SUPPORTING INFORMATION

Hollow microspheres and aqueous phase behavior of pH-responsive poly(methyl methacrylate–*co*–methacrylic acid) copolymers with a blocky comonomer distribution

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Below are the raw data, in support of derivative results and/or of statements in the manuscript. In our opinion, these raw data are probably important for the review process, however we do not feel they are necessary in case of publication.

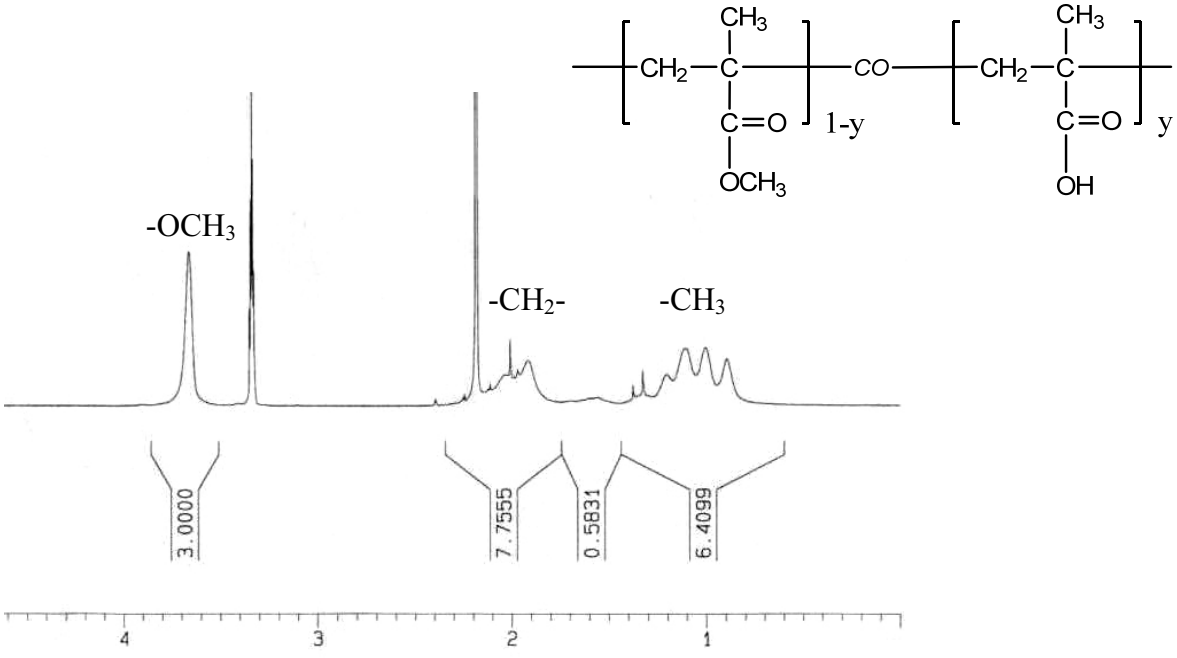

Figure S1. The relevant part of the ^{1}H-NMR spectrum of the BB60 copolymer. The copolymer's methacrylic-acid content is determined by NMR at 61±1 mol% MAA, in quantitative agreement with the composition obtained by potentiometric titration (*i.e.*, 63.80 ± 0.01 mol% of MAA; (*cf.* Fig.1)

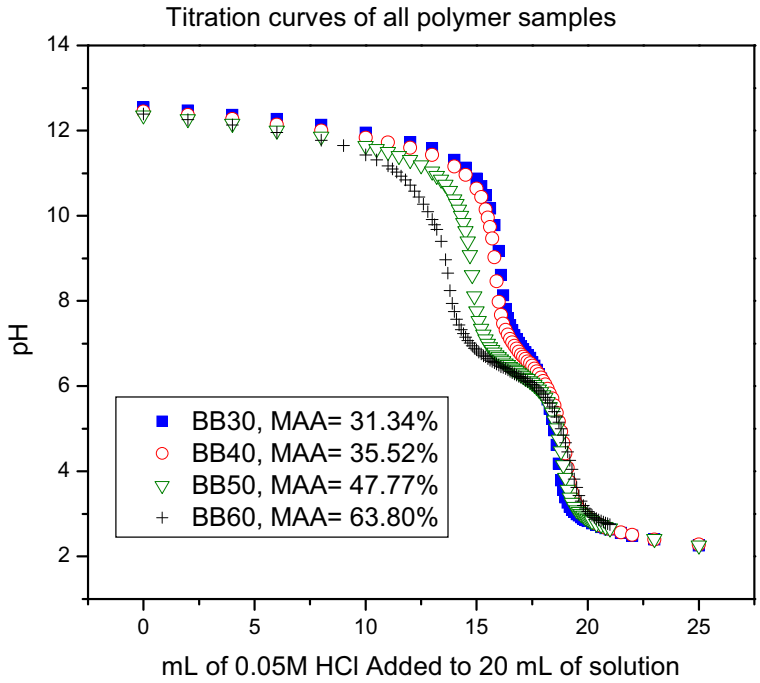

Figure S2 Potentiometric titration curves for all four copolymers in fig. 1a (0.2 wt% copolymer solutions, in standarized NaOH, titrated with 0.05M HCl). The MAA units are ionized and hydrophilic originally (at high pH), become protonated (neutral) and hydrophobic upon addition of HCl. Based on these data, it is possible to accurately calculate the MAA-content of the copolymers and their effective pKa (*cf.* fig. 1)

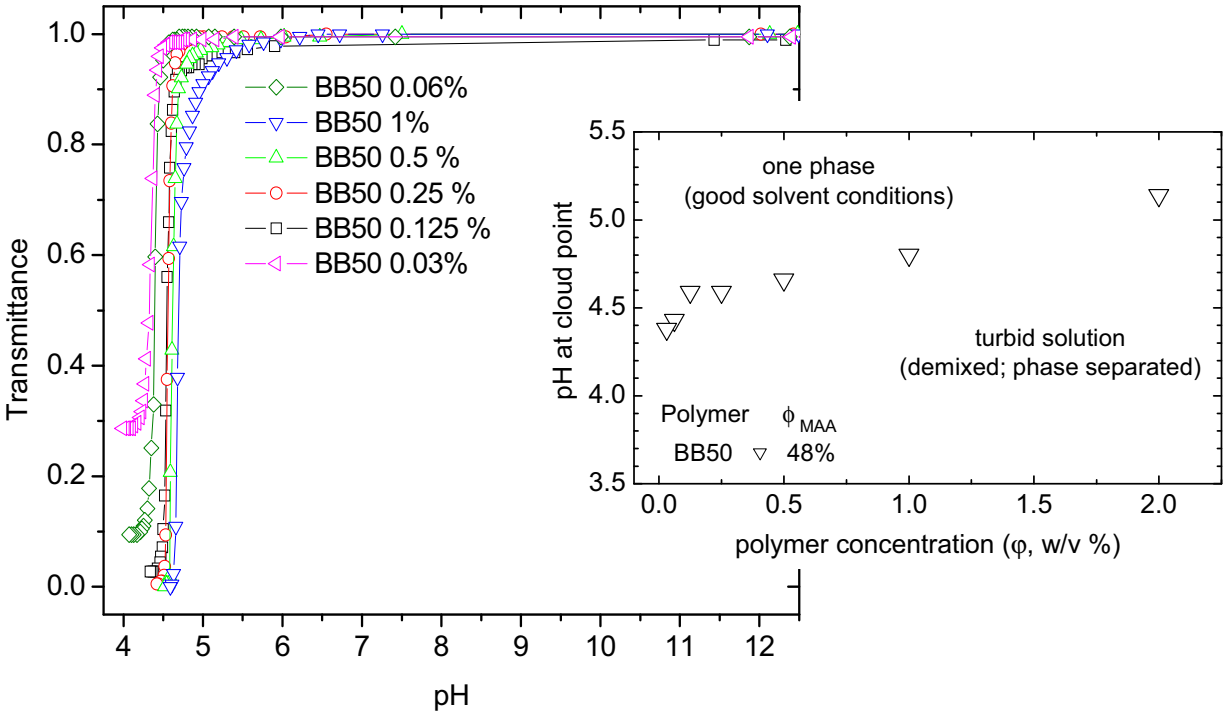

Figure S3 Turbidity (cloud point) curves of aqueous solutions of the BB50 copolymer, measured as a function of pH at different concentrations. **Inset:** Dependence of the pH-onset of phase-separation (*cf.* cloud point or binodal pH) on the copolymer concentration in water (0.125 and 1.0 w/v % values tabulated in fig.1a); The concentration dependence of the cloud point pH is strongly reminiscent of micellar phase diagrams. BB50 is the polymer used for preparation of microcapsules (*cf.* figs. 2 and 3).

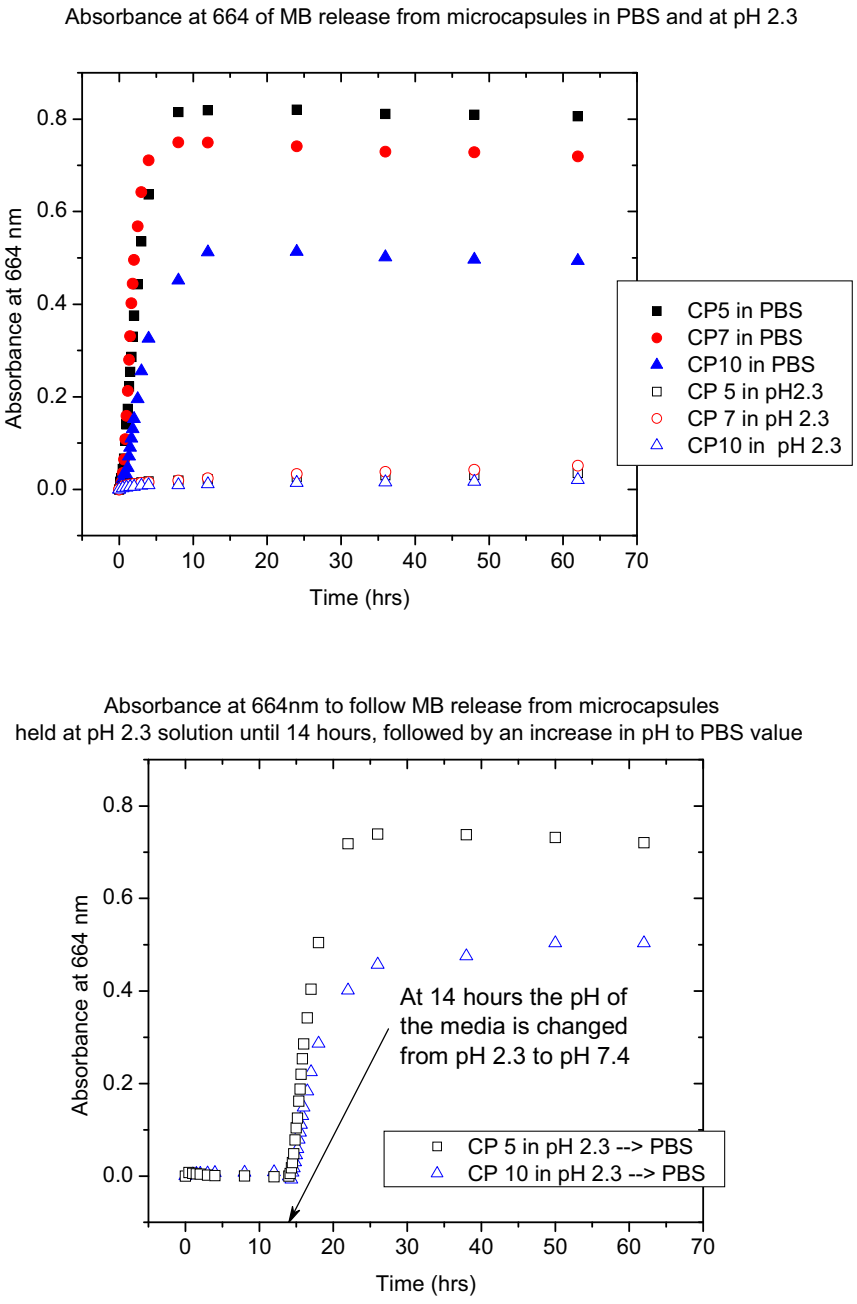

Figure S4 Raw data (UV-vis absorbance *vs.* time of capsules in solution) for the release results shown in fig. 3. Release of MB from various microcapsule systems (CP5 is the c_5 in fig. 2; CP7 is the c_7, *etc.*).
(**top**) Release in PBS (filled symbols) and in pH 2.3 aqueous solution (open symbol, no significant release was observed for any system at these conditions). The ultimate amount of methylene blue released in PBS media, has a high value for CP5 and decreases for CP7 and CP10, respectively.
(**bottom**) pH-triggered release from microcapsules (CP5 and CP10). At the 14 hours mark the media pH was abruptly increased from a pH 2.3 to pH 7.4 (PBS value).

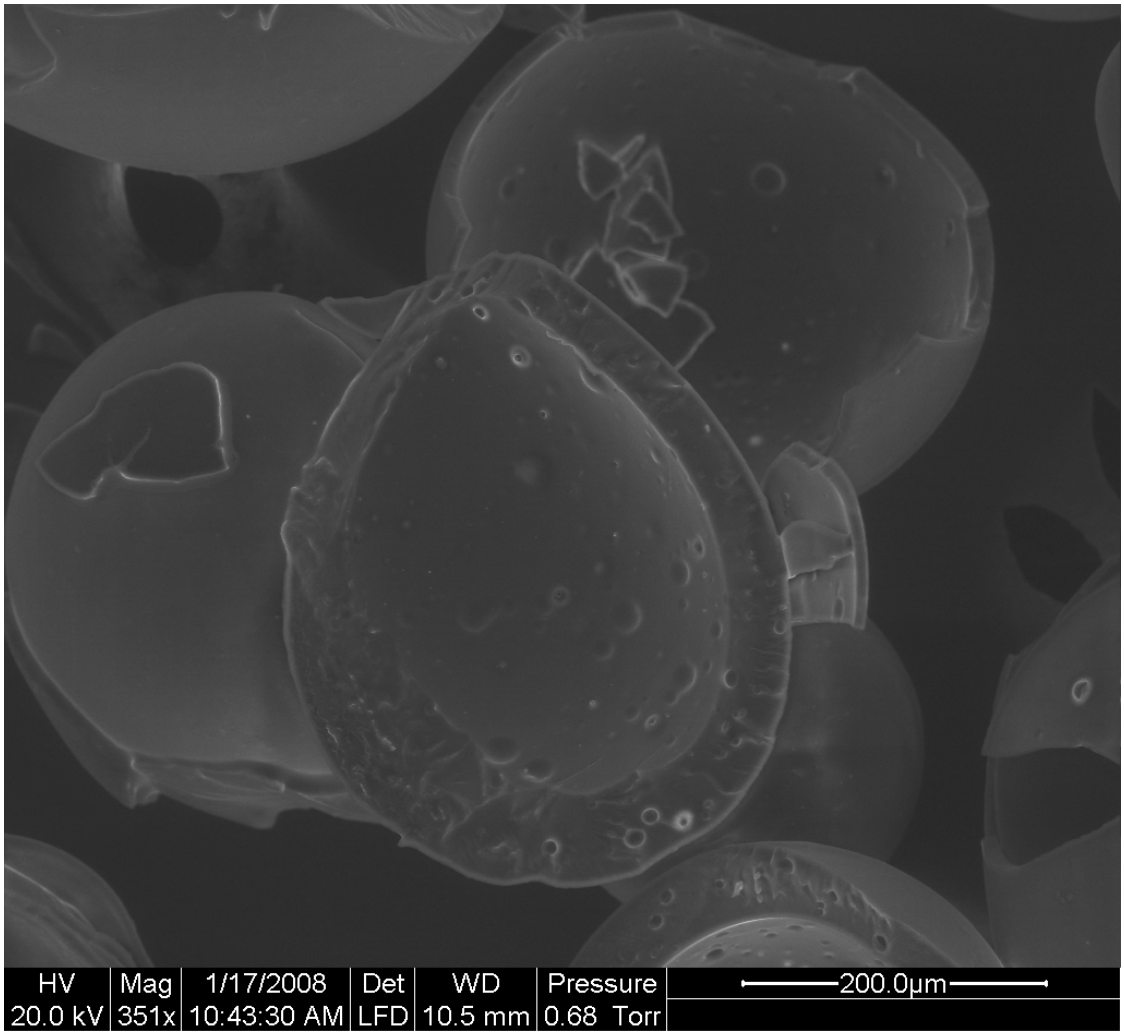

Figure S5. An SEM image of the c_{10} microcapsules (*cf.* fig. 2) focusing on a capsule with an average wall thickness for this system.