Supplementary Material

Acceleration and improved control of aqueous RAFT/MADIX polymerization of vinylphosphonic acid in the presence of alkali hydroxides

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Scheme S1: Carboxy-functional xanthate chain transfer agent X1 (2-[(ethoxythiocarbonyl)thio] propionic acid).

Figure S1: \textsuperscript{31}P\{\textsuperscript{1}H\} NMR analysis of the reaction mixtures and products during the X\textsubscript{1}-mediated RAFT/MADIX polymerization of VPA. VPA conversion = (a+b)/(a+b+c) and DPn\textsubscript{NMR} = (a+b)/b.

Figure S2: \textsuperscript{1}H NMR analysis of the reaction mixtures and products during the free radical or RAFT/MADIX polymerization of VPA. VPA conversion = b/(a+b).
Generation of a calibration curve using SEC-DRI-MALS data

Each VPA sample was analyzed by SEC using DRI-MALS detection, generating molecular weight data for each sample as a function of elution volume. In theory, these points should be superposable to form a single master curve. In practice, errors resulting from the low scattering intensity of low molecular weight polymers led to significant deviations from the master curve, especially at the high and low molecular weight shoulders of the molecular weight distribution where signal intensity is low. Additionally, MALS measures 1/MW rather than MW directly. As a result, random variation in 1/MW leads to systematic overestimation of MW.

To minimize the effect of these errors, a master calibration curve was generated for the volume range 21.1-26.9 mL by fitting a cubic equation to the combined log(MW) data obtained from MALS. Residuals were initially weighted by a factor of 1/MW to compensate for the effect of distortions in the error structure induced by the transformation of 1/MW to log(MW). However, this resulted in non-uniform residuals which increased in size with the elution volume (Figure S3a). A further empirical weighting of 1/(V-21 mL) was applied to the residuals, resulting in weighted residuals of nearly uniform magnitude (Figure S3b).

**Figure S3:** Weighted residuals of cubic fit to log(MW) vs elution volume data after applying weighting proportional to 1/MW (a) and 1/[MW×(V-21 mL)] (b)

The resulting curve of best fit is shown in Figure S4, together with the raw MW data. The master curve is approximately linear in the region 25-27 ml. Molecular weights for elution volumes of up to 30 mL were estimated by extrapolation from this region.

The full equation for the calibration curve is:

\[ \log(MW) = \begin{cases} -0.0146V^3 + 1.12V^2 - 28.8V + 252, & V \leq 25 \text{ mL} \\ -0.155V + 7.41, & V > 25 \text{ mL} \end{cases} \]
\[ \log(MW) = -0.0146V^3 + 1.12V^2 - 28.8V + \]

**Figure S4:** Calibration curve relating SEC elution time to elution volume. Dashed line shows linear extrapolation of curve used for elution volumes > 25 mL. Open circles represent molecular weights determined by DRI-MALS analysis of individual PVPA samples.
Figure S5: $^{31}\text{P}^{1\text{H}}$ NMR analysis of the reaction mixtures and products during the $X_1$-mediated RAFT/MADIX polymerization of VPA in presence of different concentration of NaOH.
Figure S6: Variation in total UV absorption as a function of polymerization time for polymerizations in the presence of NaOH at degrees of dissociation (α) of 0, 0.5 and 1.0. Total UV detector response for the elution volume range 23-35 min was normalized according to the total DRI response over the same range. Graph shows the deviation from the mean UV response for the period 2-8 h.
Figure S7: Variation in total UV absorption as a function of polymerization time for polymerizations in the presence of LiOH, NaOH, KOH and NH₄OH at degrees of dissociation (α) of 1.0. The polymerization at α = 0 is shown for comparison. Total UV detector response for the elution volume range 23-35 min was normalized according to the total DRI response over the same range. Graph shows the deviation from the mean UV response for the period 2-8 h.