

## Supporting information

### Method

#### Synthesis of branching agents:

Allyl isopropyl carbonate **1**, A three necked round bottom flask equipped with a nitrogen inlet, a condenser and a pressure equalising additional funnel was charged with *isopropanol* (26g, 0.432mol.) and triethylamine (45.5g, 0.45mol). Allyl chloroformate (50g, 0.414 mol) was added slowly to the precooled *isopropanol* and triethylamine mixture. The reaction mixture was stirred for 6 hours at ambient temperature and the reaction was quenched by the addition of distilled water. The organic layer was washed with saturated sodium bicarbonate followed by distilled water. The organic layer was washed with distilled water and then dichloromethane was added. The organic later was collected and the dichloromethane was removed by rotary evaporation. The product was then redissolved in dichloromethane and washed with water once more. 250 MHz <sup>1</sup>H NMR and GC/MS confirmed the product to be allyl *isopropyl carbonate 1*. The GC chromatogram consisted of a single peak with no evidence for impurities.

<sup>1</sup>H NMR: CH\*:CH<sub>2</sub> δ 5.9; CH:CH<sub>2</sub>\* δ 5.1-5.4; (CH<sub>3</sub>)<sub>2</sub>CH\* δ 4.8; OCH<sub>2</sub>\*CH:CH<sub>2</sub> δ≈4.5; (CH<sub>3</sub>)<sub>2</sub>C δ≈1.2. GC/MS: GC, single peak, Rt time 4.42, CI MS m/z 162 (MNH<sub>4</sub><sup>+</sup>). *isopropenyl isopropyl carbonate 2*.

*Isopropenyl chloroformate* (37g, 0.3 mol) was added slowly to a mixture of precooled 2-propanol (21g, 0.35 mol) and triethylamine (36.35g, 0.36mol). The reaction procedure was similar to the above. 250 MHz <sup>1</sup>H NMR and GC/MS confirmed the product *isopropenyl 2-propyl carbonate 2*. The GC chromatogram consisted of a single peak with no evidence for impurities.

<sup>1</sup>H NMR: CH\*CH<sub>2</sub> δ≈5.75; CHCH<sub>2</sub>\* δ≈5.1-5.3; (CH<sub>3</sub>)<sub>2</sub>CH\* δ≈4.7; CH<sub>3</sub>\*CH<sub>2</sub>: δ≈1.9 (CH<sub>3</sub>)<sub>2</sub>C δ≈1.2. GC/MS: GC Rt time 6.32, CI MS m/z 162 (MNH<sub>4</sub><sup>+</sup>).

Carbonic acid allyl ester isopropoxy-ethyl ester **3**.

Allyl chloroformate (50g, 0.414mol) was added slowly to a mixture of *isopropoxy ethanol* (45.8g, 0.44mol) and triethylamine (45.5g, 0.45mol). The reaction procedure was employed as above. 250 MHz <sup>1</sup>H NMR and GC/MS confirmed the product to be allyl carbonic acid allyl ester *isopropoxy-ethyl ester 3*. The GC chromatogram consisted of a single peak with no evidence for impurities.

Carbonic acid *isopropenyl ester isopropoxy-ethyl ester, 4*

<sup>1</sup>H NMR: CH<sub>2</sub>:CH\* δ≈5.8; CH<sub>2</sub>\*:CH δ≈5.2; OCH\*CH<sub>2</sub> δ≈4.5; OCH<sub>2</sub>CH<sub>2</sub> δ≈3.5; (CH<sub>3</sub>)<sub>2</sub>CH\* δ≈3.5; (CH<sub>3</sub>)<sub>2</sub>C δ≈1.1. GC/MS: GC Rt time 8.03, CI MS m/z 189 (MH<sup>+</sup>).

*Isopropenyl chloroformate* (37g, 0.3 mol) was added slowly to a mixture of precooled *isopropoxy ethanol* (36.4g, 0.35 mol) and triethylamine (36.35g, 0.36mol). The reaction procedure was similar to the above. 250 MHz <sup>1</sup>H NMR and GC/MS confirmed the product *isopropenyl(ethoxy) isopropyl carbonate, 4*. The GC chromatogram consisted of a single peak with no evidence for impurities.

<sup>1</sup>H NMR: CH<sub>2</sub>:CH\* δ≈5.75; CH<sub>2</sub>\*:CH δ≈5.1-5.35; OCH<sub>2</sub>CH<sub>2</sub> δ≈3.5; (CH<sub>3</sub>)<sub>2</sub>CH\* δ≈3.5; CH<sub>3</sub>\*CH<sub>2</sub>: δ≈1.75; (CH<sub>3</sub>)<sub>2</sub>C δ≈1.1. GC/MS: GC Rt time 7.69, MS m/z 189 (MH<sup>+</sup>).

In each case the yields of purified products were approximately 30 wgt.%.

### Synthesis of hyper-branched poly(vinyl acetate):

Ampoules were filled with a solution of vinyl acetate, solvent, AIBN and branching agent (**1**, **2**, **3** or **4**). The ampoules were degassed using 6 freeze pump thaw cycles on a vacuum line at  $10^{-5}$  mbar. Once the degassing cycles had been completed, the ampoules were flame sealed then frozen at  $-20^{\circ}\text{C}$  until use. They were then heated at  $60^{\circ}\text{C}$  for 4 hours after which time the polymerization was quenched by freezing. The ampoules were thawed and the contents were dissolved in THF (100 ml), prior to being precipitated into 40-60 petroleum ether (1litre). The precipitated polymer was dried *in vacuo*, before being redissolved in THF, reprecipitated and dried *in vacuo*.

Polymerizations were also carried out in an autoclave. Butyl acetate (30ml), plus the monomer and branching agent were charged to the autoclave's glass liner, and the monomers were polymerized at  $150^{\circ}\text{C}$  under nitrogen. The poly(vinyl acetate), was precipitated into 40-60 pet ether and was filtered off, redissolved in THF, before precipitation in to 40-60 pet ether. This process was repeated and the polymer dried *in vacuo*.

### Calculation of Branching Efficiency (BE):

In polymerizations incorporating branching agents **1**, **3** or **4**, the branching efficiency was calculated by comparing the integrated peak areas (250 MHz  $^1\text{H}$  NMR) of the methine proton present in the *isopropyl* group of the polymerized residue of the branching agent at  $\delta \approx 3.75$  ppm and the methylene protons (**b** in **1** and **3** and **e** in **4**) at  $\delta \approx 4.25$  ppm, as follows:

$$\text{General Formula, } BE = \frac{\frac{A_{\text{methylene}}}{2} - A_{\text{methine}}}{\frac{A_{\text{methylene}}}{2}} \quad \text{where, } A_{\text{methylene}} = \text{Peak area of methylene}$$

proton,  $A_{\text{methine}}$  = Peak area of methine proton derived from branching agents.

In the examples in which **2** was used as the branching agent, the integrated peak areas of *isopropyl* methine proton,  $\delta \approx 3.7$  ppm and *isopropyl* methyl protons,  $\delta \approx 1.2$  ppm were used as follows:

$$BE = \frac{\frac{A_{\text{methyl}}}{6} - A_{\text{methine}}}{\frac{A_{\text{methyl}}}{6}}$$

### Degree of Branching calculation:

The degree of branching (DB) was calculated on the basis of the average fraction of repeat units that contained a branch, that is:

$$DB = (N_{\text{allyl carbonate}} \times BE) / (N_{\text{allyl carbonate}} + N_{\text{vinyl acetate}})$$

*N*<sub>allyl carbonate</sub> is derived from integration of:

Branching agent **1**, peak **b** (ESI figure 1)

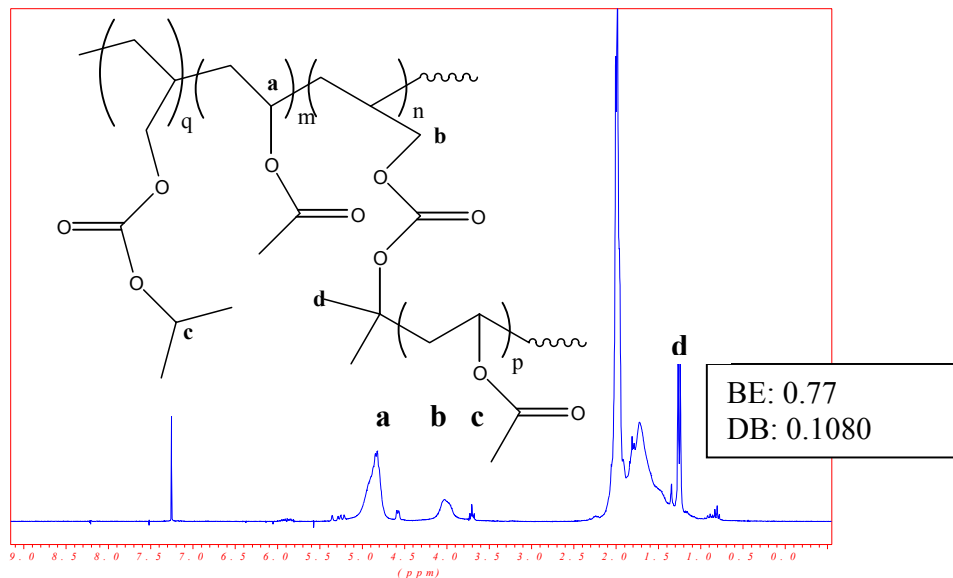
Branching agent **2**, peak **d** (ESI figure 2)

*N*<sub>vinyl acetate</sub> is derived from integration of the backbone methine from the VA residues ( $\delta$  4.7 – 5.0 ppm)

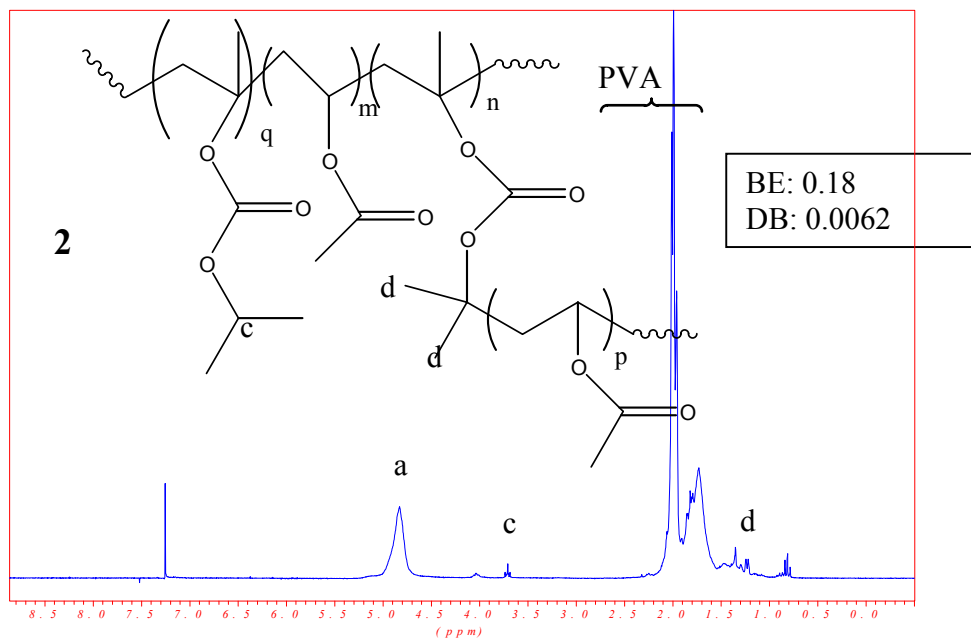
Examples of the spectra derived from polymerization with both **1** or **2** are shown in ESI figures 1 and 2. These figures also give the results of the calculations of BE and DB for these examples.

Examples of  $^1\text{H}$  NMR spectra

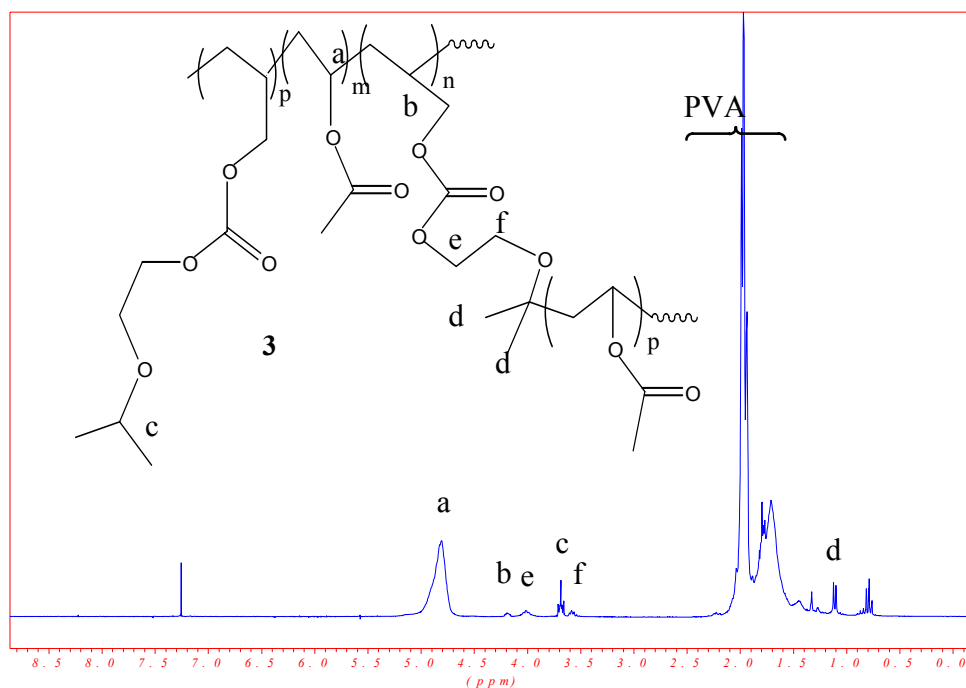
$^1\text{H}$  NMR were obtained on a Bruker AC 250 MHz spectrometer using deuterated chloroform as solvent at ambient temperature.



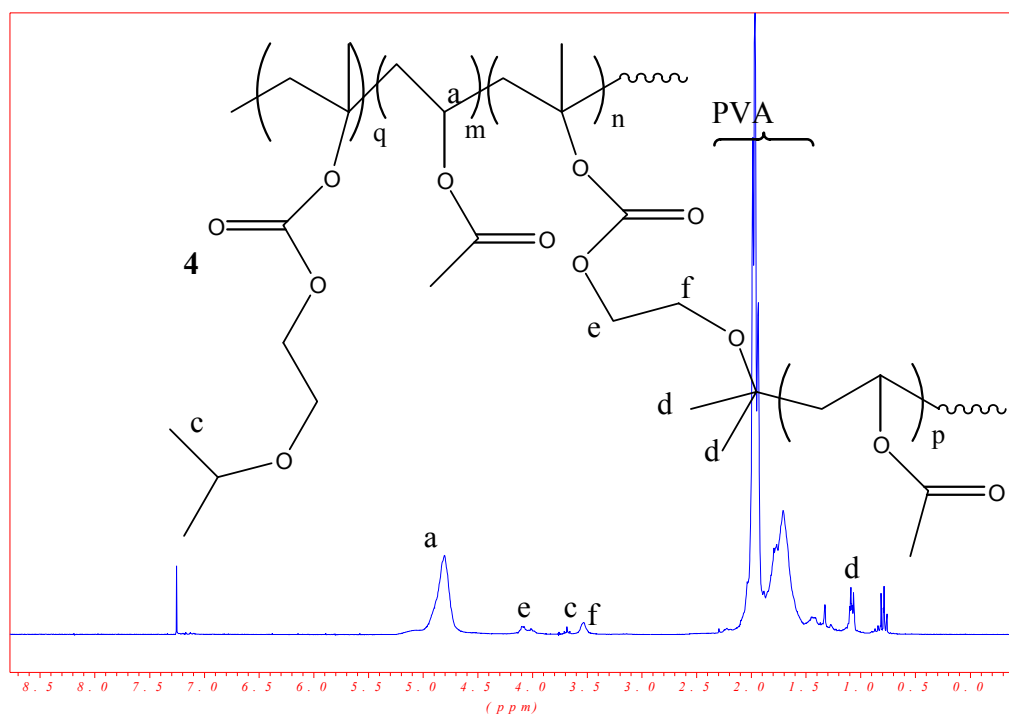
ESI Figure 1 An example of the  $^1\text{H}$  NMR spectrum of a copolymer produced from polymerization of VA and **1**



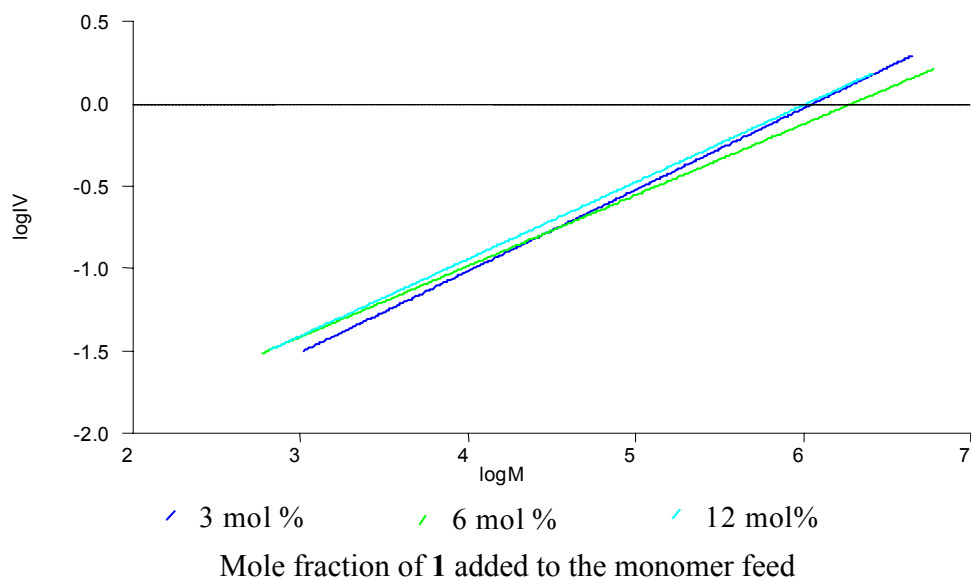
ESI Figure 2 An example of the  $^1\text{H}$  NMR spectrum of a copolymer produced from polymerization of VA and **2**



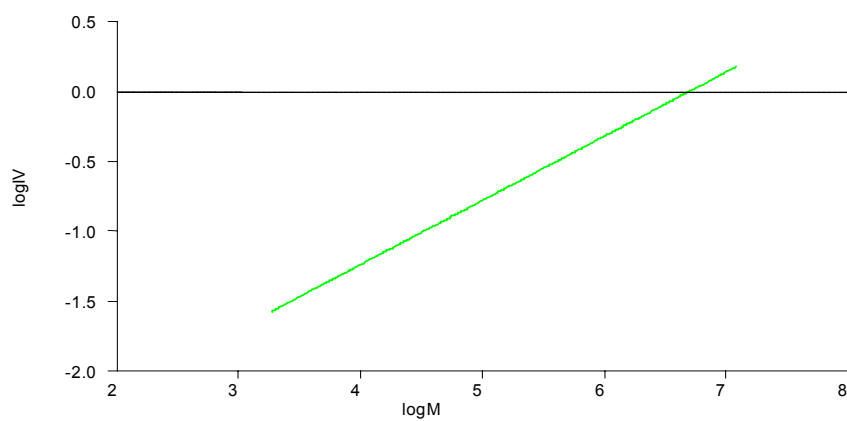
ESI Figure 3 An example of the <sup>1</sup>H NMR spectrum of a copolymer produced from polymerization of VA and **3**



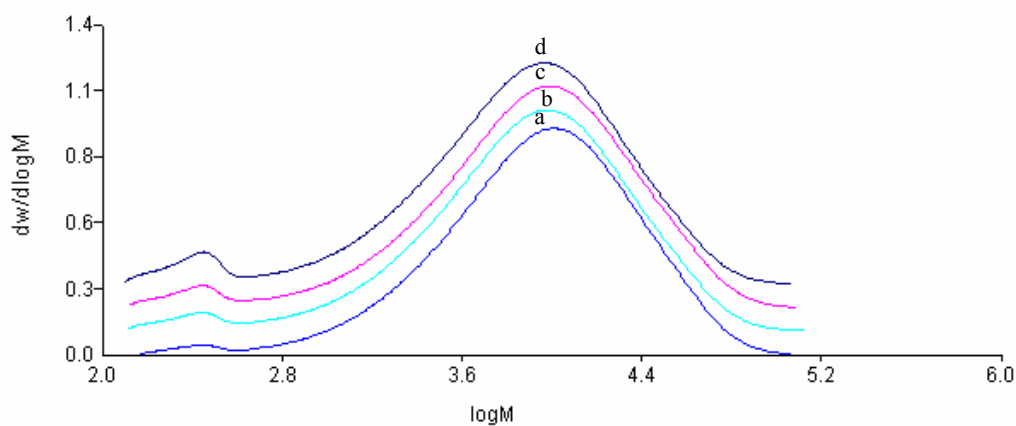
**Mark Houwink plots derived from Branched PVA prepared in the presence of 2-propanol at 60°C**



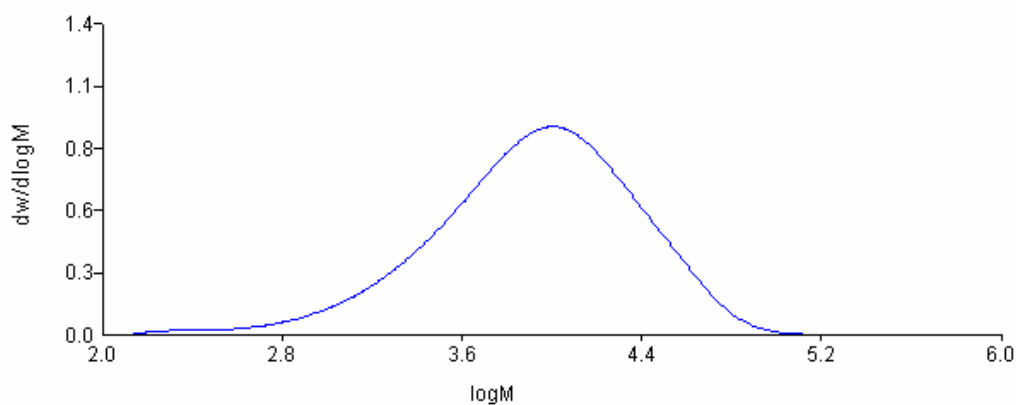
$$[\text{VA}] = 5.4 \text{ mol dm}^{-3}$$



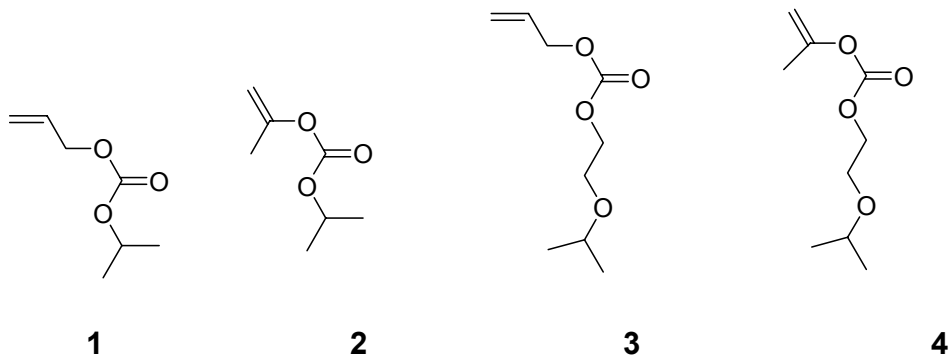
$$[\text{VA}] = 4.3 \text{ mol dm}^{-3}, \text{ fraction of 1 in monomer feed} = 3 \text{ mol.}\%$$



SEC nominal molecular weight distributions for polymerizations of VAc in the presence of **2** at 150°C in n-butyl acetate, (a) VAc: CTA = 1:0.03; (b) VAc: CTA = 1: 0.06; (c) VAc: CTA = 1: 0.12 and (d) VAc: CTA = 1: 0.24.



SEC nominal molecular weight distributions for polymerizations of VAc in absence of branching monomer at 150°C in n-butyl acetate.



**Structures of allylic carbonate comonomers**