

Supporting Information:

Reversible Complexation of Iminophenylboronates with Mono- and Dihydroxy Methacrylate Monomers and their Polymerization at Low Temperature by Photoinduced ATRP in One Pot

Elkin Amado and Jörg Kressler*

Department of Chemistry, Martin Luther University Halle-Wittenberg, D-06099 Halle (Saale),
Germany.

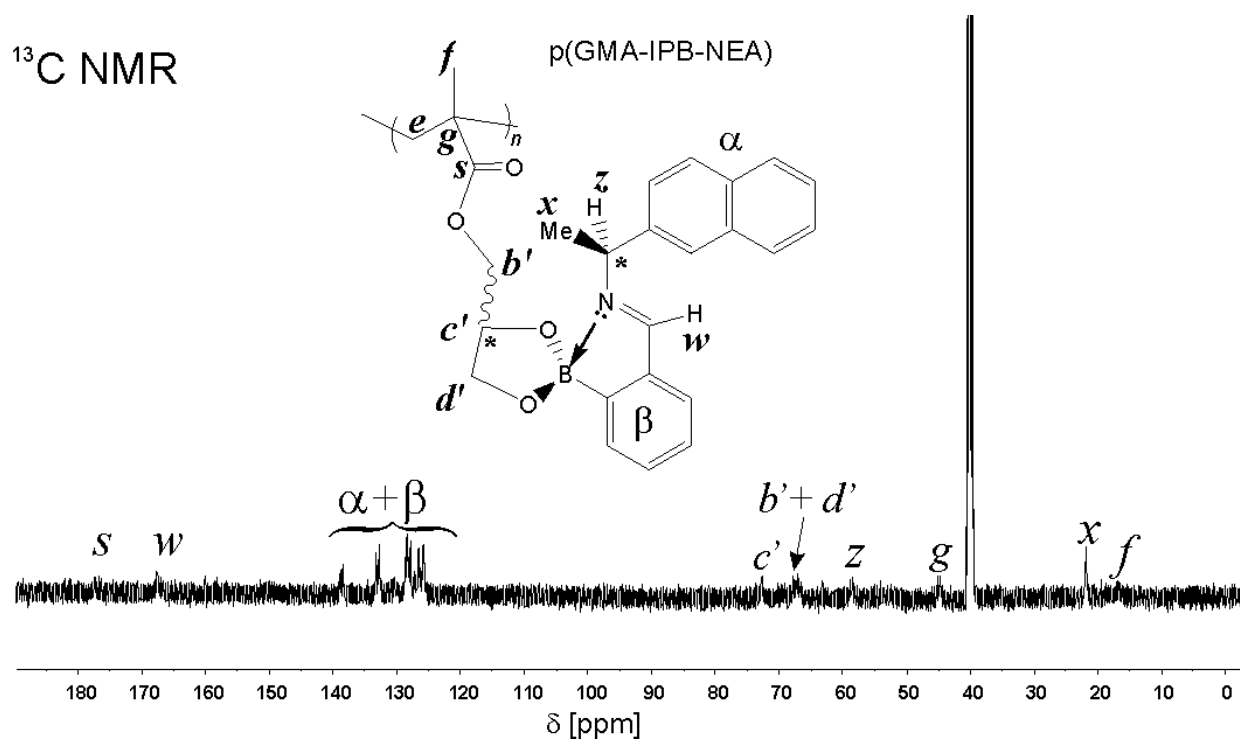


Figure S1. ¹³C NMR spectra (DMSO-*d*₆, 126 MHz) of (a) p(GMA-IPB-NEA), poly(IPB methacrylate) from the esterification of GMA with FPBA and amine **2**.

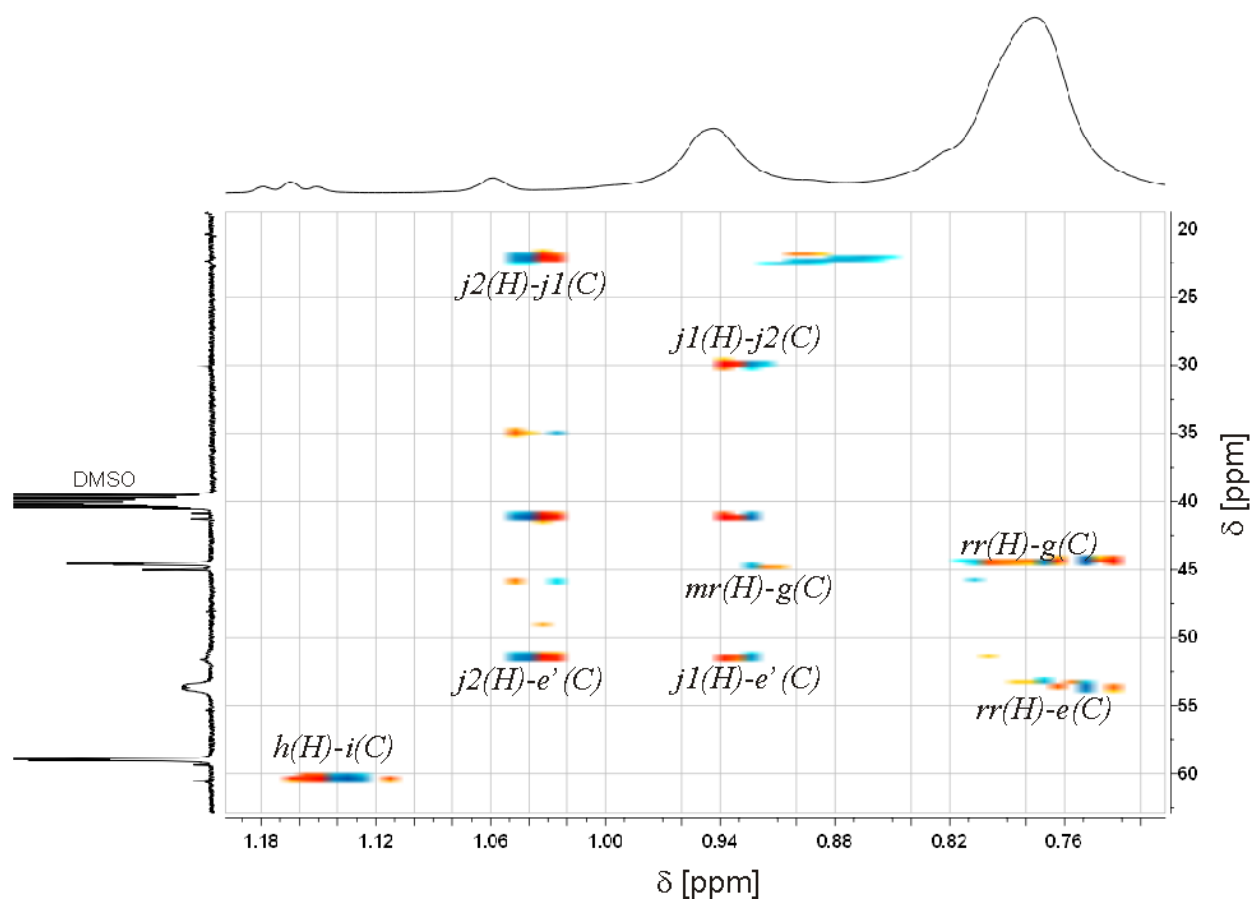


Figure S2. ^1H - ^{13}C gHMBCAD NMR spectrum of pHEMA obtained after decomplexation of p(HEMA-IPB-NEA) polymerized by photo-induced ATRP (0 °C, 20 h). See structure in Figure 5b for peaks assignment.

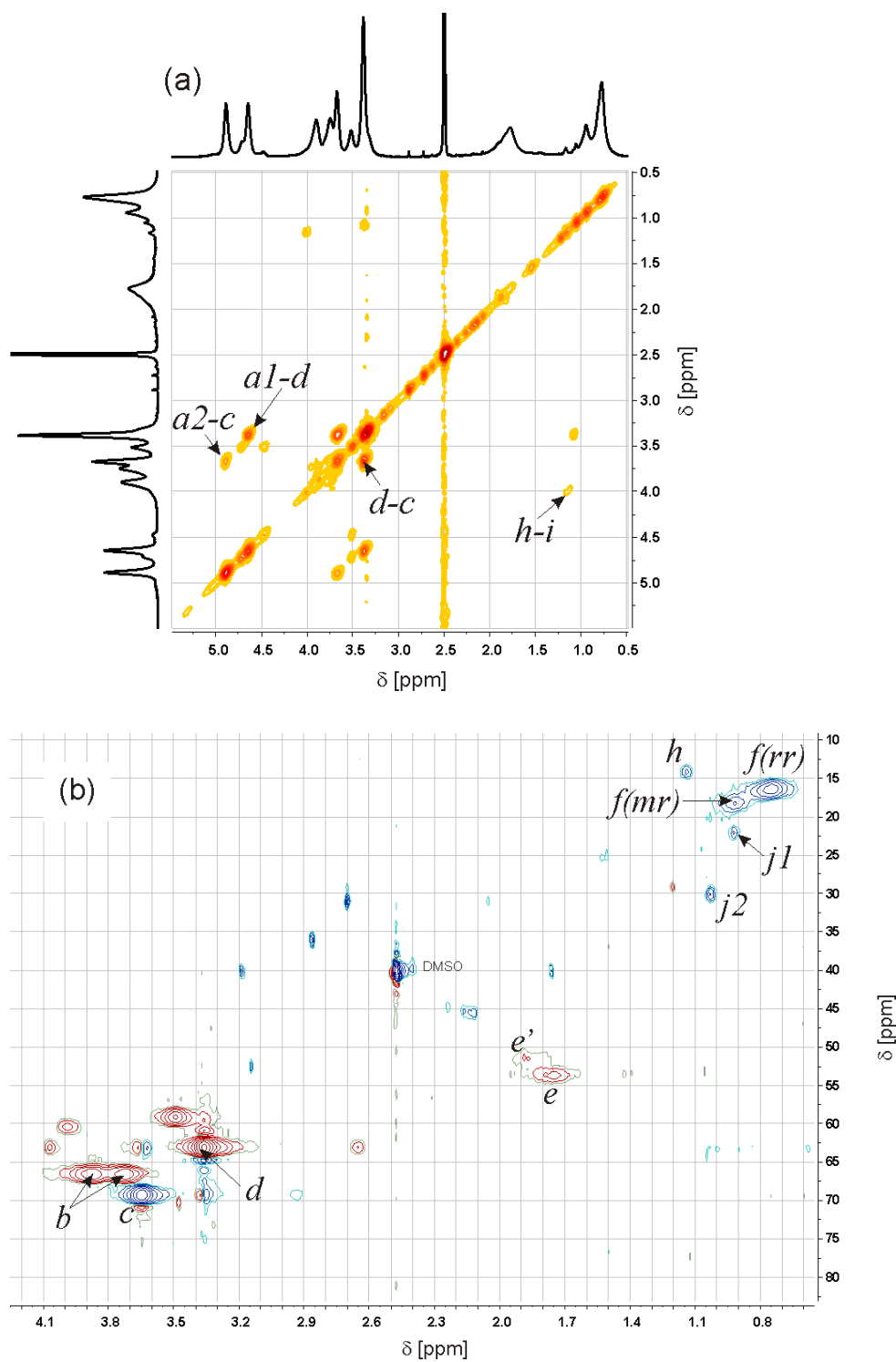


Figure S3. (a) ^1H - ^1H COSY, and (b) multiplicity edited ^1H - ^{13}C gHSQCAD NMR spectra of pGMA polymerized by classical ATRP (0 °C, 6 d). See structure in Figure 2b for peaks assignment.

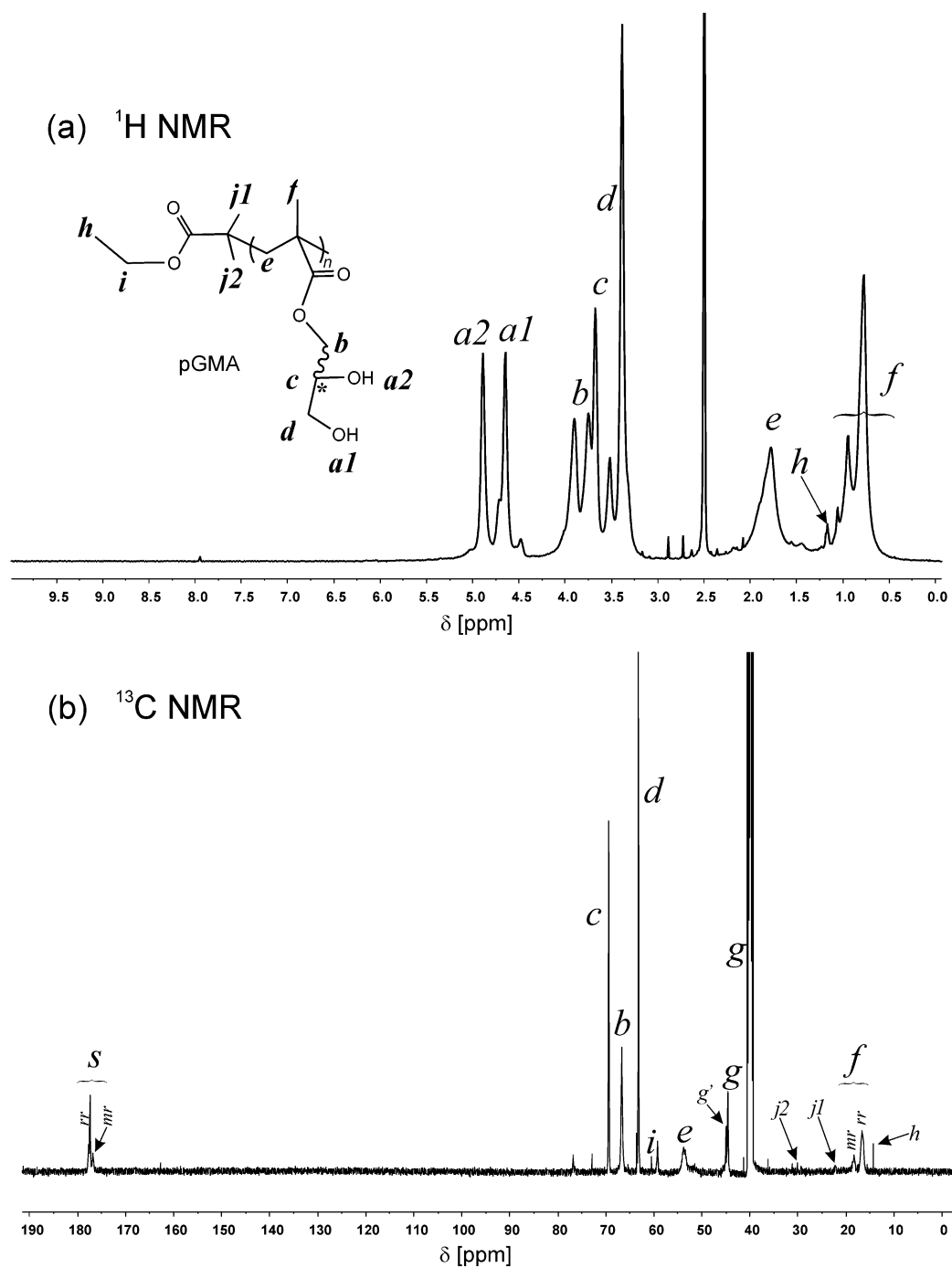


Figure S4. (a) ^1H NMR spectrum ($\text{DMSO-}d_6$, 500 MHz) of pGMA polymerized by classical ATRP (0°C , 6 d). (b) Corresponding ^{13}C NMR spectrum ($\text{DMSO-}d_6$, 126 MHz).

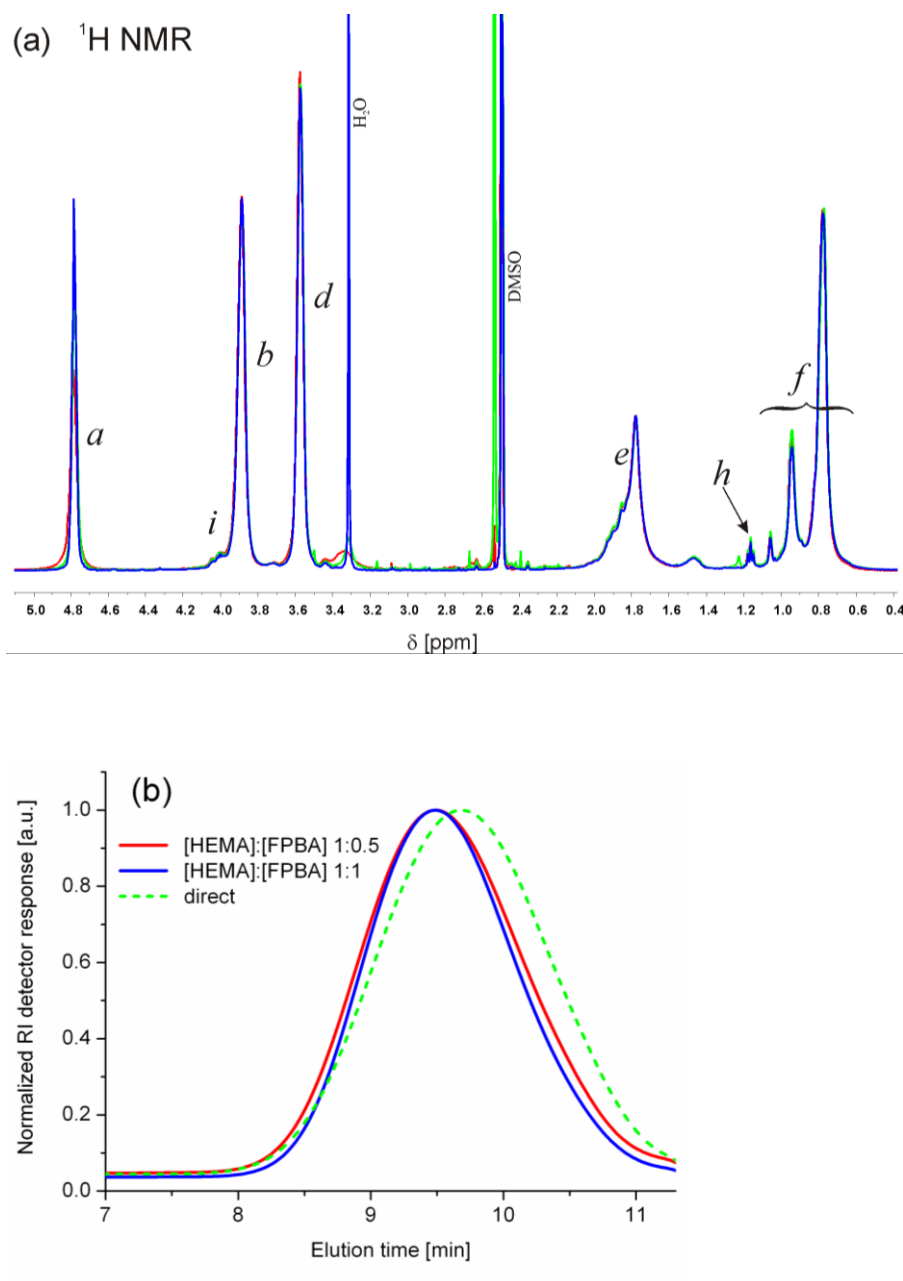


Figure S5. (a) ^1H NMR spectra (DMSO- d_6 , 500 MHz) of pHEMAs obtained after decomplexation of p(HEMA-IPB-NEA) polymerized by photo-induced ATRP (0 °C, 20 h, HMTETA) with the stoichiometric amount of complexing iminoboronate (red) *versus* twice that amount (blue), entries 7 and 4, Table 2, respectively. The pHEMA obtained under the same conditions but through direct polymerization of HEMA (entry 10, Table 2) is also included for comparison (green). (b) Corresponding SEC chromatograms (DMF, 40 °C).

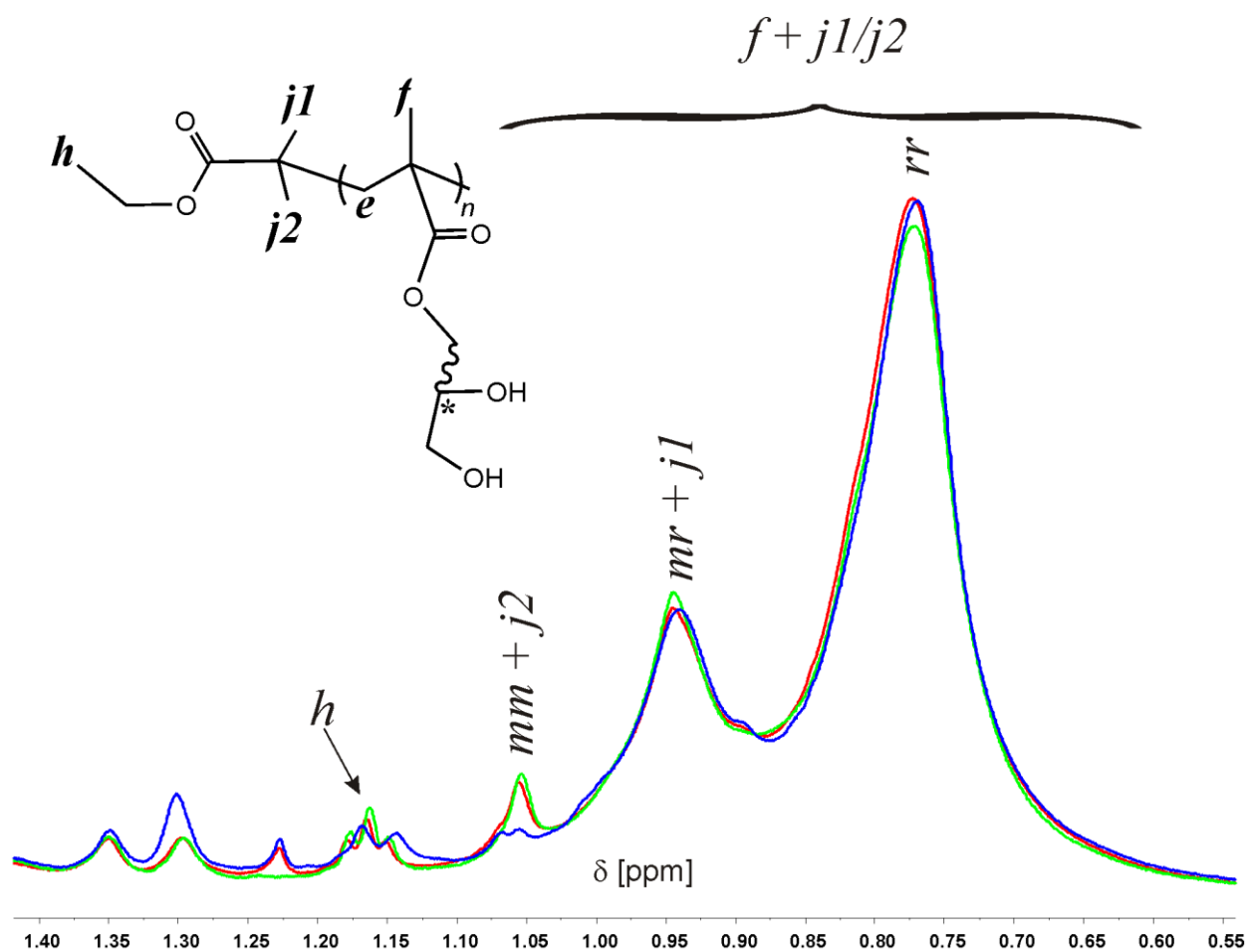


Figure S6. ^1H NMR spectra (DMSO- d_6 , 500 MHz) of pGMAs obtained after decomplexation of the poly(IPB methacrylate)s of p(GMA-IPB-MBA)s polymerized by: classical ATRP (0 °C, 5 d, red), photo-induced ATRP (0 °C, 18 h, green), and UV initiated free radical polymerization (AIBN, 10 °C, 48h, blue).

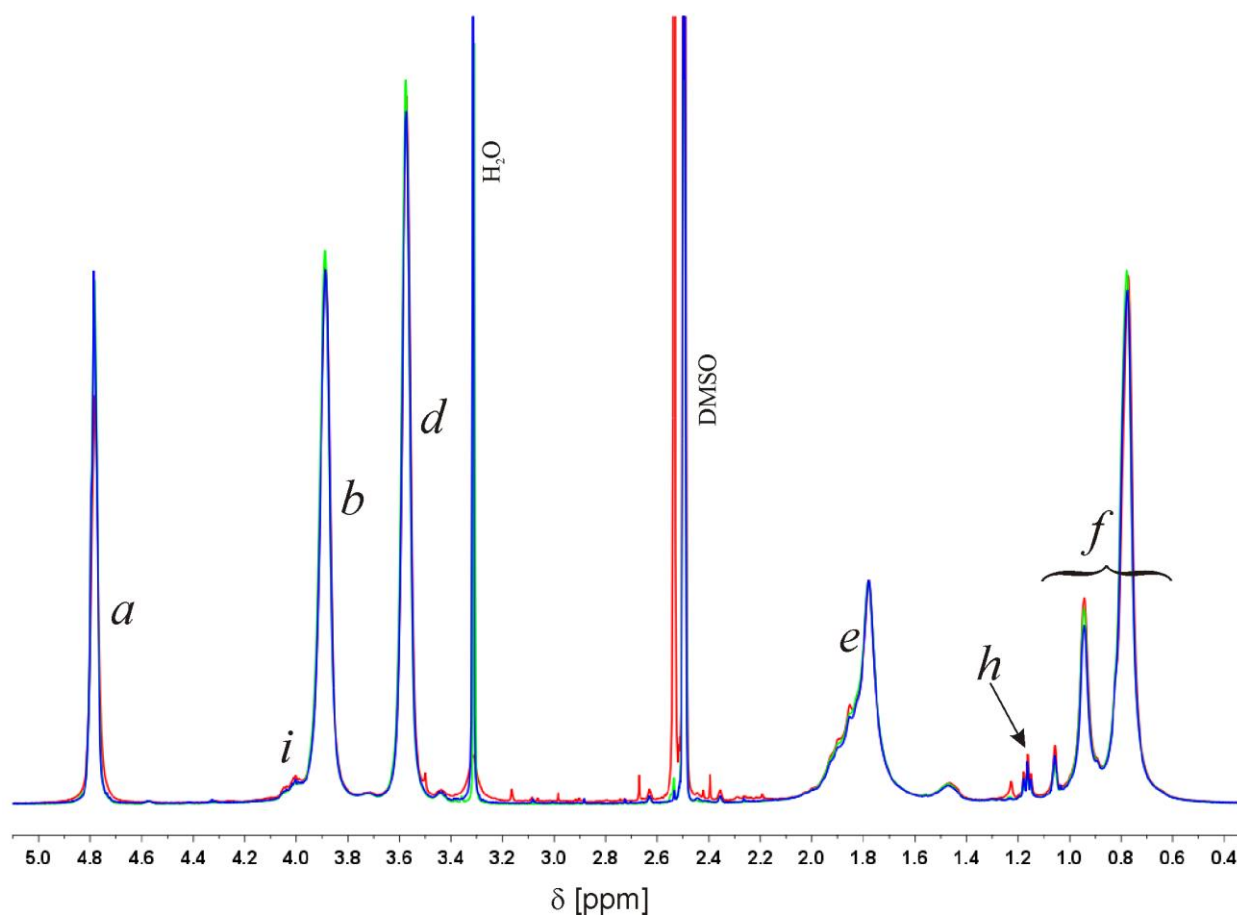


Figure S7. ^1H NMR spectra ($\text{DMSO-}d_6$, 500 MHz) of pHEMAs obtained after decomplexation of p(HEMA-IPB-NEA) polymerized by classical ATRP (0 °C, 6 d, green), and by photo-induced ATRP (0 °C, 20 h, blue), entries 1 and 4, Table 2, respectively. The pHEMA obtained under the same conditions by classical ATRP (0 °C, 6 d) but through direct polymerization of HEMA (entry 10, Table 2) is also included for comparison (red).

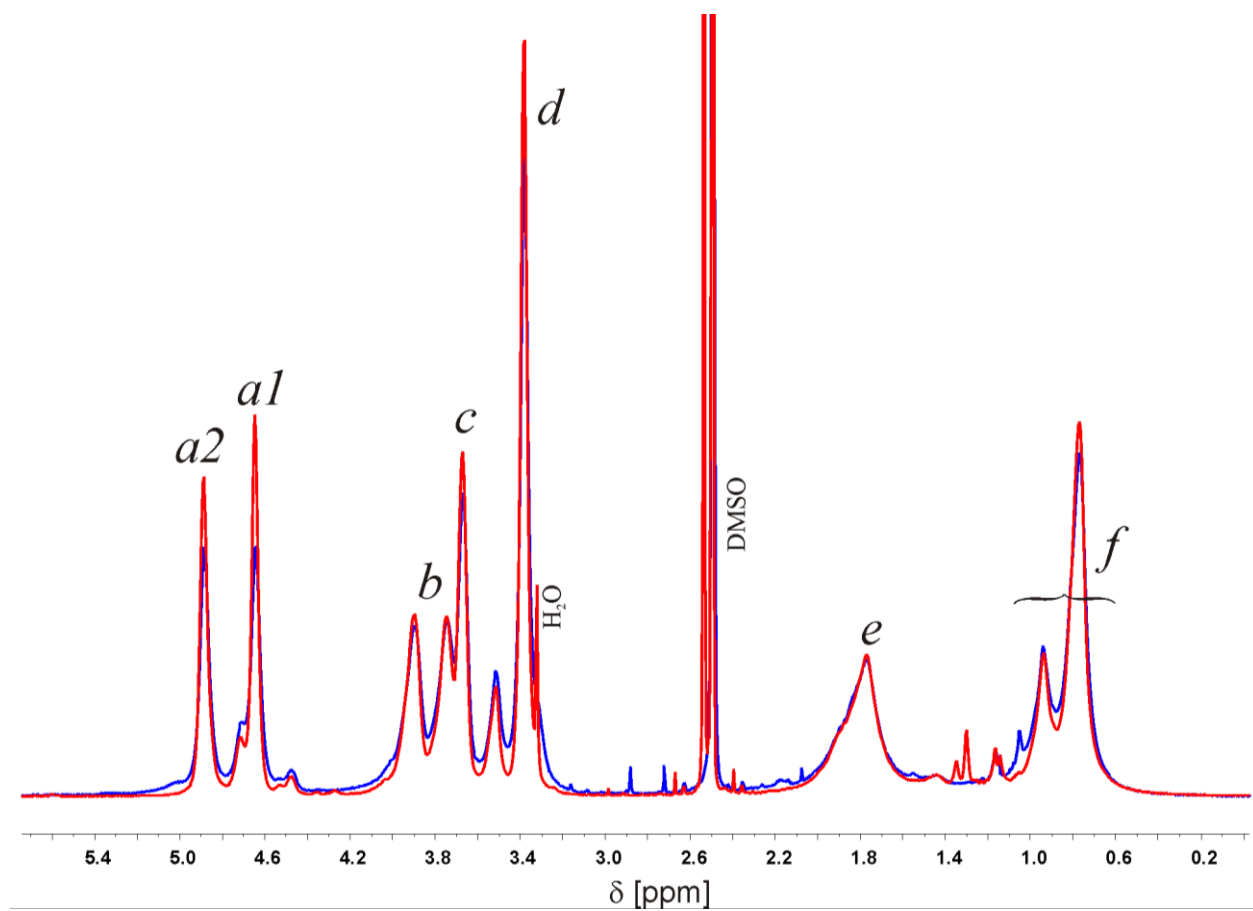


Figure S8. ^1H NMR spectrum ($\text{DMSO-}d_6$, 500 MHz) of pGMA polymerized by classical ATRP (0 °C, 6 d, entry 8 Table 1, blue) and by UV initiated free radical polymerization (AIBN, 10 °C, 48 h, entry 2, Table 1, red).

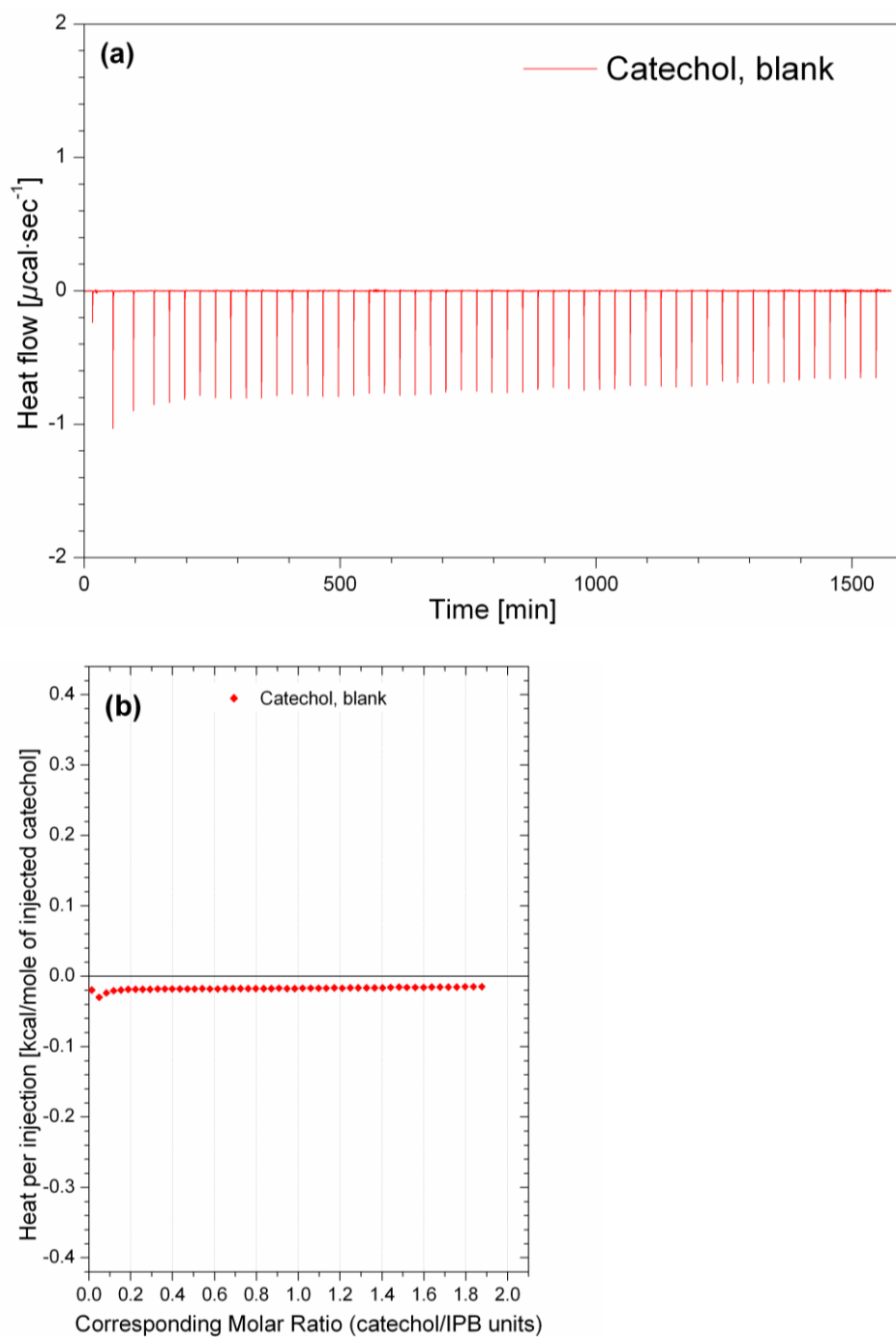


Figure S9. (a) Experimental isothermal titration calorimetry curve (298 K) for the titration of a 200 mM solution of catechol into pure DMSO. (b) Heat of dilution obtained by integration of the titration peaks.