Supplementary Information

Graft copolymers of hydroxyethyl cellulose by a ‘grafting to’ method: $^{15}\text{N}$ labelling as a powerful characterisation tool in ‘click’ polymer chemistry

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RAFT Polymerisations

Synthesis of RAFT agents 5 and 8 are shown in Schemes S1 and S2 respectively.

![Scheme S1: Preparation of O-ethyl S-prop-2-ynyl carbonodithiolate (5)](image)

![Scheme S2: Synthesis of alkyne-terminated trithiocarbonate (8)](image)

Polymerisation of NVP ad NIPAAM are shown in Schemes S3 and S4.
Scheme S3: RAFT polymerisation of NVP

Scheme S4: RAFT polymerisation of NIPAAm

Selected data for PVP and PNIPAAm prepared by RAFT are shown in Figures S1-4.
**Figure S1:** Solution state $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of poly(N-vinylpyrrolidone) (PVP) 10 ($\text{DP}_{\text{targeted}}$=10)

![Graph showing the NMR spectrum of poly(N-vinylpyrrolidone) (PVP) 10](image)

**Figure S2:** Results of SEC analysis of poly(N-vinylpyrrolidone) (PVP) ($\text{DP}_{\text{targeted}}$=10)
Figure S3: Solution state $^1$H NMR spectrum (400 MHz, CDCl$_3$) of PNIPAAM 12

Figure S4: Results of the SEC analysis of PNIPAAM$_{10}$ polymerised using trithiocarbonate 8 (black) and xanthate 5 (orange) as chain transfer agent
The xanthate (5) that was used to polymerise NVP was also used to polymerise NIPAAm (Figure S4). However, only 60% monomer conversion was obtained after overnight reaction and the molecular weight distribution was broader compared to that obtained with the trithiocarbonate ($D_M = 1.5$ vs. 1.2).

CuAAC Coupling Reactions

Scheme S5: CuAAC between N₃-HEC and transfer agent

Scheme S6: CuAAC reaction between N₃-HEC and alkyne-terminated PVP₁₀

The numbering scheme used in the NMR characterisation of HEC-g-PVP is shown in Figure S5.
Figure S5: Numbering of the molecular structure of HEC-g-PVP$_{10}$, where $x$ and $y$ represent the degree of functionalization.
**Scheme S6:** CuAAC between alkyne-ended PNIPAAM$_{10}$ and partially labelled N$_3$-HEC

The FTIR spectrum of the coupled product, showing the disappearance of the azide peak, is shown in Figure S6.

**Figure S6:** FT-IR spectrum of (a) HEC-g-PNIPAAM$_{10}$ and (b) N$_3$-HEC