

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI) FOR:

When Mayo falls Short ($C_{tr} \gg 1$): The use of Cumulative Chain Length Distribution Data in the Determination of Chain Transfer Constants (C_{tr}) for Radical Polymerizations.

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CONTENT OF ESI:

- S1. Molecular weight distributions as obtained from SEC analysis, $dw(\log M)$, obtained for the free radical polymerization of vinyl acetate at 333.15 K in presence of various amounts of *n*-dodecanethiol as chain transfer agent.
- S2. Natural logarithmic versions of the chain length distributions, $P(i)$ at various stages of monomer conversion, obtained for the free radical polymerization of vinyl acetate at 333.15 K in presence of various amounts of *n*-dodecanethiol as chain transfer agent.
- S3. Example GC chromatogram showing the elution behaviour of the reactants.
- S4. GC calibration Equation, data and fit.
- S5. $dw/d \log M$ distribution of the poly(vinyl acetate) sample used for triple detection analysis and the determined intrinsic viscosity $[\eta]$ as a function of MW with the fitted K and α values.

S1. Molecular weight distributions

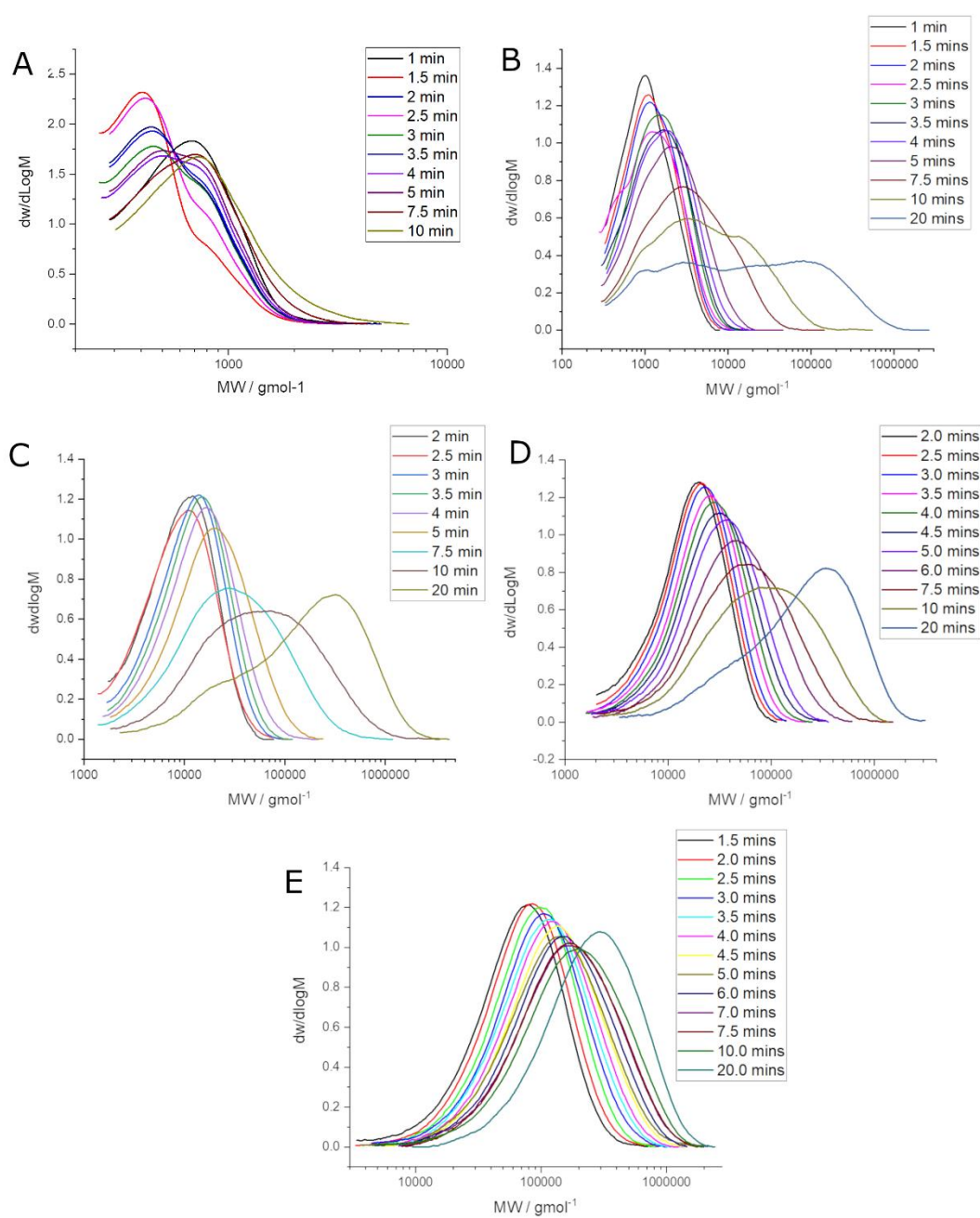


Figure S1: Molecular weight distributions, $dw/d\log M$ as a function of molecular weight (gmol^{-1}), were A, B, C, D and E correspond to $[\text{DDT}]_{p=0}/[\text{VA}]_{p=0} = 1 \times 10^{-2}$, 1×10^{-3} , 1×10^{-4} , 5×10^{-5} and 1×10^{-5} respectively.

S2. $\ln P(i)$ plots as a function of time

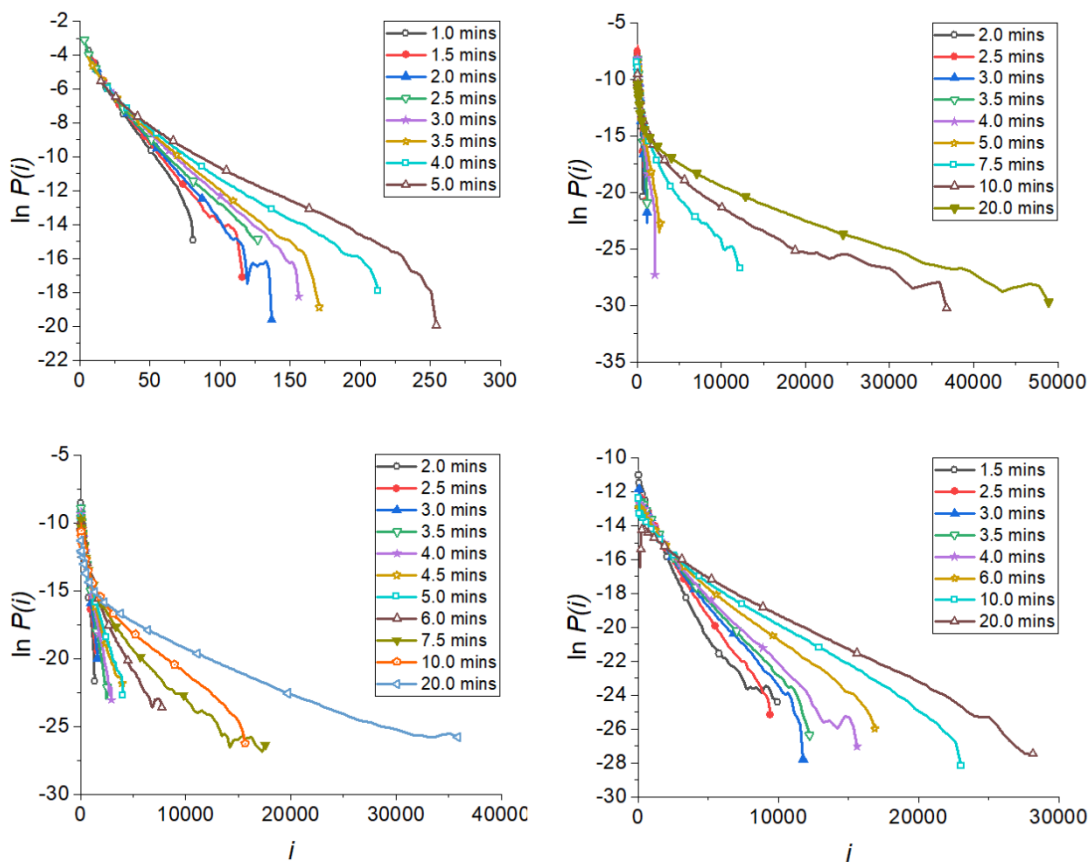


Figure S2: $\ln P(i)$ distributions at increasing polymerisation times where $[DDT]_{p=0}/[VA]_{p=0} = 1 \times 10^{-3}$ (top left), 1×10^{-4} (top right), 5×10^{-5} (bottom left) and 1×10^{-5} (bottom right) respectively.

S3. Example GC chromatogram

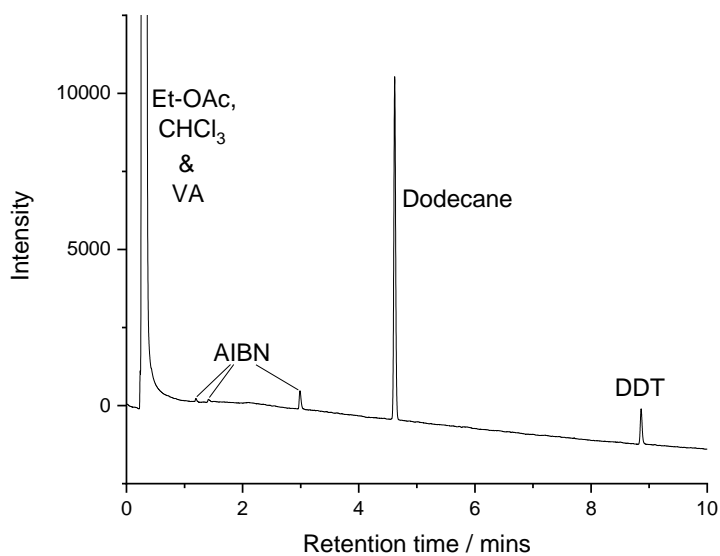


Figure S3: Example GC chromatogram showing the elution behaviour of the reactants.

S4. GC calibration Equation, data and fit

$$y = bx + c$$

Where $b = 1.0032$ and $c = 2.066 \times 10^{-3}$

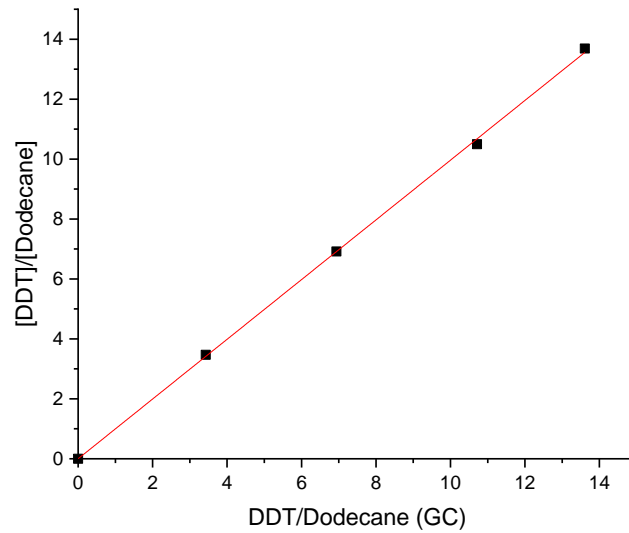


Figure S4: Calibration plot showing the relationship between the [DDT]/[Dodecane] ratio and the ratio of the signals recorded in the GC chromatogram.

S5. Determination of Mark-Houwink-Sakurada parameters

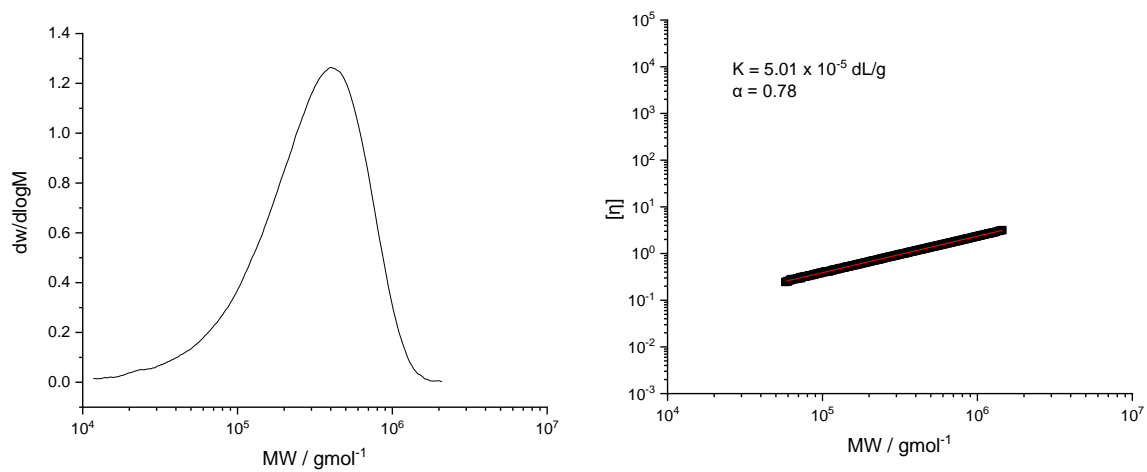


Figure S5: $dw/d \log M$ distribution of the poly(vinyl acetate) sample used for triple detection analysis (left) and the determined intrinsic viscosity $[\eta]$ as a function of MW with the fitted K and α values.