



Cite this: *Polym. Chem.*, 2015, **6**, 4185

Received 26th March 2015,

Accepted 4th May 2015

DOI: 10.1039/c5py00444f

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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,¹ 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 $1 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ and k_p of 1×10^4 , 3×10^4 and $5 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ were displayed separately in ref. 1, but are superimposed here (Fig. 1a). In ref. 1 it is implied that none of the k_p 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_p and k_t , giving a residual functionality of $-\infty$. Furthermore, if the residual functionality measured at intermediate conversions is taken into account, it is evident from Fig. 1 that a k_p of $5 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ fits the data reasonably well.

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

$$[\text{dead polymer}]_t = k_t [\text{P}^*]^2 t \quad (1)$$

This assumes that k_t is independent of chain length and the radical concentration, $[\text{P}^*]$, is constant throughout the reaction. The reaction is first order in monomer concentration, such that conversion increases with time according to eqn (2).

$$\text{conv} = 1 - e^{-k_p^{\text{app}} t} \quad (2)$$

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† Electronic supplementary information (ESI) available: Details of NLLS fitting procedure. See DOI: 10.1039/c5py00444f

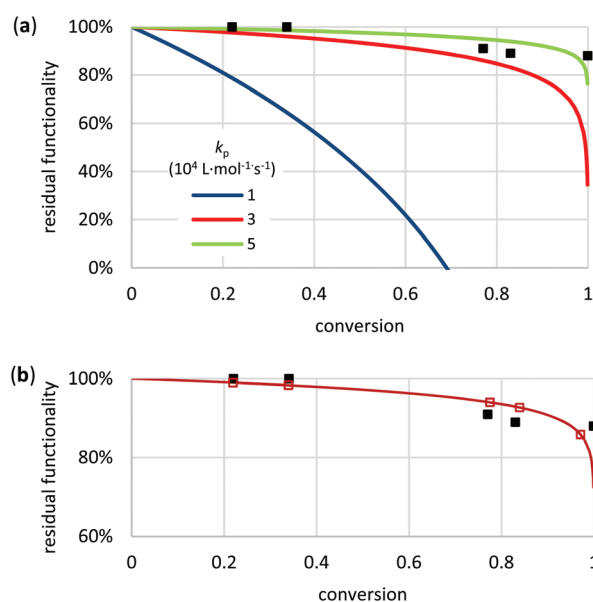


Fig. 1 (a) Measured residual functionality as a function of conversion superimposed on model predictions using $k_t = 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_p = 1 \times 10^4$, 3×10^4 , or $5 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ (combination of Fig. 8b and Fig. 10 from ref. 1). (b) Nonlinear least squares fit to the data assuming errors in both variables. Open squares show the closest approach of the curve of best fit to the data points. The curve shown corresponds to k_t/k_p^2 of $0.047 \text{ s mol L}^{-1}$, with standard error of $0.013 \text{ s mol L}^{-1}$.

In this equation, k_p^{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 is given by eqn (3).

$$[\text{P}^*] = \frac{k_p^{\text{app}}}{k_p} \quad (3)$$

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

$$f_{\text{PBr}} = 1 - \frac{[\text{dead polymer}]_t}{[\text{I}]_0} \quad (4)$$

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

$$f_{\text{PBr}} = 1 + \frac{k_t k_p^{\text{app}}}{k_p^2 [I]_0} \ln(1 - \text{conv}) \quad (5)$$

Fitting eqn (5) to the measured conversion and residual functionality data gives k_t/k_p^2 of $0.047 \pm 0.013 \text{ s mol L}^{-1}$ (Fig. 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 , $1 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, this corresponds to a k_p of $4.6 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ and a radical concentration of $1.7 \times 10^{-6} \text{ M}$. If k_p is taken to be $1 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$, then a value for k_t of $4.7 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ is obtained, with a radical concentration of $7.7 \times 10^{-6} \text{ M}$ (not $7.7 \times 10^5 \text{ M}$ 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_p 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.

The k_p value of $1 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ is that of dodecyl acrylate (DA) in bulk at 100 bar (published value: $9.97 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$),^{§2} and may not be applicable to OEOMEA in water at atmospheric pressure. In alkyl methacrylates, higher propagation rate coefficients are observed for bulkier side chains.³ The same trend is believed to occur in acrylates,⁴ and the oligoethylene oxide group of OEOMEA is twice as long as the dodecyl group of DA. Strong solvent effects on propagation rate coefficients have been observed in water for monomers that, like OEOMEA, are capable of forming hydrogen bonds, such as *N*-vinyl pyrrolidone (20-fold increase in k_p)^{5,6} methacrylic acid (5-fold increase in k_p)⁷ and *N*-isopropyl acrylamide (3-fold increase in k_p).⁸ Thus, a k_p of $4.6 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ appears possible.

Similarly, the true value of k_t is unknown and may be significantly lower than the value of $10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ used in ref. 1. While no source is given for this value, it corresponds to the k_t of methyl acrylate as measured by multiple groups.^{9–11} For the polymerization of DA, a much lower value of around $10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ has been reported.^{12,13} In this context, a value of k_t for OEOMEA in water of $4.6 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ does not seem impossible. Termination rate constants in radical polymerizations are sensitive to many factors including chain length^{9–14} and viscosity,^{15,16} and can be as low as $10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ in extreme cases.^{16,17}

[‡] The full range of values of k_p and k_t that are consistent with the experimental data is shown in Fig. S3 of the ESI[†].

[§] Ref. 98 cited in ref. 1 (ref. 8 in this Comment) does not provide a value for k_p of DA.

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_t (0.5 – $10 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$), k_p (1 – $5 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$), and $[P^*]$ (2 – $8 \times 10^{-6} \text{ M}$). 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 CuBr_2 but not with each other, further evidence would be required to support this hypothesis.

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