

$$f_{PB} = 1 + \frac{k_t k_{app}}{k_p^2[I]_0} \ln(1 - \text{conv})$$

(5)

Fitting equation 5 to the measured conversion and residual functionality data gives $k_t/k_o$ of 0.047 ± 0.013 s·mol·L$^{-1}$ (Figure 1b). As both conversion and residual functionality were measured by NMR, it was assumed that each parameter would be subject to errors of similar magnitude. A nonlinear least squares fitting algorithm assuming errors in both variables was used to fit the data. The maximum distance between a data point and the curve of best fit is less than 4%.

Using the proposed value of $k_t$, $1 \times 10^8$ L·mol$^{-1}$·s$^{-1}$, this corresponds to a $k_o$ of $4.6 \times 10^9$ L·mol$^{-1}$·s$^{-1}$ and a radical concentration of $1.7 \times 10^6$ M. If $k_o$ is taken to be $1 \times 10^9$ L·mol$^{-1}$·s$^{-1}$, then a value for $k_t$ of $4.7 \times 10^6$ L·mol$^{-1}$·s$^{-1}$ is obtained, with a radical concentration of $7.7 \times 10^6$ M (not $7.7 \times 10^5$ M as was stated in ref. 1). The radical concentrations are higher than typical values of $10^7$-$10^9$ M obtained in controlled radical polymerizations, but still physically realistic. As neither $k_o$ nor $k_t$ data are available for OEOMEA in water, it is impossible to say which pair of values more closely resembles the true situation.

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† Electronic Supplementary Information (ESI) available: details of NLLS fitting procedure. See DOI: 10.1039/x0xx00000x
In summary, the residual functionality vs conversion data presented in ref. 1 are consistent with a conventional radical termination mechanism involving diffusion-controlled bimolecular termination, with physically realistic values of $k_1$ (0.5-10 × 10^8 L·mol⁻¹·s⁻¹), $k_p$ (1-5 × 10^4 L·mol⁻¹·s⁻¹), and [P*] (2-8 × 10^4 M). Superimposing the experimental data on the model predictions reveals reasonable agreement between theory and data, confirmed by nonlinear least squares fitting. While the data do not rule out a mechanism involving adsorbed radicals which are capable of reacting with monomer and CuBr₂ but not with each other, further evidence would be required to support this hypothesis.

Notes and references

† The full range of values of $k_p$ and $k_1$ that are consistent with the experimental data is shown in Figure S3 of the ESI.
‡ Reference 98 cited in ref. 1 (reference 8 in this Comment) does not provide a value for $k_p$ of DA.