**Supporting Information**

# Determination of the Compositional Profile for Tapered Copolymers of Ethylene Oxide and 1,2-Butylene Oxide by In-situ-NMR

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## Algorithms

The integration of the kinetic equations was done using subroutine DC04 from the Harwell Subroutine Library (HSL) (see reference 31 in article). This subroutine implements a variable order Backward Differentiation Formula (BDF) method, also known as Gear's method, of order 1 to 5.

The resulting development of concentrations was fitted to the data obtained from NMR by subroutine VA05 from HSL. The implemented method is a compromise between three different algorithms for minimising a sum of squares, namely Newton-Raphson, Steepest Descent and Marquardt. Moreover it automatically obtains and improves an approximation to the first derivative matrix following the ideas of Broyden.

In a first attempt, errors of the fit parameters were estimated from the covariance matrix. This is also the usual procedure in commercial data fitting software. This method is very efficient because it is based on data already present from the fit subroutine (VA05 here). But it is known that it gives too optimistic estimated for non-linear problems with a high number of

free parameters as the one here. Indeed, the errors for the kinetic constants obtained in this way were suspiciously small.

Therefore we used a bootstrap method described in reference 1. It is based on re-weighting the experimental data with randomly chosen numbers and performing the identical fit for each of these 'replica data sets'. Because the data values themselves are not changed, each of these fits should result in the same parameters if they had zero errors. Conversely, the deviation of the 'replica' parameters from that of the original fit reflects the uncertainty of the fit procedure, including effects of non-linearity, possible secondary minima etc.

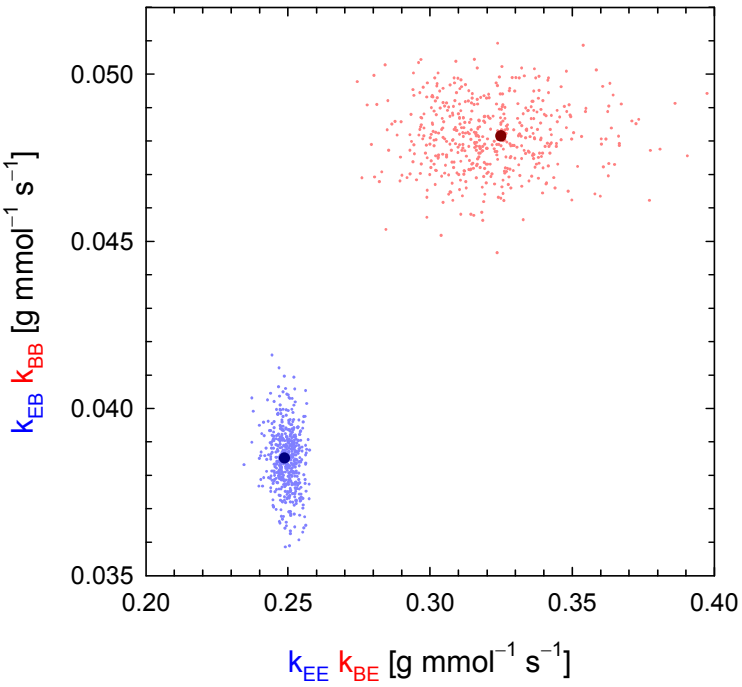


Fig. 1: Fit results underlying the bootstrap estimation of the errors of the kinetic constants. The blue points represent $k_{EE}$ and $k_{EB}$, the red points $k_{BE}$ and $k_{BB}$. The larger point represents the original fit with uniformly weighted data. The small points represent the fit results from the bootstrap replicas.

The bootstrap method was used with 100 and 500 replicas. There were significant increases of the error bars of the kinetic constants compared to the standard method, with a factor between 2 and 9. Interestingly, the (fitted) initial concentrations did not show a big increase in their errors, in some cases even a reduction. The extension to 500 replicas did not yield a significant change of the error estimates compared to 100. Nevertheless, the 500-replica estimates were used in the main paper. Fig. 7 shows the kinetic constants from all 500 replica fits.

Another advantage of this method is that the replica fits contain the correlation between the parameters. Therefore, they allow a direct calculation of the ratios and products of kinetic constants taking into account that the operands involved may be correlated.

**References**

(1) Rubin, D. B. *Ann. Stat.* **1981**, *9*, 130–134.