Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supplementary Information

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

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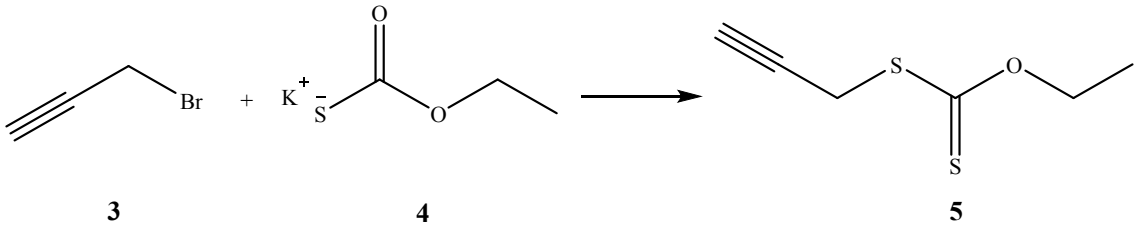
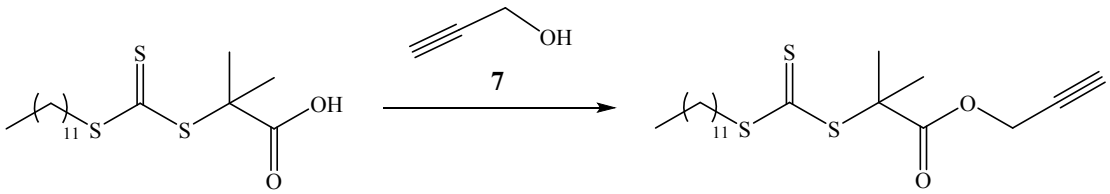
RAFT Polymerisations

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



3 **4** **5**

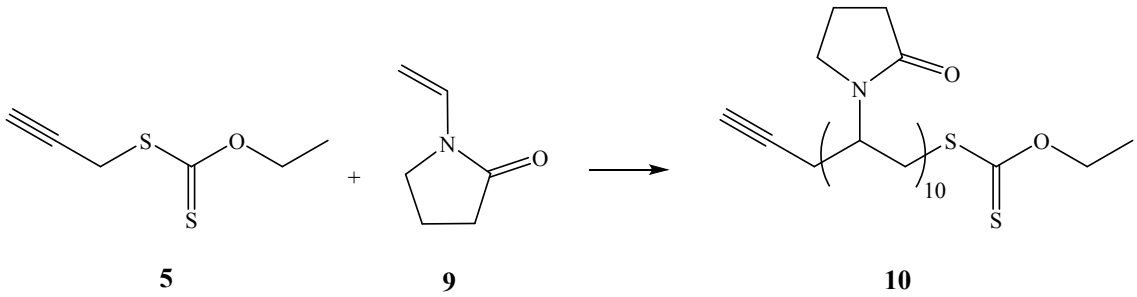
Scheme S1: Preparation of O-ethyl S-prop-2-ynyl carbonodithiolate (**5**)



6 **8**

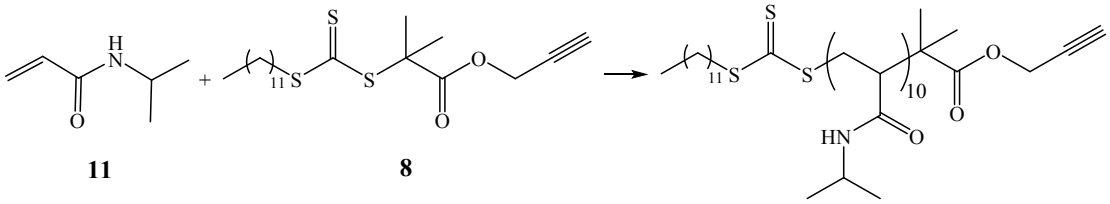
Scheme S2: Synthesis of alkyne-terminated trithiocarbonate (**8**)

Polymerisation of NVP ad NIPAAM are shown in Schemes S3 and S4.



5 **9** **10**

Scheme S3: RAFT polymerisation of NVP



11 **8** **12**

Scheme S4: RAFT polymerisation of NIPAAM

Selected data for PVP and PNIPAAM prepared by RAFT are shown in Figures S1-4.

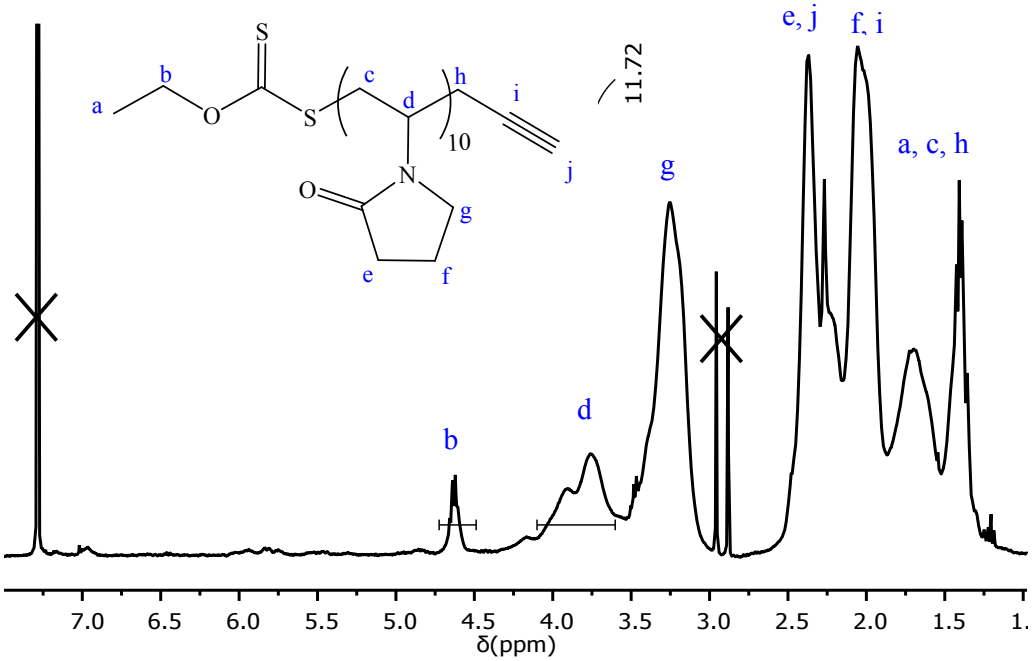


Figure S1: Solution state ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of poly(N-vinylpyrrolidone) (PVP) **10** ($DP_{targeted}$ =10)

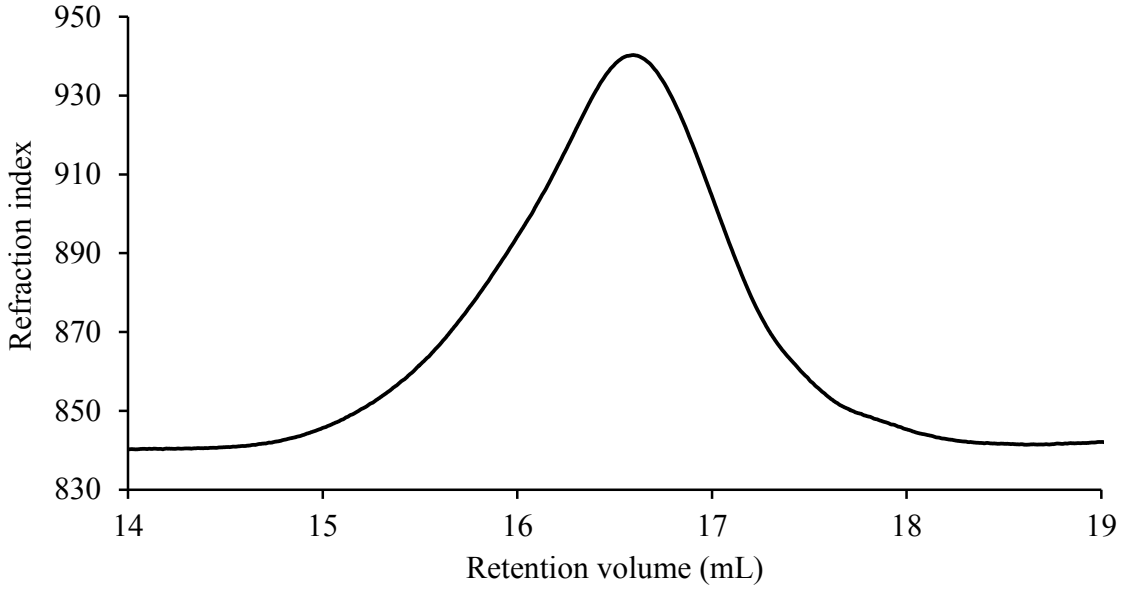


Figure S2: Results of SEC analysis of poly(N-vinylpyrrolidone) (PVP) ($DP_{targeted}$ =10)

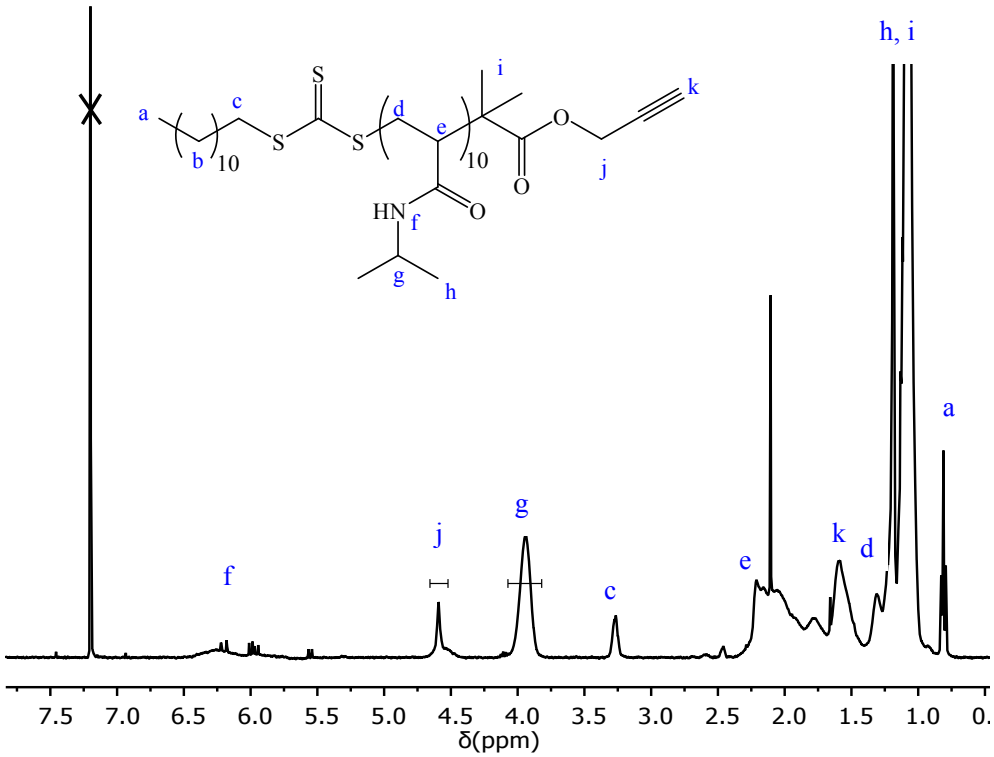


Figure S3: Solution state ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PNIPAAM **12**

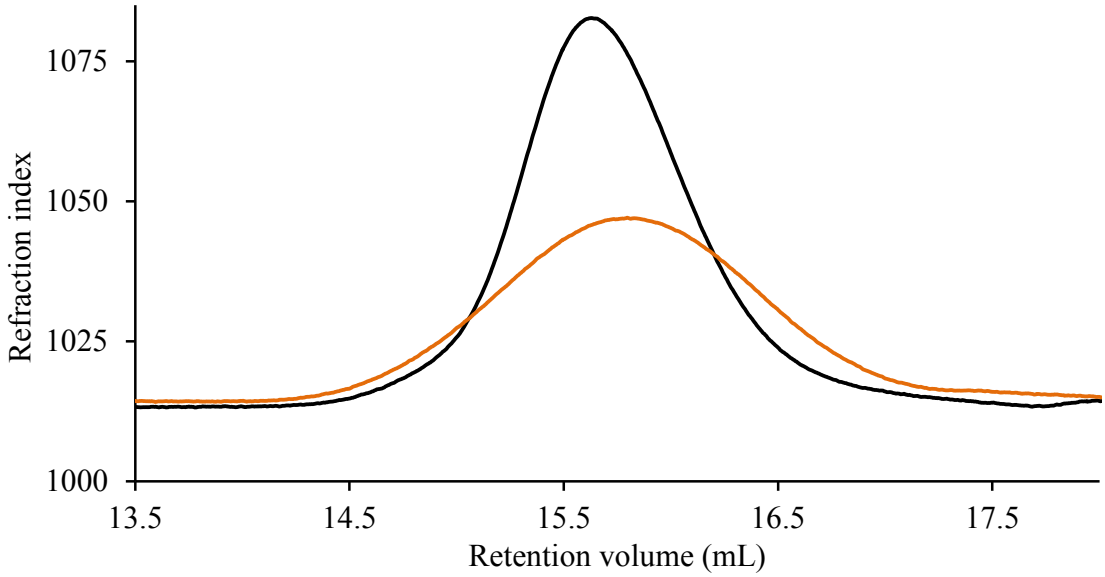
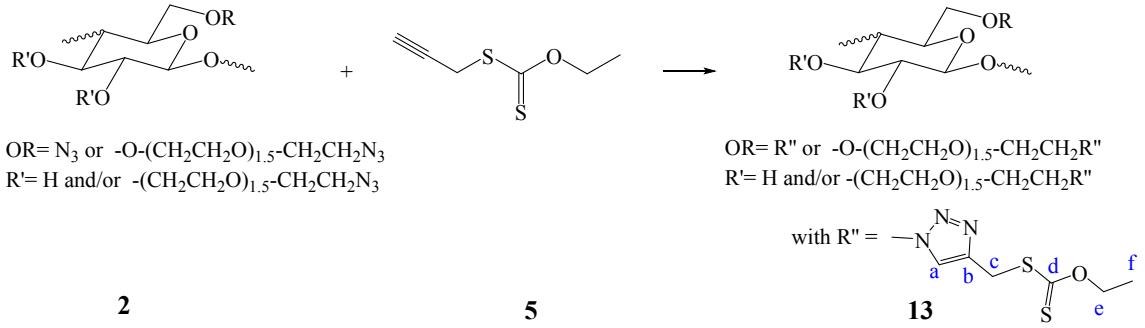


Figure S4: Results of the SEC analysis of $PNIPAAM_{10}$ polymerised using trithiocarbonate **8** (black) and xanthate **5** (orange) as chain transfer agent

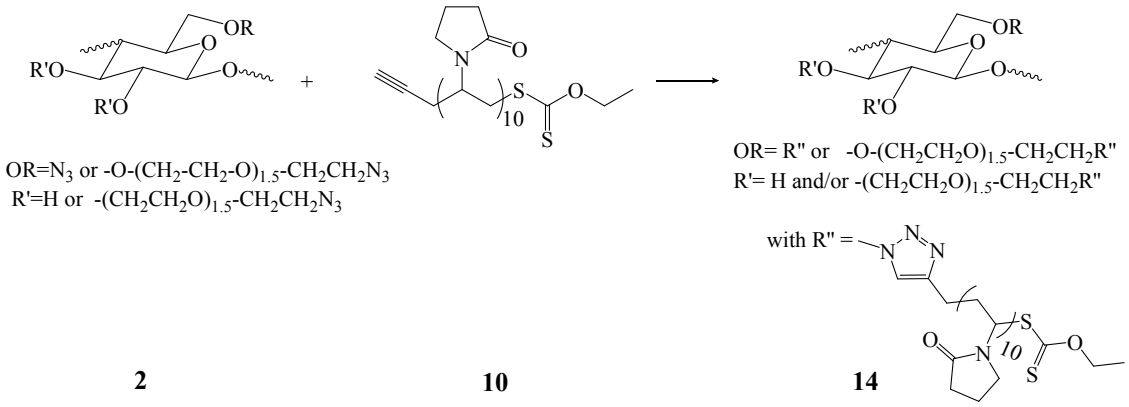
The xanthate (**5**) that was used to polymerise NVP was also used to polymerise NIPAAM (Figure S4). However, only 60% monomer conversion was obtained after overnight reaction and the molecular weight distribution was broader compared to that obtained with the trithiocarbonate ($Đ_M$=1.5 vs. 1.2).

CuAAC Coupling Reactions



2 **5** **13**

Scheme S5: CuAAC between N_3-HEC and transfer agent



2 **10** **14**

Scheme S6: CuAAC reaction between N_3-HEC and alkyne-terminated PVP_{10}

The numbering scheme used in the NMR characterisation of HEC-g-PVP is shown in Figure S5.

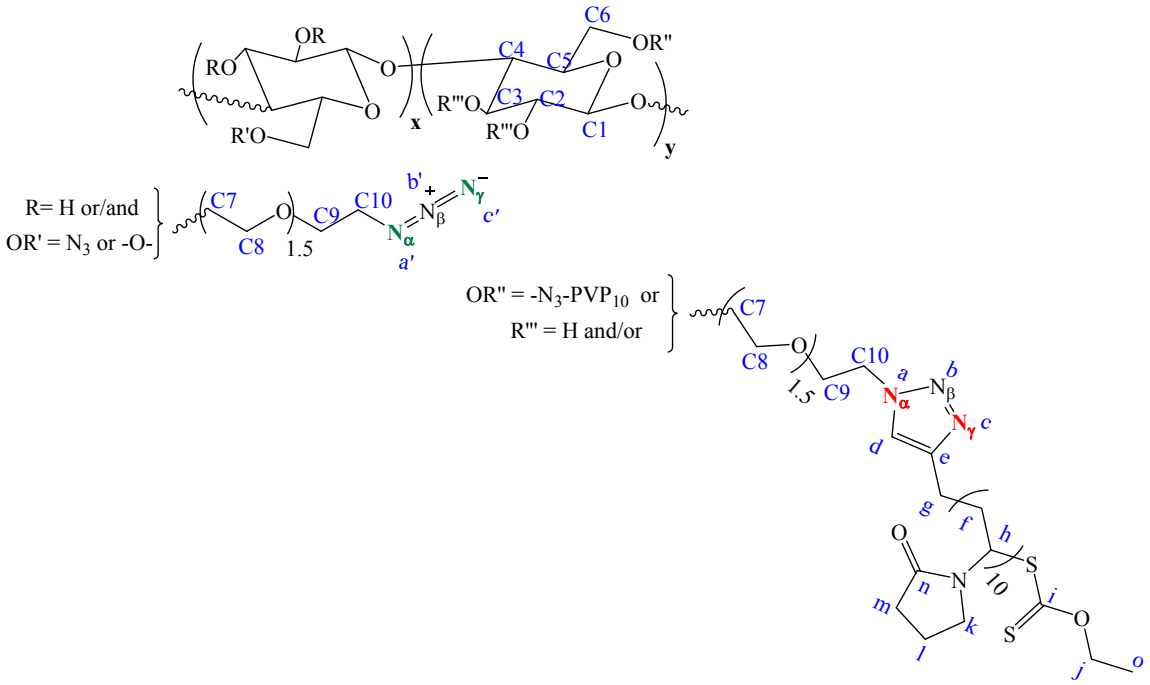
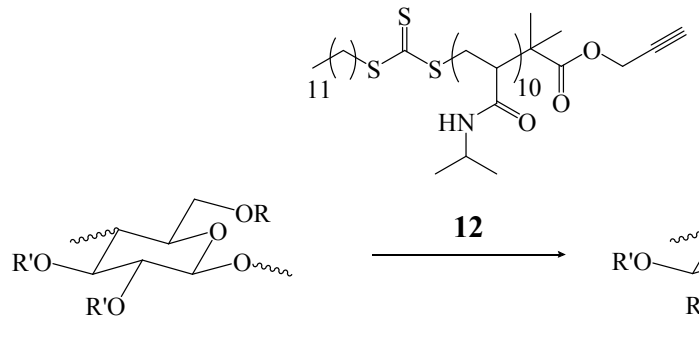


Figure S5: Numbering of the molecular structure of HEC-g-PVP_{10}, where x and y represent the degree of functionalization

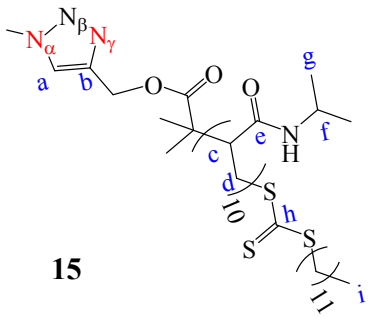


OR=N_3 or -O-$(CH_2$-CH_2-O$)_{1.5}$-$CH_2CH_2N_3$
R'=H or -$(CH_2CH_2O)_{1.5}$-$CH_2CH_2N_3$

2

OR= R" or -O-$(CH_2CH_2O)_{1.5}$-CH_2CH_2R"
R'= H and/or -$(CH_2CH_2O)_{1.5}$-CH_2CH_2R"

with R" =



15

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.

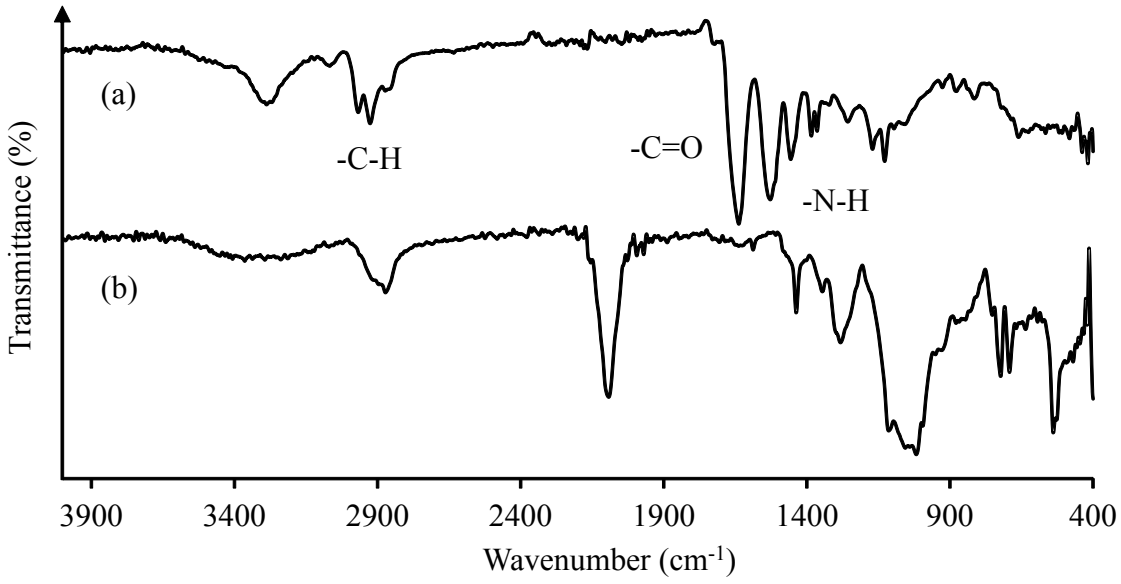


Figure S6: FT-IR spectrum of (a) HEC-g-$PNIPAAM_{10}$ and (b) N_3-HEC