Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Maximizing macromonomer content produced by starved-feed high temperature acrylate/methacrylate semi-batch polymerization

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Proton NMR Analysis

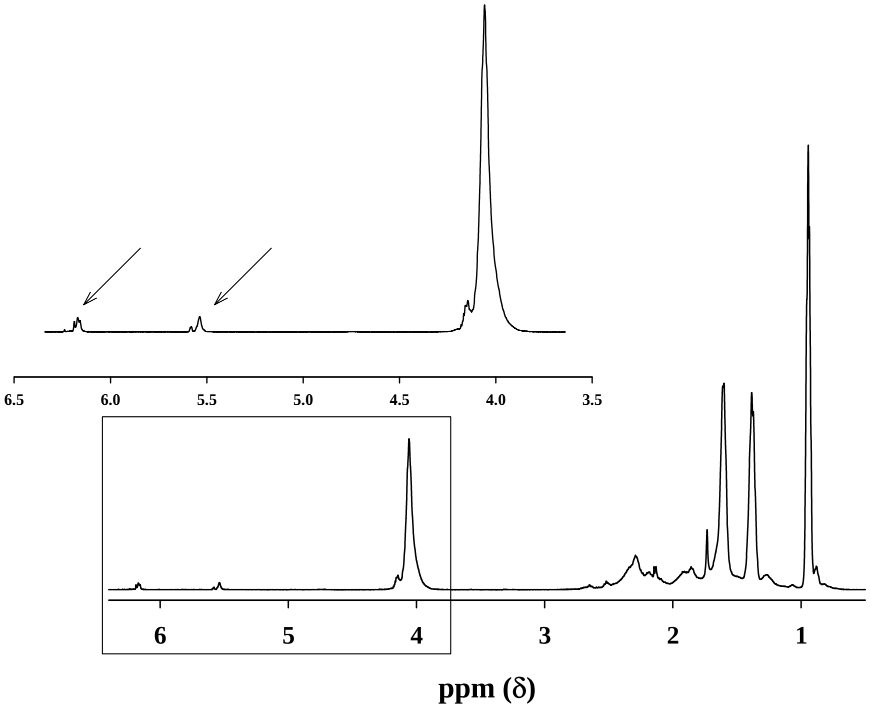

Fig. S1 ^{1}H NMR spectrum of poly(BA); inset exhibits the cis and trans olefinic protons with respect to the the O-C$\underline{H}_2$- group of the ester group

The unsaturated end-group appear in the 5.0–6.5 ppm range depending on the adjacent monomer unit; the *cis*-proton with respect to the CH_3 in butoxy group (Scheme 3) resonances at a lower magnetic field than the trans-proton with identical intensity. In the case of copolymers, the olefinic protons exhibit different chemical shifts depending on the adjacent monomer units. Dependence of the chemical shift of the olefinic proton resonances can be conveniently used to monitor exchange of the end-group. Figure S2 shows the resonances of poly(BA) (5.45 and ca. 6.07 ppm) and poly(BMA) (5.31 and ca. 6.04 ppm) chain terminal double bond end group and the BA/BMA copolymers end-group shifting towards lower resonances with increasing BMA composition.

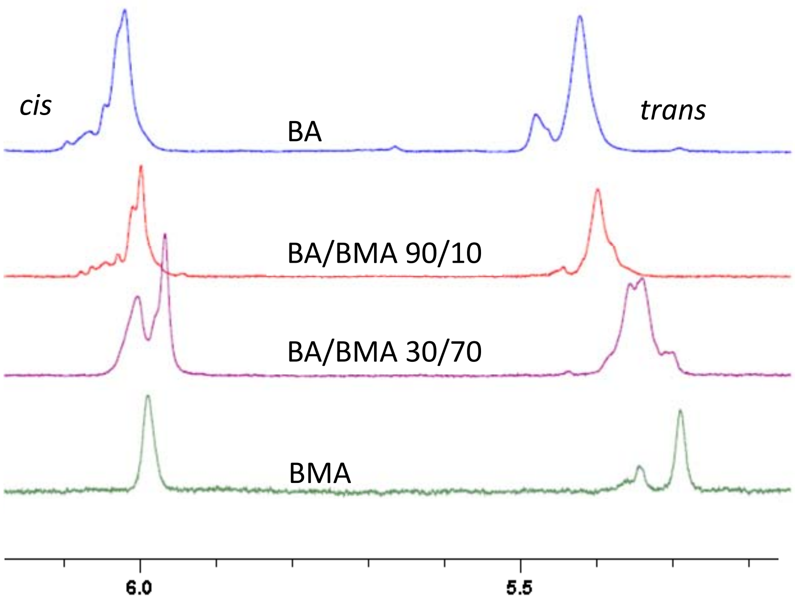

Fig. S2 Unsaturation region of BA and BMA homopolymers compared to copolymers

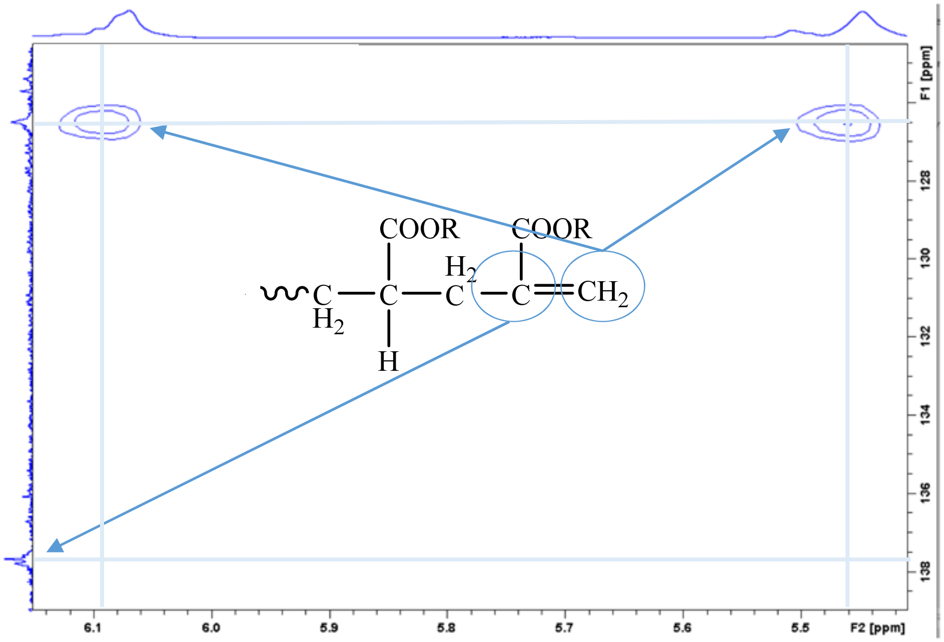

Fig. S3 Unsaturation detection of BA homopolymer with HSQC NMR

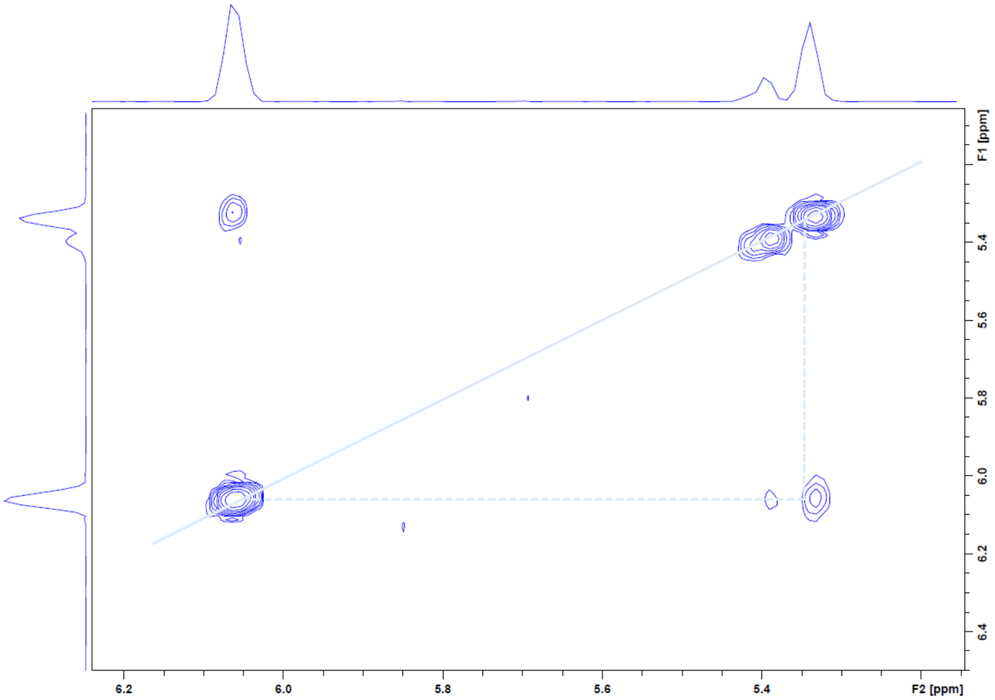

Fig. S4 Unsaturation end group of BMA homopolymer using COSY NMR to show the *cis* and *trans* coupling protons

^{13}C NMR spectra

$$\%C_4 = \frac{1}{10.5457} \times 100 = 9.48$$

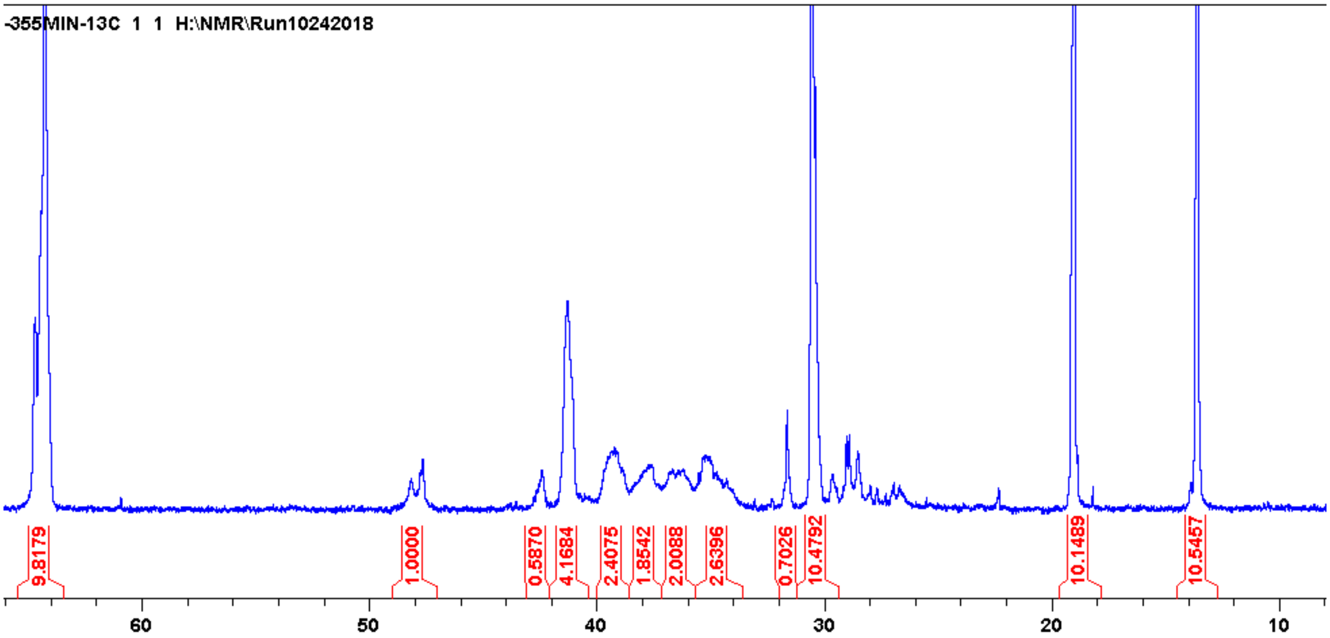

Fig. S5 The ^{13}C NMR spectra of poly(BA) isolated after 6h of reaction time; quaternary carbon appears at 47-48 ppm with branching level calculated relative to the methyl group in basis of 100 repeat units contained in the polymer

From the DEPT spectrum shown in Fig. S6, together with a well-known experimental fact that phase of DEPT spectrum is positive for methyl and methane carbons and negative for methylene carbon and nonobservable for quaternary carbon, we can easily assign the peaks based on carbon species (number of coupling protons). If all carbons at 47-48 ppm are a quaternary nature, no signal would be observed in a DEPT spectrum. For BA/BMA copolymer, however, the spectrum clearly shows an intense negative peak in this area, indicating a CH2 group (negative).

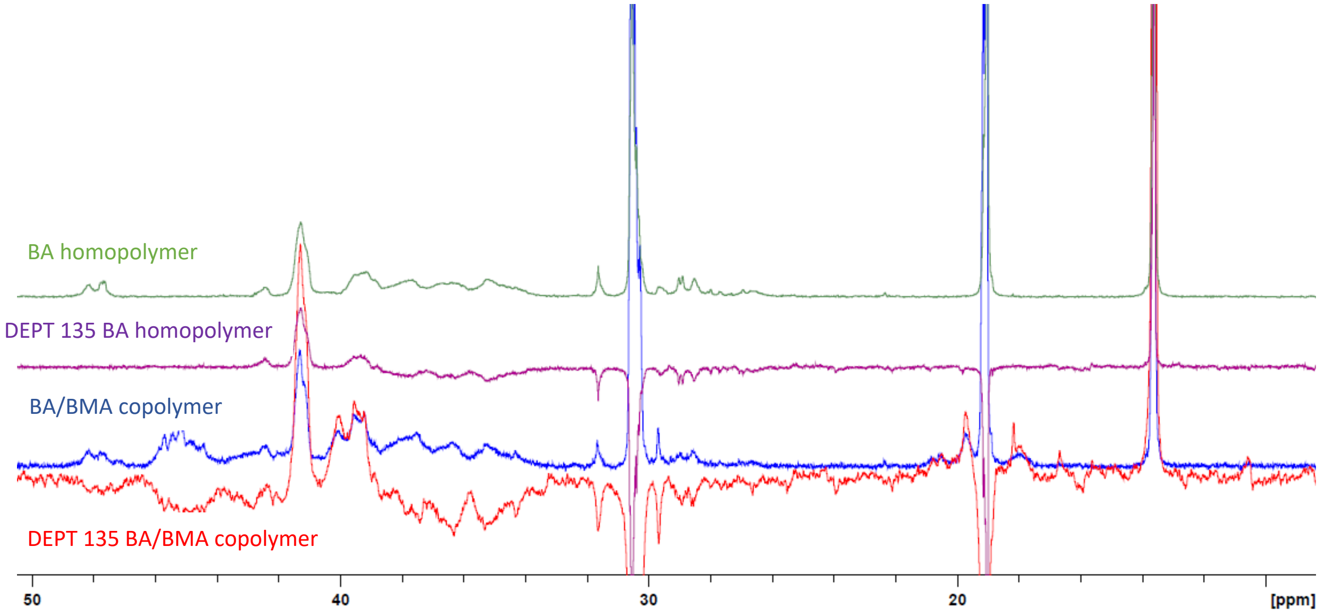

Fig. S6 Zoom into DEPT 135 spectra for BA homopolymer and BMA/BA copolymer

Free monomer levels measured for BA/BMA semi-batch copolymerizations

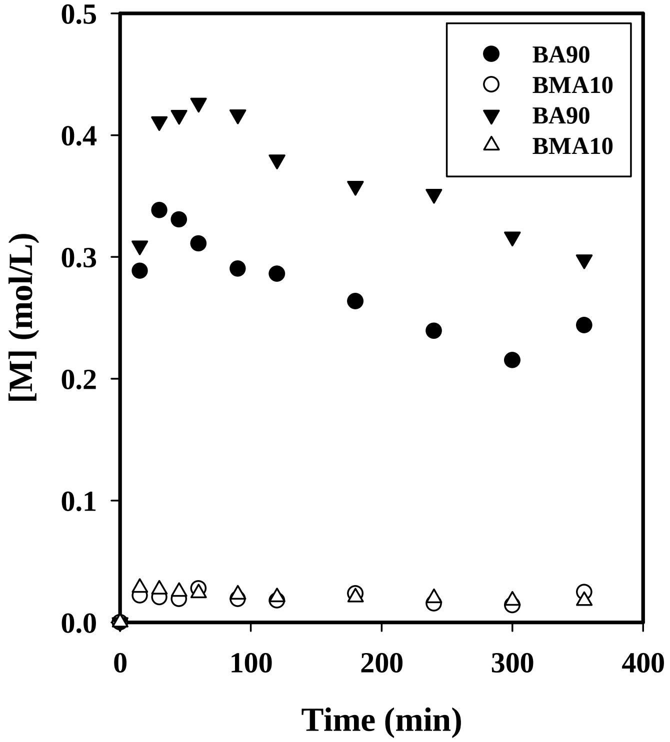

Fig. S7 Free monomer levels from BA/BMA 90/10 copolymerizations at 140 °C and 65 wt% final solids with 0.5 (○,•) and 0.2 (Δ,▼) mol% TBPA

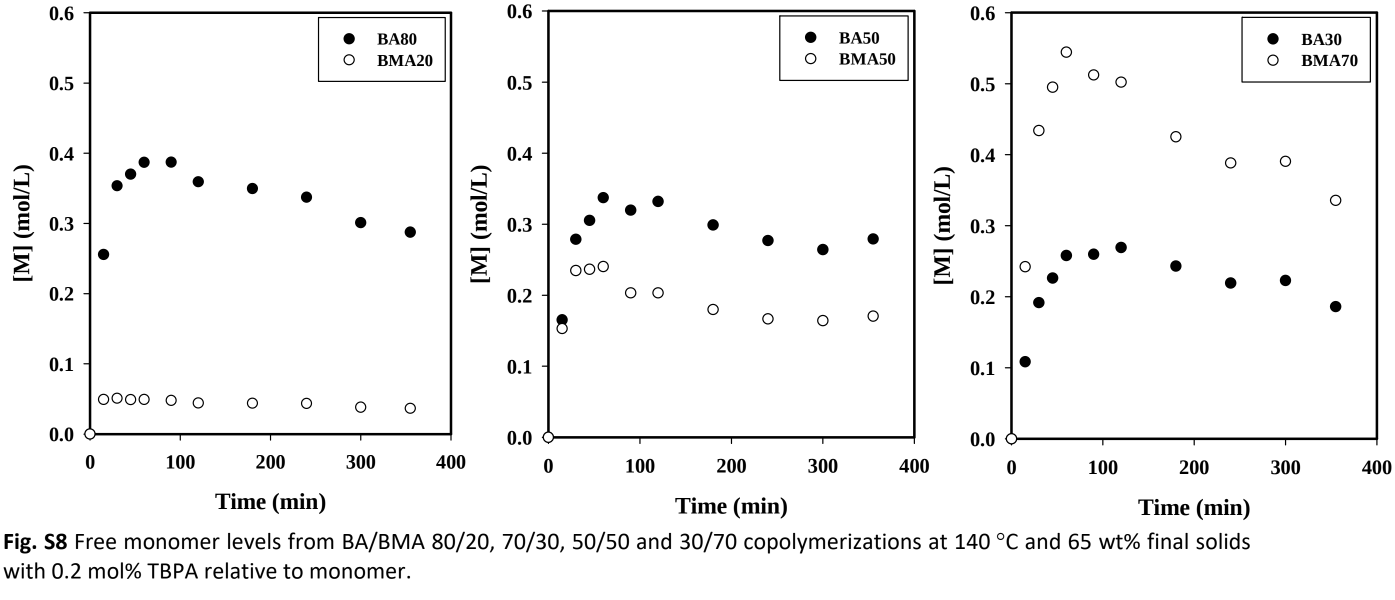

Fig. S8 Free monomer levels from BA/BMA 80/20, 70/30, 50/50 and 30/70 copolymerizations at 140 °C and 65 wt% final solids with 0.2 mol% TBPA relative to monomer.

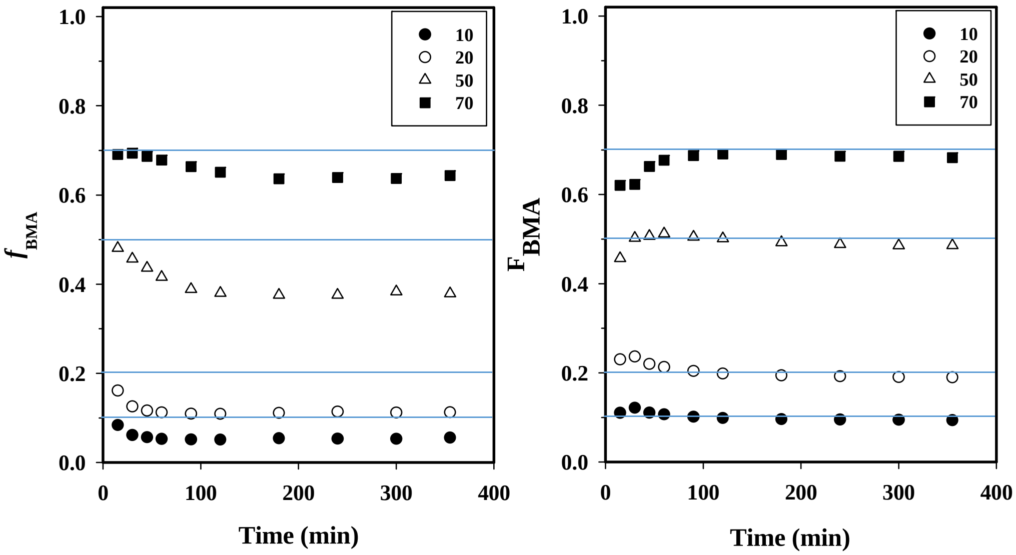

Fig. S9 BMA molar fraction in comonomer (left, measured by GC) and copolymer (right, estimated from material balances) during semi-batch reactions at 140 °C and 65 wt% final solids with 0.2 mol% TBPA relative to monomer. Horizontal lines indicate the molar fraction of BMA corresponding to feed mixtures containing 10, 20, 50 and 70 wt% BMA .