Hydrocarbon based stabilisers for the synthesis of cross-linked poly(2-hydroxyethyl methacrylate) particles in supercritical carbon dioxide

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Supporting Information

Calculation of the VAc:VPi composition

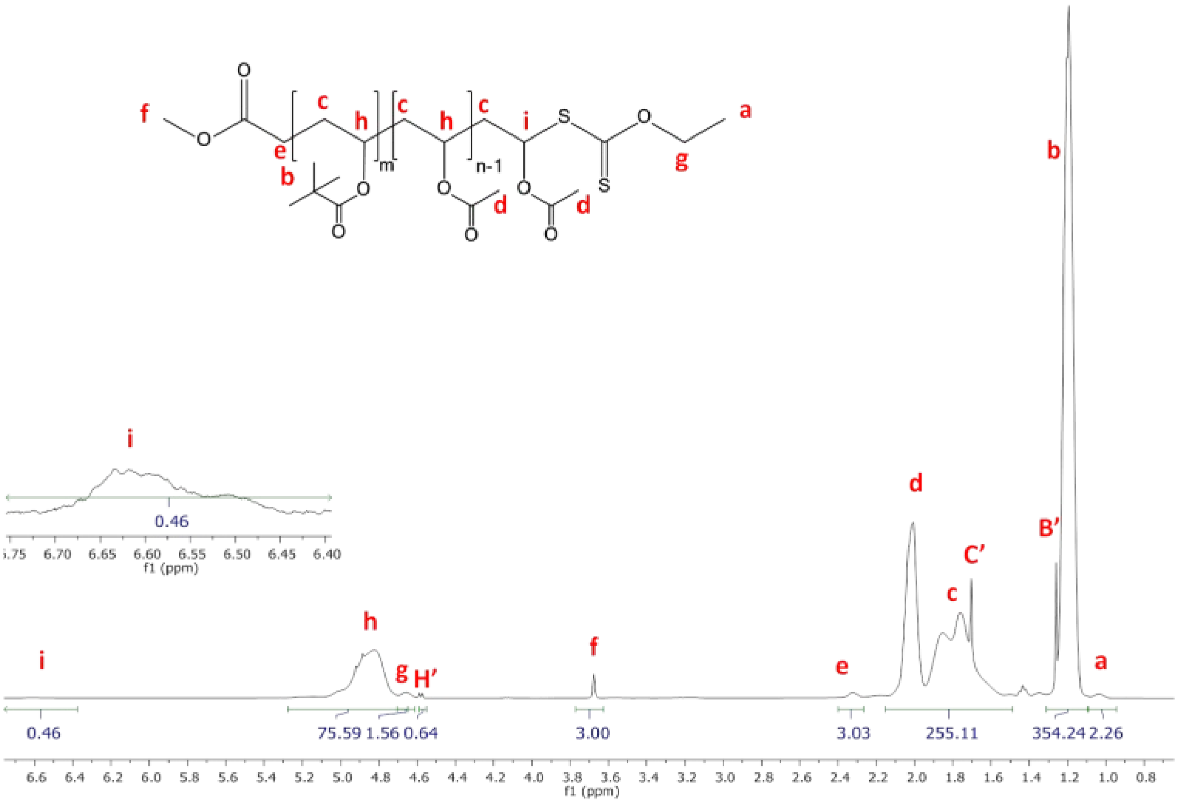

Figure S1: ^{1}H-NMR spectrum for a standard P(VAc-*stat*-VPi) copolymer.

VAc:VPi ratios were calculated by comparison of the peaks b, c and d. Example calculation is shown below:

VPi (9H from ^{t}Bu) = 354.24/9 = 39.36

5VAc (3H from CH_3 + 2H from CH_2) + 2VPi (2H from CH_2) = 255.11

5VAc + 2x39.36 = 255.11 $\rightarrow$ VAc= 35.27

% VAc = [VAc / (VAc + VPi)]x100 = [35.27/ (35.27+39.36)]x100 = 47%

Monomeric residual signals were found and highlighted as H', C' and B'.

Molar mass calculation by NMR

Considering as an example the NMR spectrum given in Figure S1, M_n values obtained by NMR were calculated from the degree of polymerisation obtained from the integration of the resonance *h* when calibrating signal *f* to 3.

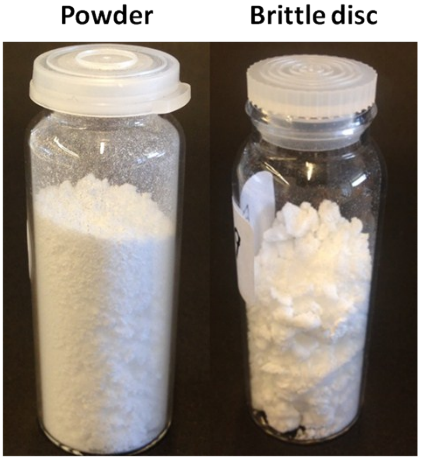

Figure S2: Representative products taken straight after depressurisation of the autoclave. The left hand-side is a free flowing powder, the right hand-side is a brittle disc that was chiselled out from the reactor.

Table S1: DMA results of the PHEMA particles

Entry	Stabiliser ($w_{stabiliser}/v_{monomer}$ %)	Cross-linker ($v_{cross\text{-}linker}/v_{monomer}$ %)	Peak 1 (°C)	Peak 2 (°C)
1	10	0	57.5	98.5
2	10	1	53.5	101
3	10	3	53.6	106.5

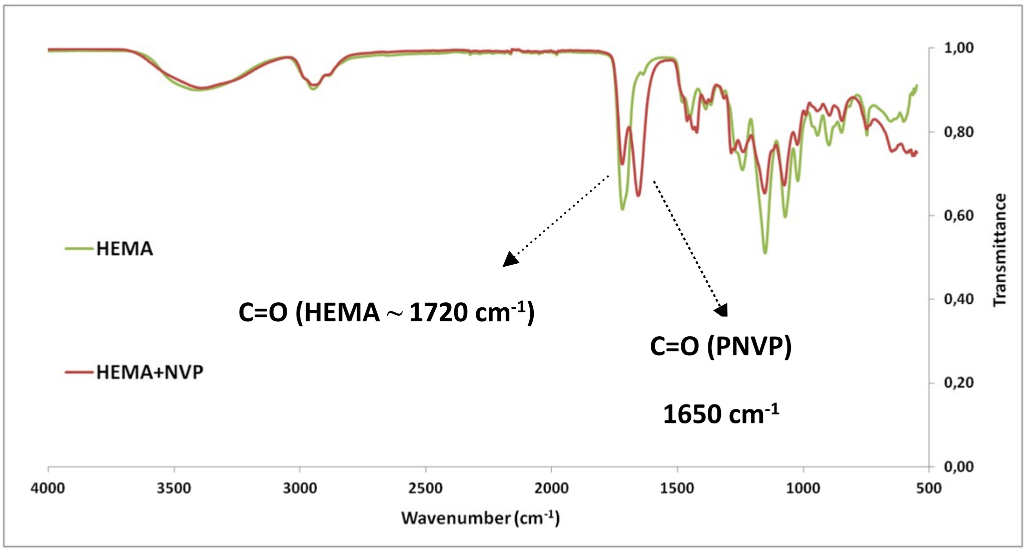

Figure S3: ATR FTIR spectra for PHEMA and P(HEMA-*co*-NVP) clearly demonstrating the introduction of carbonyl features corresponding to NVP.

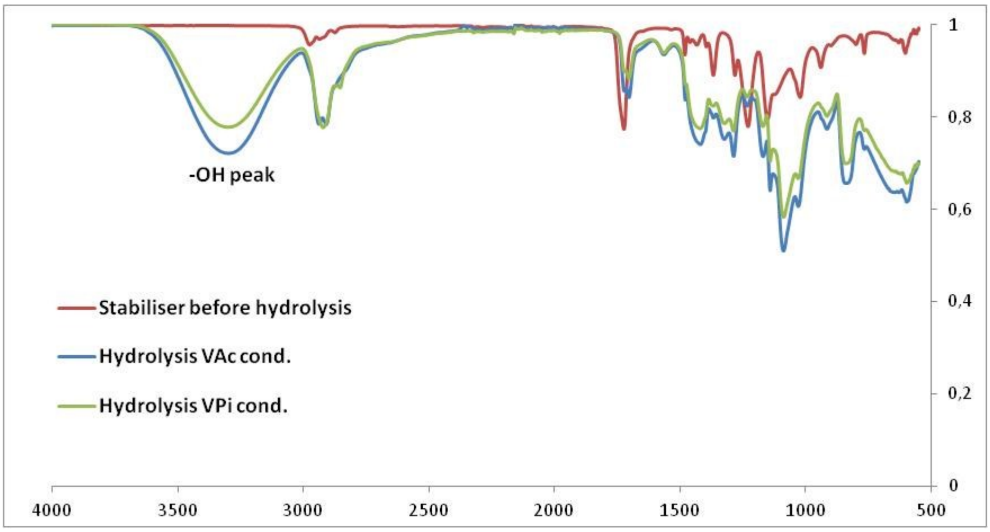

Figure S4: FTIR-ATR spectra of the P(VAc-*stat*–VPi) (Table 1, Entry 15) stabiliser before (red) and after hydrolysis under two different sets of hydrolysis conditions (see the experimental section). The data clearly show that hydrolysis has occurred with the appearance of –OH functionalities. Some loss of carbonyl moieties is also observed.

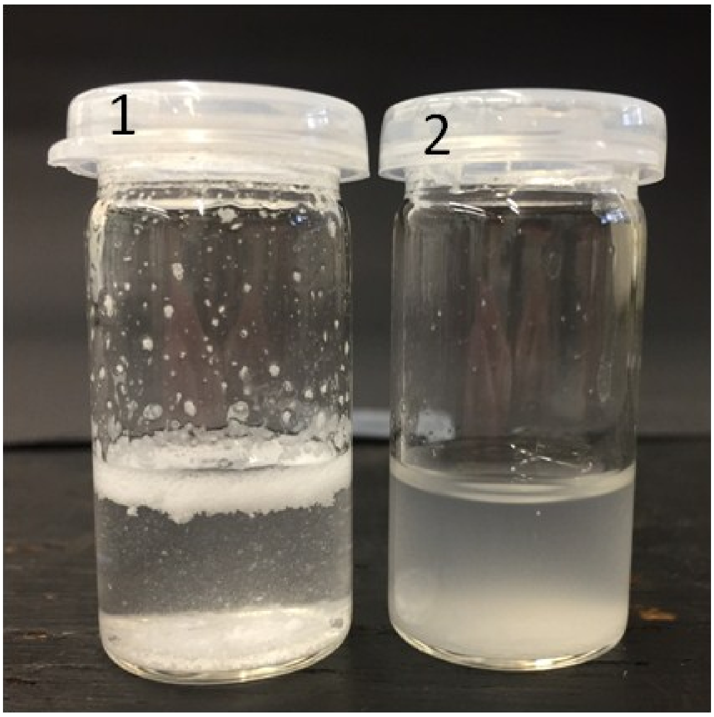

Figure S5: PHEMA particles synthesized in the presence of PEO-*b*-PFDA before hydrolysis (1) and after hydrolysis (2) dispersed in water with a known concentration 5 mg mL^{-1}. Some improvement is clearly seen for PEO-*b*-PFDA stabiliser but may be attributable to hydrolysis of the C=O bonds present on the stabiliser leading to an improvement of the water dispersability. More importantly, the stability of this dispersion is much lower compared to the P(VAc-*stat*-VPi) hydrolysed particles. After less than 15 minutes the PEO-*b*-PFDA stabilised particles start to phase separate and a clear water phase is visible. By contrast the dispersion of particles from P(VAc-*stat*-VPi) is stable for ca. 48 minutes.