

**Understanding copolymerisation
kinetics for the design of functional
copolymers *via* free radical
polymerisation**

Supporting Information

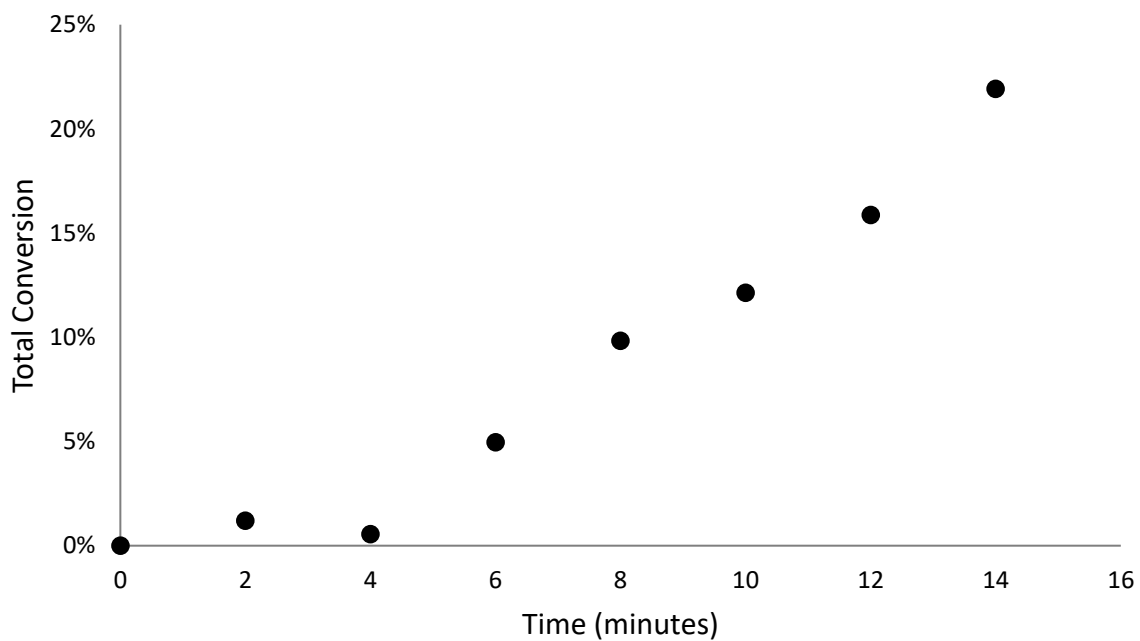


Figure S1. Samples from the early stages of the copolymerisation of MMA with PEGMEM₅₀₀

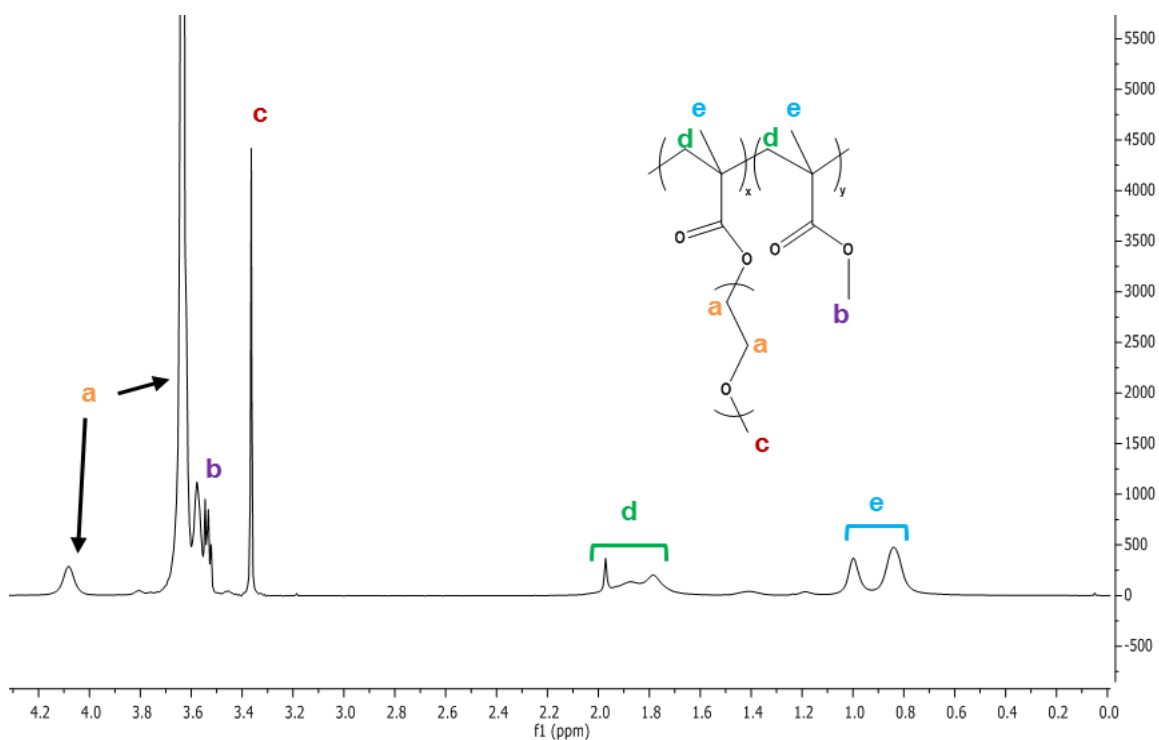


Figure S2. Typical ¹H NMR spectrum of P(MMA-*stat*-PEGMEM).

Calculation of mole fraction of monomer in copolymer:

$$x = \frac{c}{3 \text{ (protons)}} \quad 1$$

$$y = \frac{e-c}{3 \text{ (protons)}} \quad 2$$

$$F_{PEGMEM} = \frac{x}{(x+y)} \quad 3$$

$$F_{MMA} = \frac{y}{(x+y)} \quad 4$$

where x and y are the mole fractions of PEGMEM₅₀₀ and MMA units in the polymer chain respectively (eqns 1 and 2), and F_{PEGMEM} and F_{MMA} are the mole fractions of PEGMEM₅₀₀ and MMA in the copolymer respectively (eqns 3 and 4).

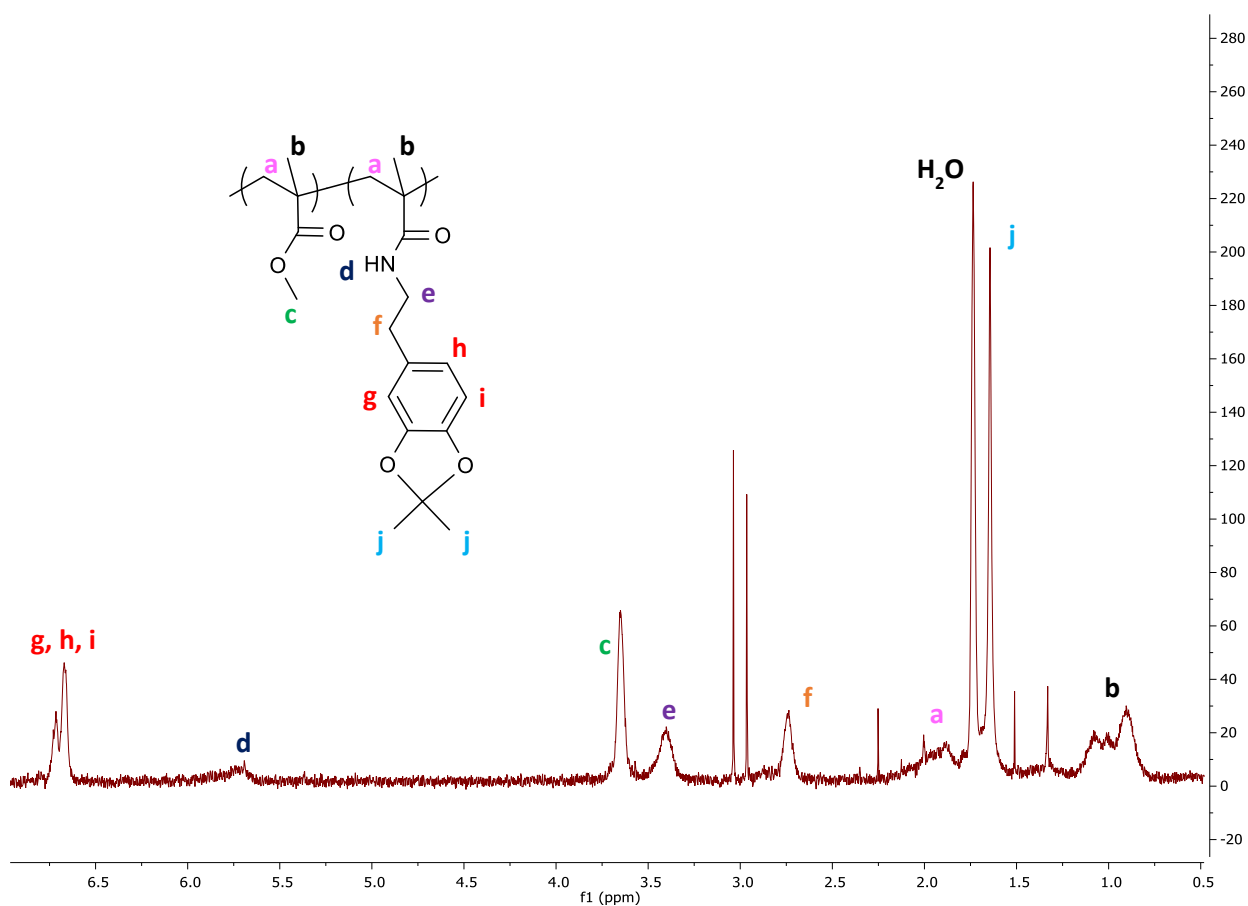


Figure S3. Typical ¹H NMR spectrum of P(MMA-*stat*-ADMA).

Calculation of mole fraction of monomer in copolymer:

$$x = \frac{b-(g+h+i)}{3 \text{ (protons)}} \quad 1$$

$$y = \frac{g+h+i}{3 \text{ (protons)}} \quad 2$$

$$F_{MMA} = \frac{x}{(x+y)} \quad 3$$

$$F_{ADMA} = \frac{y}{(x+y)} \quad 4$$

where x and y are the mole fractions of PEGMEM₅₀₀ and MMA units in the polymer chain respectively (eqns 1 and 2), and F_{PEGMEM} and F_{MMA} are the mole fractions of PEGMEM₅₀₀ and MMA in the copolymer respectively (eqns 3 and 4)).

Determination of Reactivity Ratios with the Fineman-Ross and Kelen-Tüdös Models

In the Fineman-Ross method, G is plotted against H for each experiment, which yields a straight line of gradient r_1 and intercept r_2 (eqn 3). G and H (eqns 4 and 5) are derived from the monomer feed mole fraction (f_{mon}) and the mole fraction of each in the resulting copolymer (F_{mon}):

$$G = r_1 H - r_2 \quad 1$$

where,

$$G = \frac{F_1}{F_2} \left(1 - \frac{f_2}{f_1} \right) \quad 2$$

$$H = \left(\frac{F_1}{F_2} \right)^2 \left(\frac{f_2}{f_1} \right) \quad 3$$

Kelen and Tüdös refined the Fineman-Ross equation by the introduction of an arbitrary constant (α) to distribute the data more uniformly and eliminate bias from certain experimental data points.³⁰ The previously defined values, G and H can be modified, giving values ξ and η (eqns 6-9) where r_1 and r_2 are the reactivity ratios of monomers 1 and 2 and G and H are variables defined from the Fineman-Ross technique. H_{min} and H_{max} are the minimum and maximum values of H determined from the data. Reactivity ratios r_1 and r_2 can be calculated by plotting ξ versus η for each experiment. This yields a straight line, where $\eta = r_1$ at $\xi = 1$ and $\eta = -r_2 / \alpha$ at $\xi = 0$.

$$\eta = \left(\frac{r_1+r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad 4$$

where,

$$\eta = \frac{G}{\alpha+H} \quad 5$$

$$\xi = \frac{H}{\alpha+H} \quad 6$$

$$\alpha = (H_{min}H_{max})^{\frac{1}{2}} \quad 7$$

The Fineman-Ross and Kelen-Tüdös plots for each copolymerisation system are shown in Figure S4.

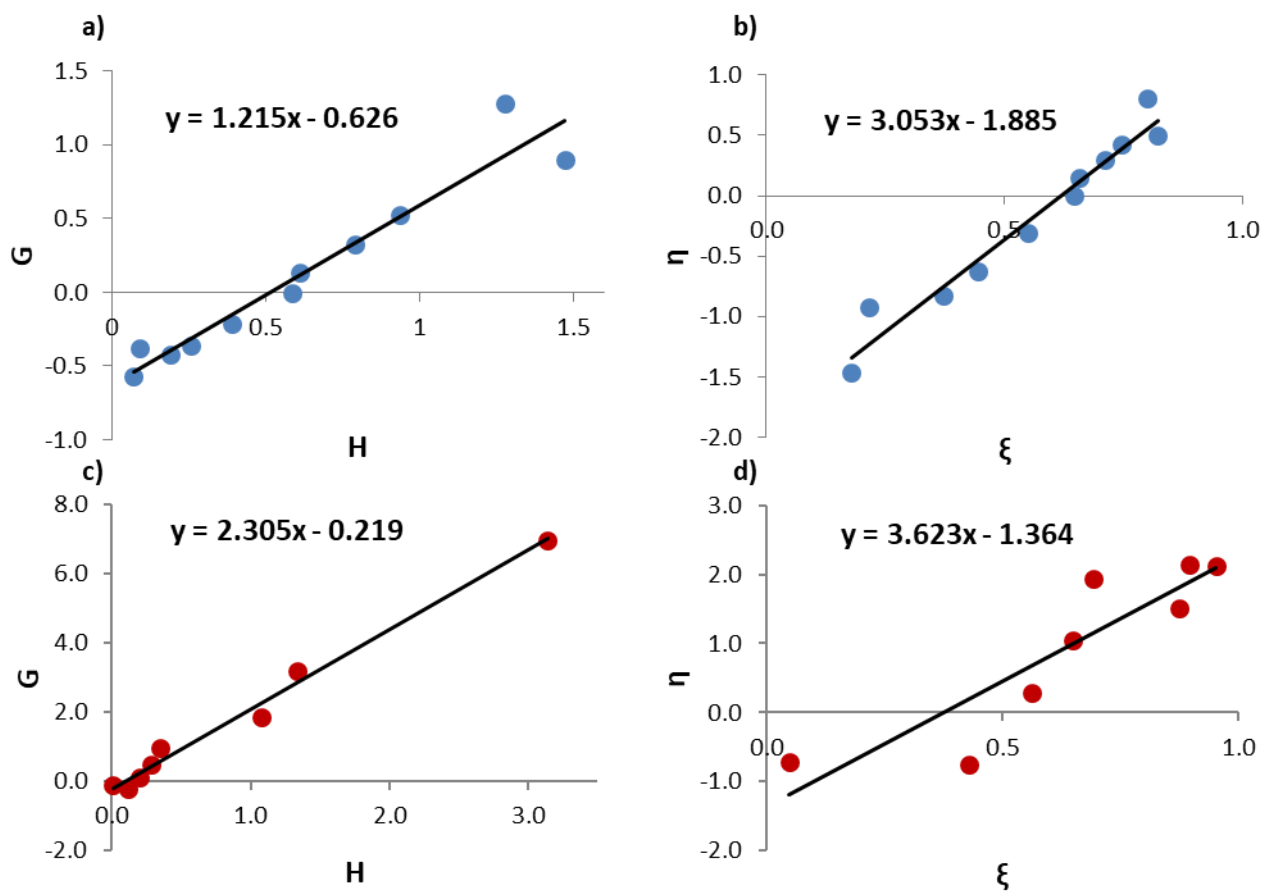


Figure S4. Fineman-Ross (a, c) and Kelen-Tüdös (b, d) plots to estimate reactivity ratios (r_1 and r_2) of P(MMA-co-PEGMEM₅₀₀) (a and b) and P(MMA-co-ADMA) (c, d).

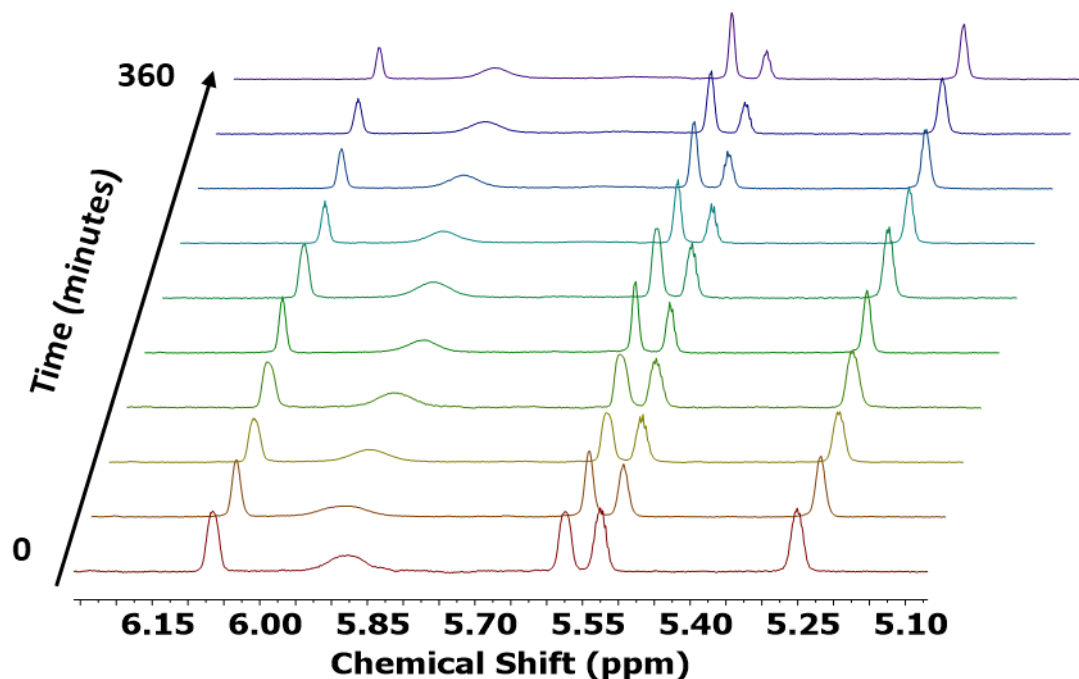


Figure S5. Stacked ¹H NMR spectra of samples (0 – 360 min) from the copolymerisation of MMA and ADMA in dioxane with equimolar feed ratios at 70 °C in CDCl₃. The monomer vinyl group peaks are displayed: MMA (δ 5.52 and 6.06 ppm) and ADMA (δ 5.25 and 5.57 ppm). Peak at 5.88 ppm is due to ADMA acrylamide proton (-CH₂-NH-) (broad).

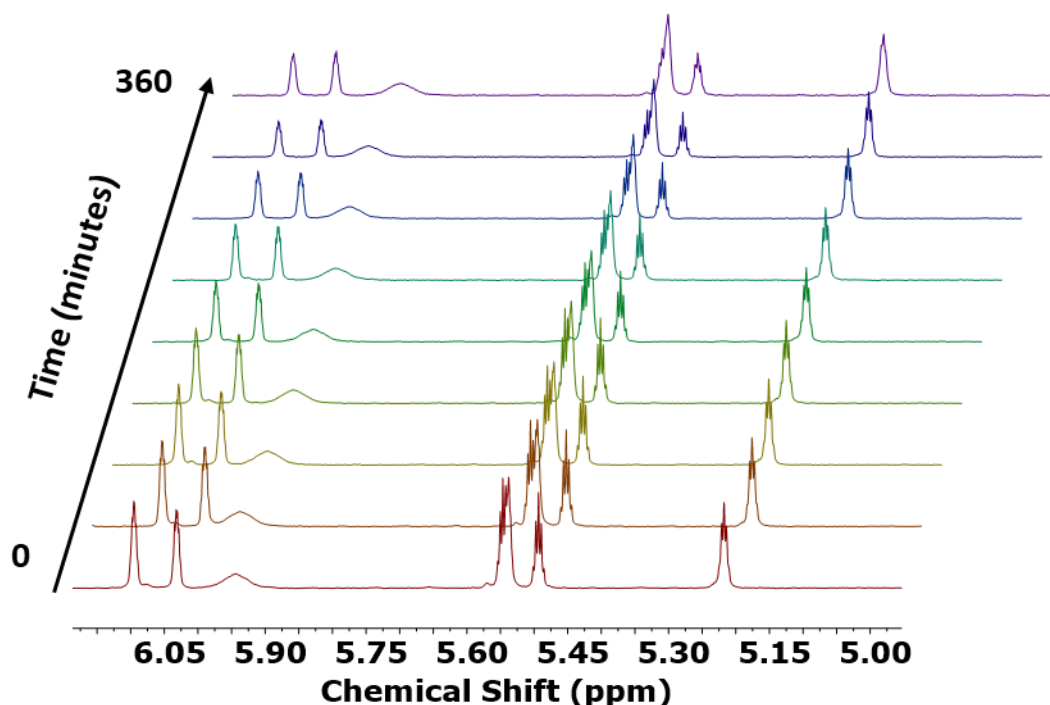


Figure S6. Stacked ¹H NMR spectra of samples (0 – 360 min) from the terpolymerisation of MMA, ADMA and GMA in dioxane with equimolar feed ratios at 70 °C in CDCl₃. The monomer vinyl group peaks are displayed: MMA (δ 5.49 and 6.03 ppm), ADMA (δ 5.22 and 5.54 ppm) and GMA (δ 5.54 and 6.10 ppm). Peak due to ADMA acrylamide proton (-CH₂-NH-) (broad) at 5.94 ppm.

The slight difference in chemical shifts of vinyl peaks of MMA in the MMA/PEGMEM(/MAA) spectra (Figures 3 and 5 – main manuscript) and the MMA/ADMA(/GMA) spectra (Figures S5 and S6) is simply because the samples were not worked up prior to analysis. Thus, the reaction solvents (propanediol and dioxane) are still present and in the case of the MMA/PEGMEM spectra, the chemical shift of the vinyl protons are impacted by the H-bonding solvent (propanediol) and in the case of the MMA/ADMA spectra, the solvent is not H-bonding (dioxane). H-bonding solvents are known to promote the reactivity of these monomers by H-bonding to the carbonyl group and this will also impact upon the chemical shifts of vinyl protons.