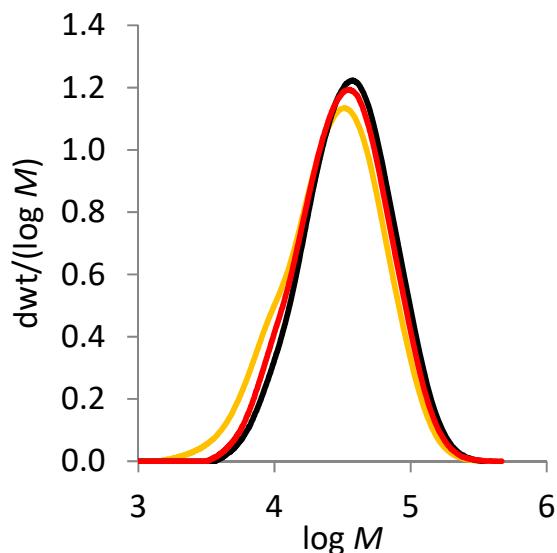


**Supporting Information**

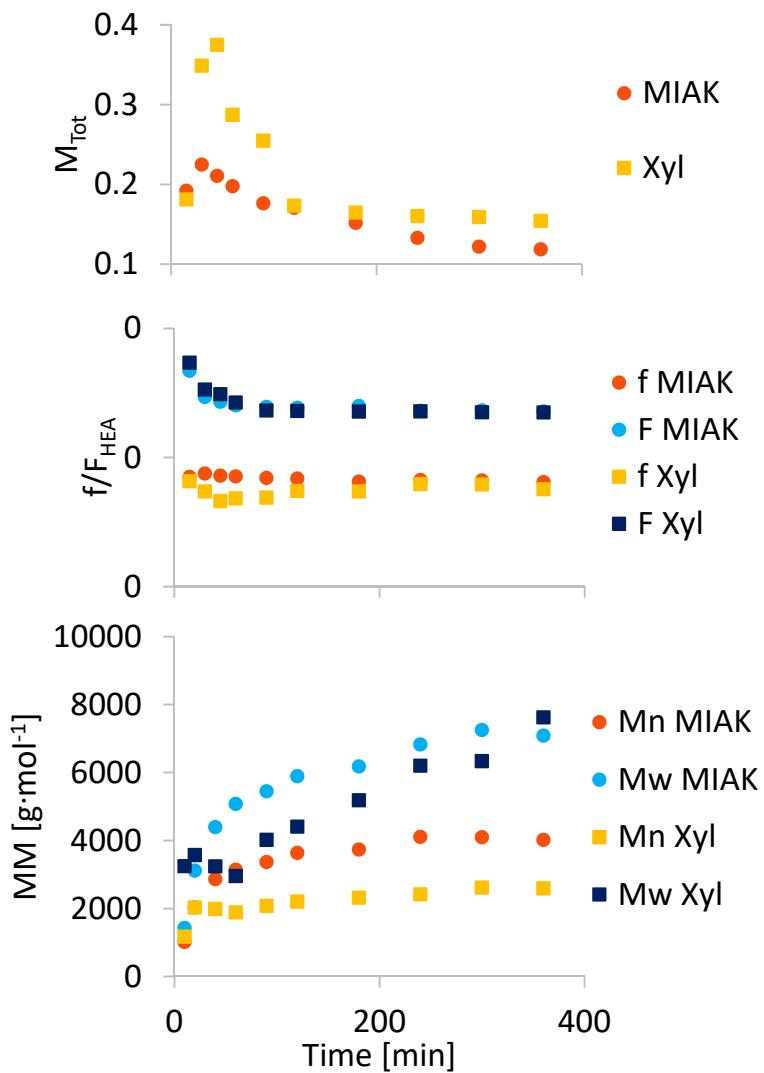
**The effect of hydrogen bonding on radical semi-batch copolymerization of butyl acrylate and 2-hydroxyethyl acrylate**

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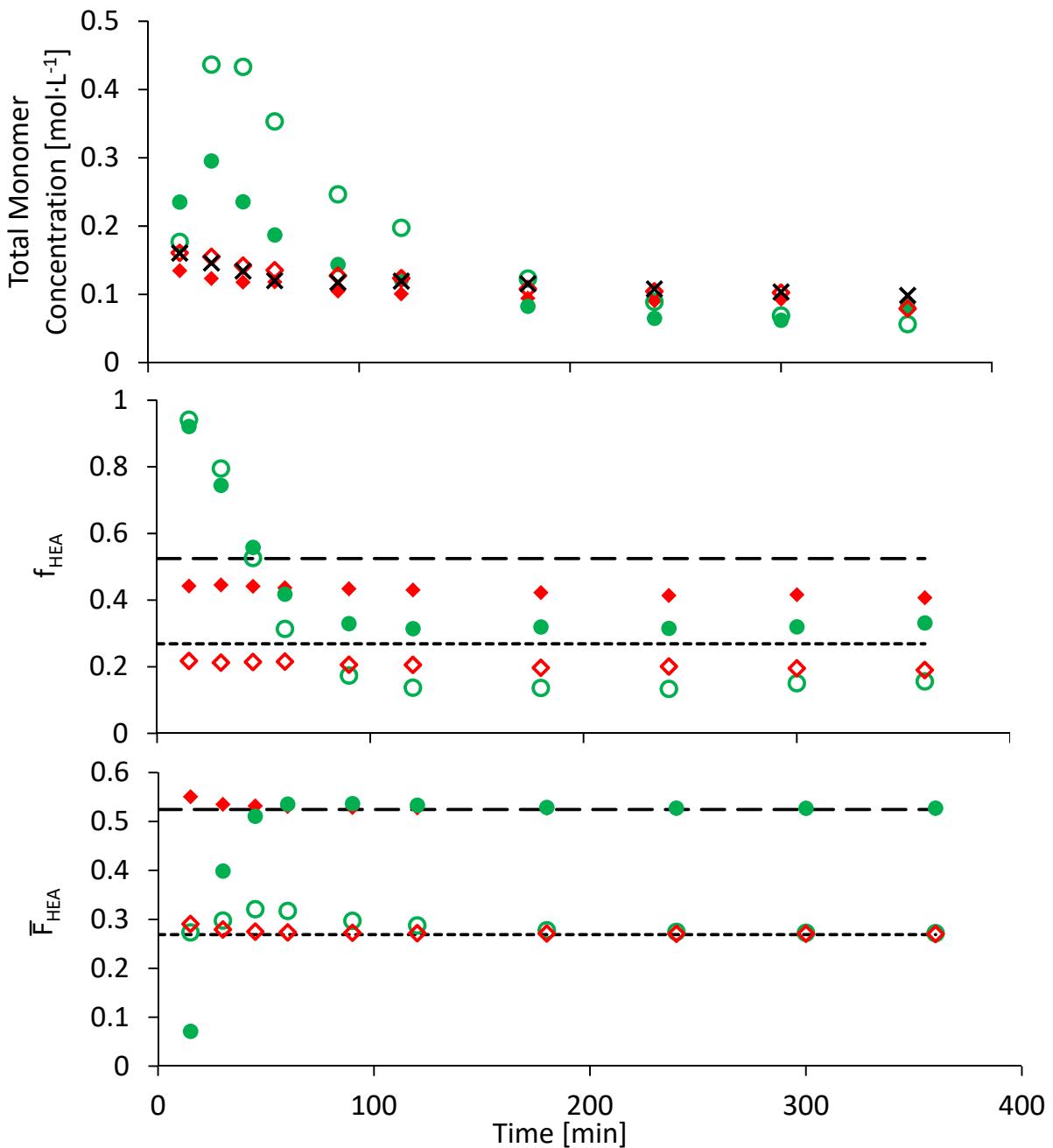
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**Figure S1:** MMDs of three poly(BA) samples produced by 30 min batch reactions of 25 v% BA in 75 v% xylenes, illustrating excellent reproducibility of the experimental procedures.

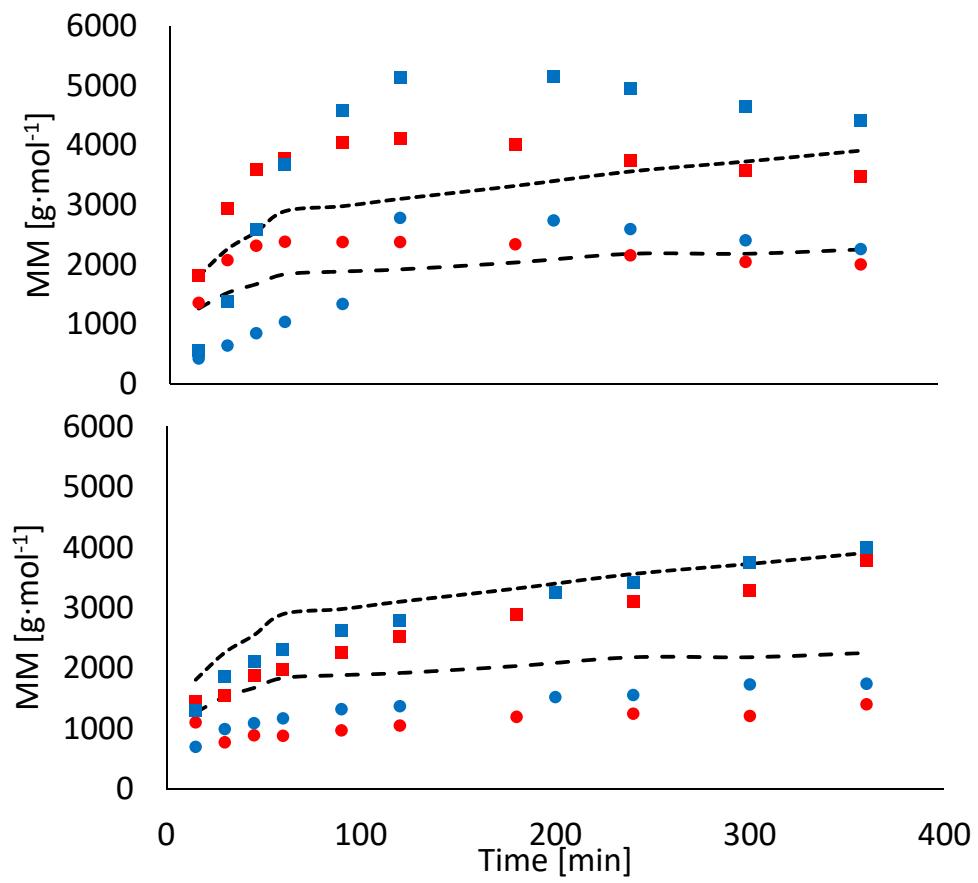


**Figure S2:** Evolution of total free monomer (top) and number-average ( $M_n$ ) and weight-average ( $M_w$ ) polymer molar masses (bottom) formed by copolymerization of BA/HEA with 25 wt% HEA in the feed under semi-batch conditions at 138 °C in xylenes (Xyl) and methyl isoamyl ketone (MIAK).

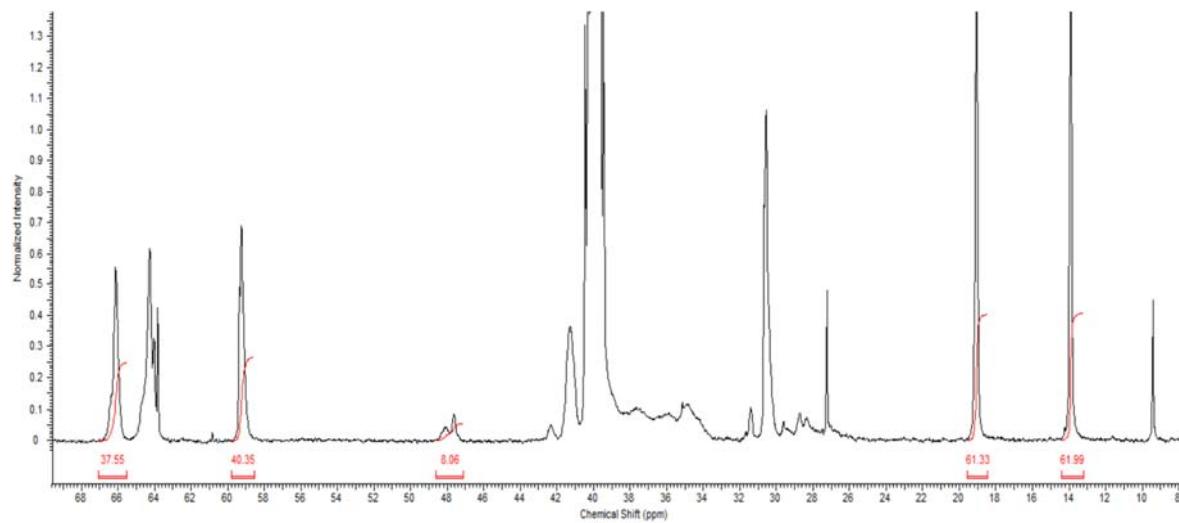


**Figure S3:** Total free monomer concentration (top), HEA molar fraction in the comonomer ( $f_{\text{HEA}}$ ) (middle) and copolymer ( $\bar{F}_{\text{HEA}}$ ) (bottom) for BA/HEA semibatch copolymerizations at 138 °C in PeOH (■) and DMF (□) with 25 wt% (○, △) and 50 wt% (●, ◆) HEA in the comonomer feed.

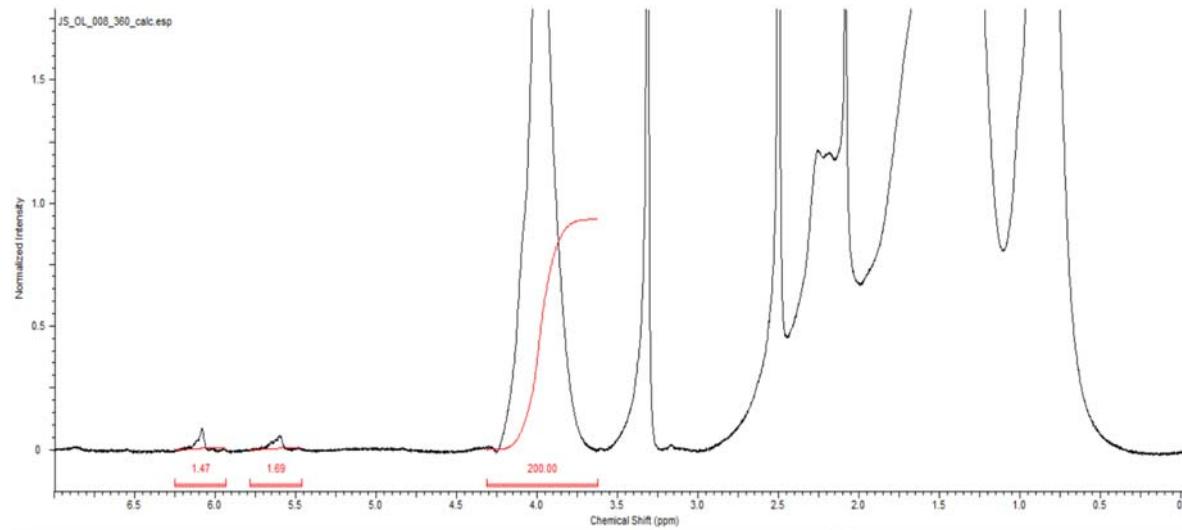
Monomer concentration profile also shown for BA homopolymerization in PeOH (x).



**Figure S4:**  $M_n$  (●) and  $M_w$  (■) values determined for BA/HEA copolymers with 25 wt% (■) and 50 wt% (■) HEA synthesized in PeOH (top) and DMF (bottom) under semi-batch conditions at 138 °C. Lines indicate results for BA homopolymerization in PeOH ( $M_n = \cdots$ ,  $M_w = ---$ ).



**Figure S5:** Quantitative  $^{13}\text{C}$ -NMR spectrum for BA/HEA copolymer prepared via semi-batch reaction in BPi at 138 °C, with the quaternary carbon peak observable at 48 ppm.



**Figure S6:**  $^1\text{H}$ -NMR spectrum for BA homopolymer prepared via semi-batch reaction in BPi at 138 °C, with residual macromonomer signals at 5.6 and 6.1 ppm.