SUPPLEMENTARY INFORMATION

for

Unusual kinetics of poly(ethylene glycol) oxidation with cerium(IV) ions in sulfuric acid medium and implications for copolymer synthesis

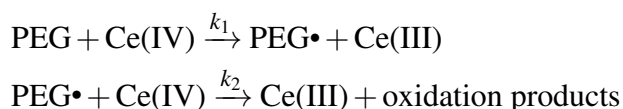Jan K. Szymański, Fernando Temprano-Coleto,
and Juan Pérez-Mercader

1 Materials and methods

Materials.   Ammonium cerium(IV) nitrate (ACN, Sigma), poly(ethylene glycol) (PEG, $\overline{M}_w$ = 1500 g/mol, Sigma), stock 5 mol/L sulfuric acid (Sigma) and stock 6 mol/L nitric acid solutions (Sigma) were used as received. The stock solution of ACN was prepared by dissolving it in 3 mol/L sulfuric acid and the final concentration of Ce(IV) was 0.208 mol/L.

Procedures.   Poly(ethylene glycol) was dissolved in deionized (12 MΩ water) in a polyurethane spectrophotometric cuvette and the appropriate amounts of stock nitric and/or sulfuric acid solutions were added to ensure that the desired concentrations of protons and HSO_4^- ions were maintained. This was followed by heating the solution to 40°C and a predetermined amount of the stock solution of cerium(IV) was then added, at which point the reaction started immediately. The changes in the Ce^{4+} ion concentration were monitored by recording the absorbance of the solution at 427 nm (the absorbtion maximum of the ion under consideration) on-line with a fiber optics USB spectrophotometer (Ocean Optics), while the solution temperature was controlled by a temperature probe connected to a hotplate (CAT Scientific).

2 Quasi-stationary state approximation (QSSA) for poly(ethylene glycol) radicals

Assuming the following reaction scheme, where Ce(IV) might refer to any of the cerium(IV)-sulfate complexes ($CeSO_4^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_3^{2-}$) we have

$$PEG + Ce(IV) \xrightarrow{k_1} PEG\bullet + Ce(III)$$

$$PEG\bullet + Ce(IV) \xrightarrow{k_2} Ce(III) + \text{oxidation products}$$

and assuming further that any radicals formed in the first step are immediately consumed in the second, one expects their concentration changes to be very small, i.e. d[PEG•]/dt = 0. From introducing this assumption into the above kinetics, one obtains the following expression for the concentration of the radicals:

$$[PEG\bullet] = (k_1/k_2)[PEG]$$

which, when substituted into the differential equation describing the cerium(IV) consumption, yields equation 1 from the main text:

$$\frac{d[Ce(IV)]}{dt} = -2k_1[PEG][Ce(IV)] \tag{1}$$

3 Cerium(IV) species concentrations as a function of total cerium(IV)

If we denote the total cerium(IV) concentration by [Ce(IV)], the composition of the reaction mixture with respect to the various species present can be then described as follows:

$$[Ce^{4+}] = [Ce(IV)]\frac{1}{1 + K_A R + K_A K_B R^2 + K_A K_B K_C R^3} \tag{2}$$

$$[CeSO_4^{2+}] = [Ce(IV)]\frac{K_A R}{1 + K_A R + K_A K_B R^2 + K_A K_B K_C R^3} \tag{3}$$

$$[Ce(SO_4)_2] = [Ce(IV)]\frac{K_A K_B R^2}{1 + K_A R + K_A K_B R^2 + K_A K_B K_C R^3} \tag{4}$$

$$[Ce(SO_4)_3^{2-}] = [Ce(IV)]\frac{K_A K_B K_C R^3}{1 + K_A R + K_A K_B R^2 + K_A K_B K_C R^3} \tag{5}$$

4 Fitting of the experimental results

The experimental results were fitted using MATLAB's built-in function *NonLinearModel.fit*, which is based on a Levenberg-Marquardt nonlinear least squares algorithm. The curve that was fitted to the results was the following:

$$[Ce(IV)]_t = \left([Ce(IV)]_0^{1-n} + 2k_{app}[PEG]_0(n-1)t\right)^{\frac{1}{1-n}}$$

The values for the standard errors of the fitting for both the order of reaction and rate constant were plotted using error bars.

5 Fitting and optimization of the rate constants

The chemical kinetics simulations were performed by solving the system of differential equations using MATLAB's solver *ode23s* for stiff differential systems, which is based on a modified Rosenbrock formula of order two. The fitting and optimization procedure was started by ensuring that the value of the term $k_4/[H^+]$ was such that the linear decay was reasonably well reproduced in case of $R = 0.537$; this was achieved for $k_4 = 1.562 \times 10^{-6}$. The obtained function

$$\frac{k_2[Ce(IV)]K_A R}{\sigma[H^+]} + \frac{k_3[Ce(IV)]K_A K_B R^2}{\sigma[H^+]} + 1.562 \times 10^{-6}/[H^+]$$

$$= k_{app}[Ce(IV)]^n \tag{6}$$

was fitted to the experimental series of $k_{app}[\text{Ce(IV)}]^n$ as a function of R.

The algorithm for the optimization of the kinetic constants was coded in MATLAB. The array of the time steps from the experimental absorbance measurements was used as the array of the integration steps in the simulations. The simulated curves for a selected group of values of R were plotted against their corresponding experimental curves and the error was calculated as the average of the absolute values of the differences between each point of the experimental set and its reciprocal point of the simulated set. The process was repeated sweeping a range of possible combinations of values for k_2 and k_3, and those values for which the error was minimized were selected as the final constants.

6 Cerium(IV) absorbance spectra for $R = 0.537$

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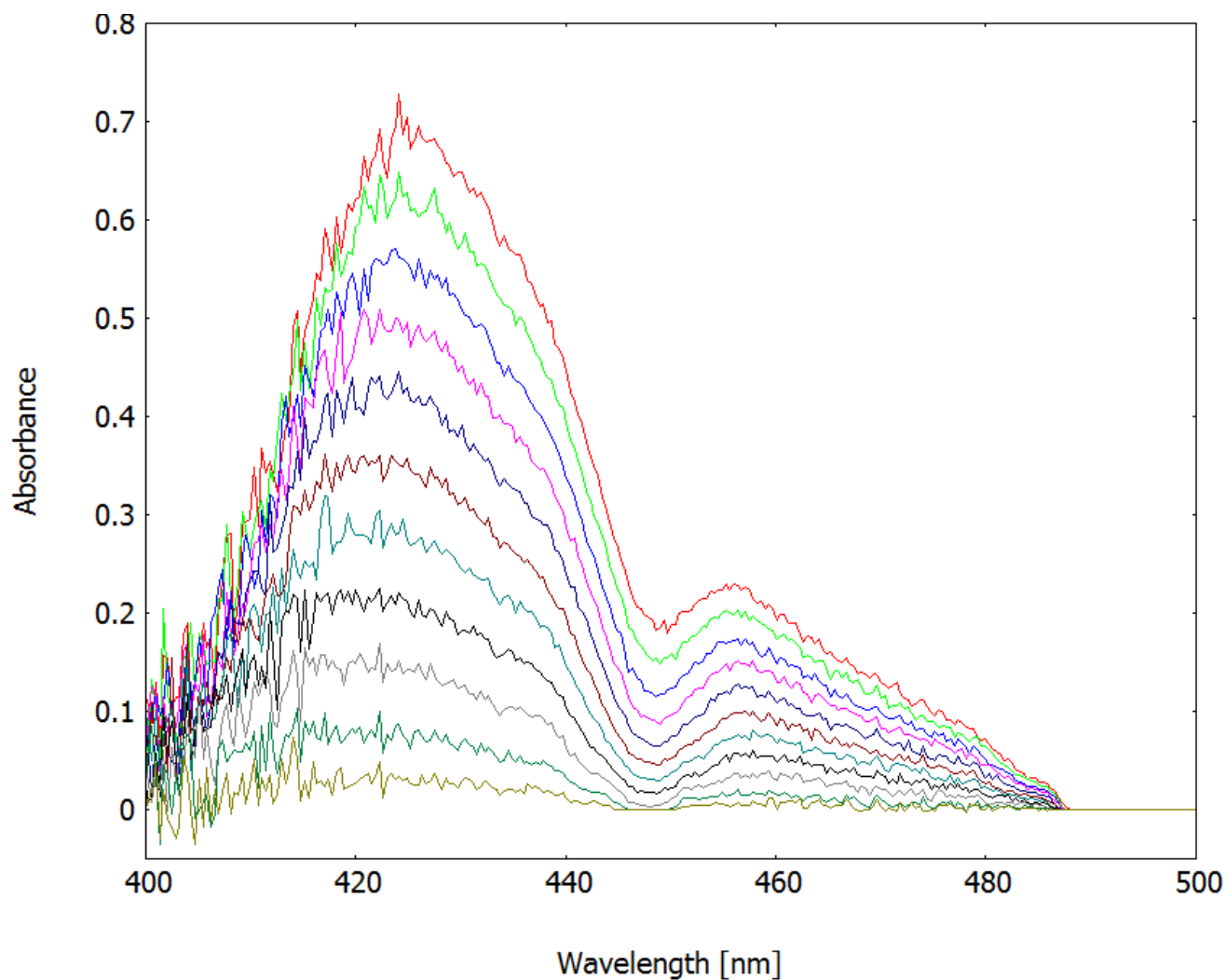
Figure 1 Overlay of experimental spectra recorded every 60 seconds around the absorbance maximum of cerium(IV) in sulfuric acid medium during oxidation of poly(ethylene glycol) at $40\,^\circ$C. $[\text{PEG}]_0 = 0.06$ mol/L, $[\text{Ce(IV)}]_0 = 6\times 10^{-4}$ mol/L, $[\text{HSO}_4^-] = 0.070$ mol/L, $[\text{H}^+] = 0.130$ mol/L and $R = 0.537$.