Electronic Supplementary Material (ESI) for Polymer Chemistry


# Supporting Information

## Tuning the upper critical solution temperature behavior of poly(methyl methacrylate) in aqueous ethanol by modification of an activated ester comonomer

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*NMR spectra of PFPMA and P1*

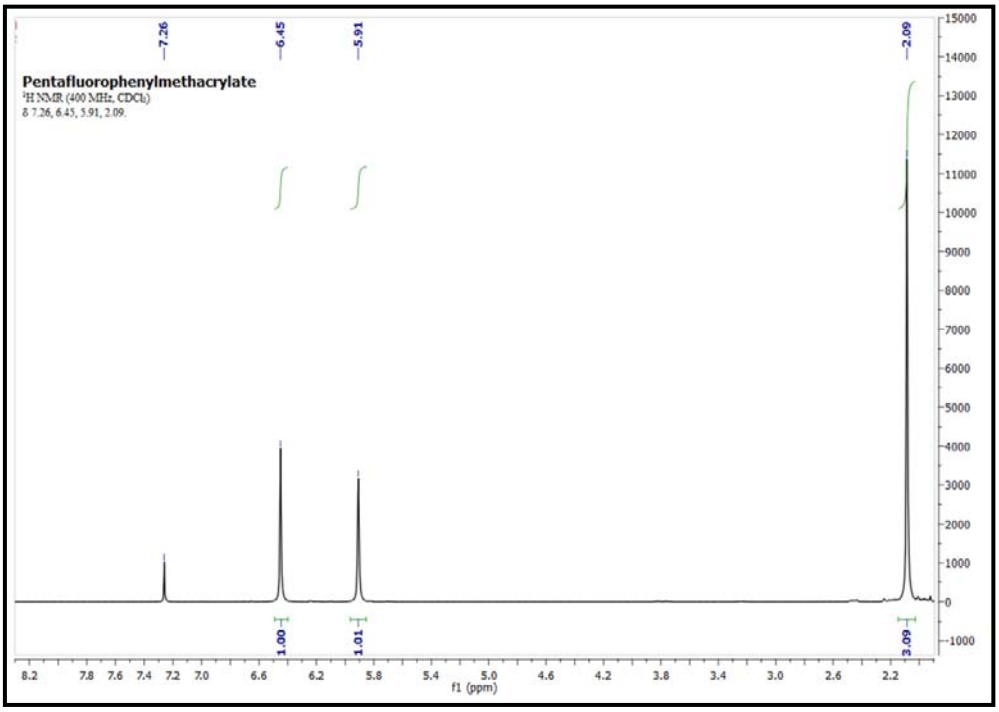



**Figure S 1:[1]H-NMR spectra of pentafluorophenyl methacrylate**

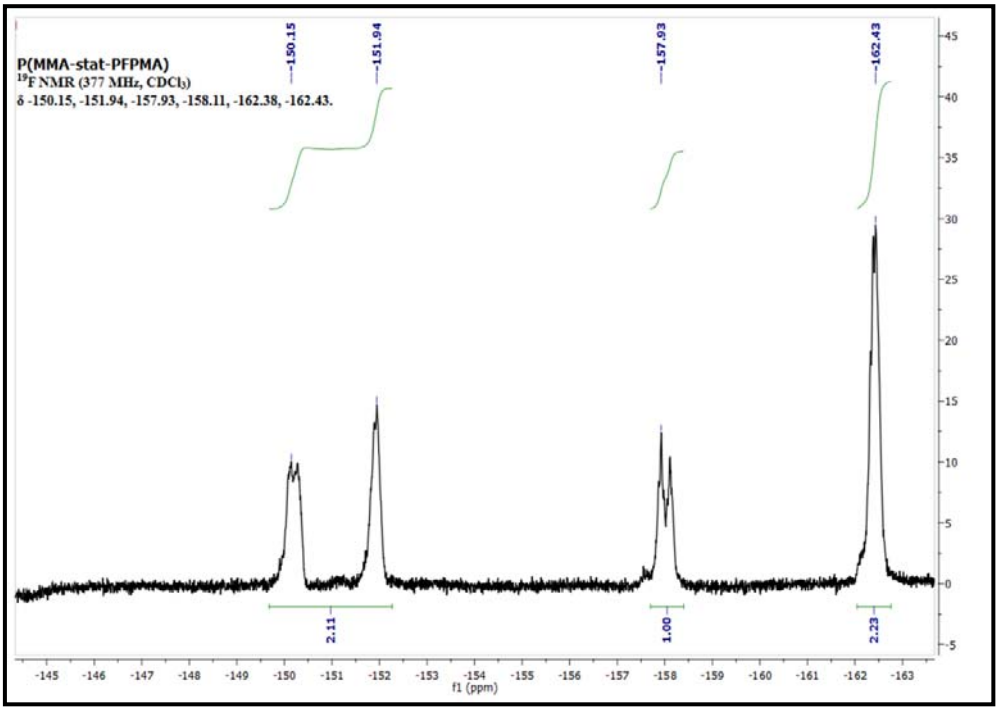



**figure S 2: [19]F-NMR spectra of the statistical copolymer PMMA-PFPMA. The NMR signal for the *ortho*-fluorine atoms is split, indicating the slight difference in the chemical environment due to the methyl group in the polymeric backbone as described in reference [1].**

*Estimation of the PFPMA content in the PMMA-PFPMA copolymer*

In order to estimate the content of the PFPMA moiety, the corresponding absorbance bands in the FT-IR spectra and the signals in the $^{1}$H-NMR spectra respectively were integrated. Due to baseline corrections and noise reductions the FT-IR spectrum usually provides an underestimated value in respect to the original one. In contrast the NMR analysis provides an overestimated value, due to phase corrections and integration uncertainties, especially when polymers were analyzed. As a result the actual value should be located in between. As consequence the average value, generated from both the NMR and FT-IR, was used.

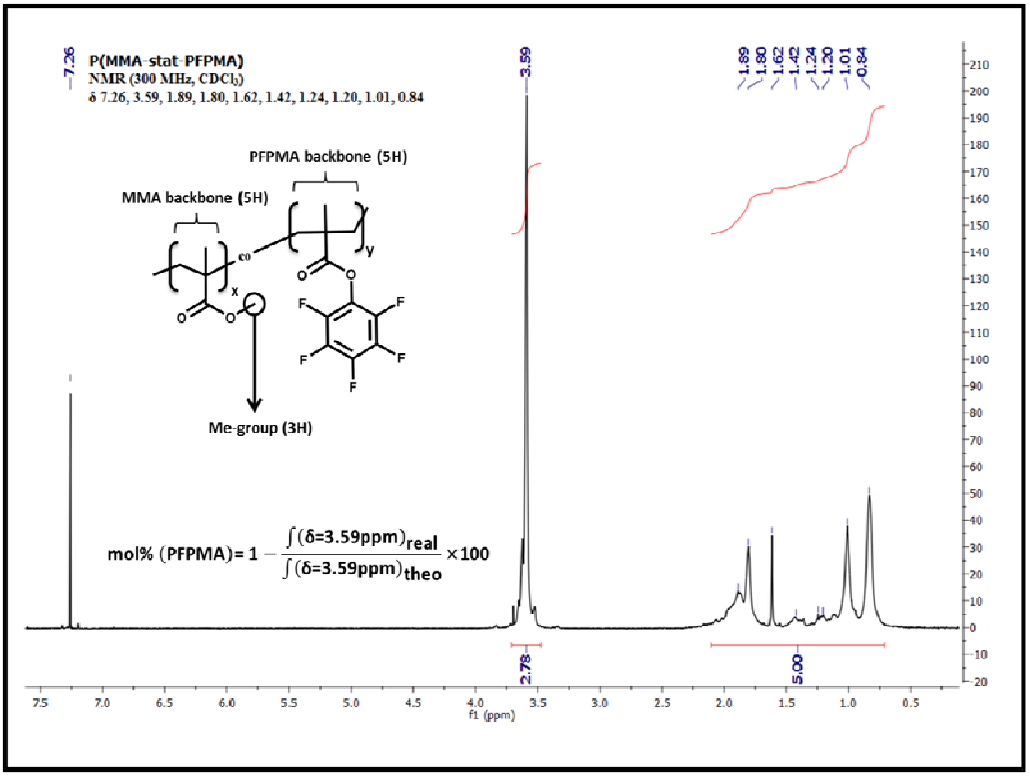



**figure S 3: NMR spectra of the statistical copolymer P(MMA-co-PFPMA), including the calculation for the estimation of the PFPMA content.**

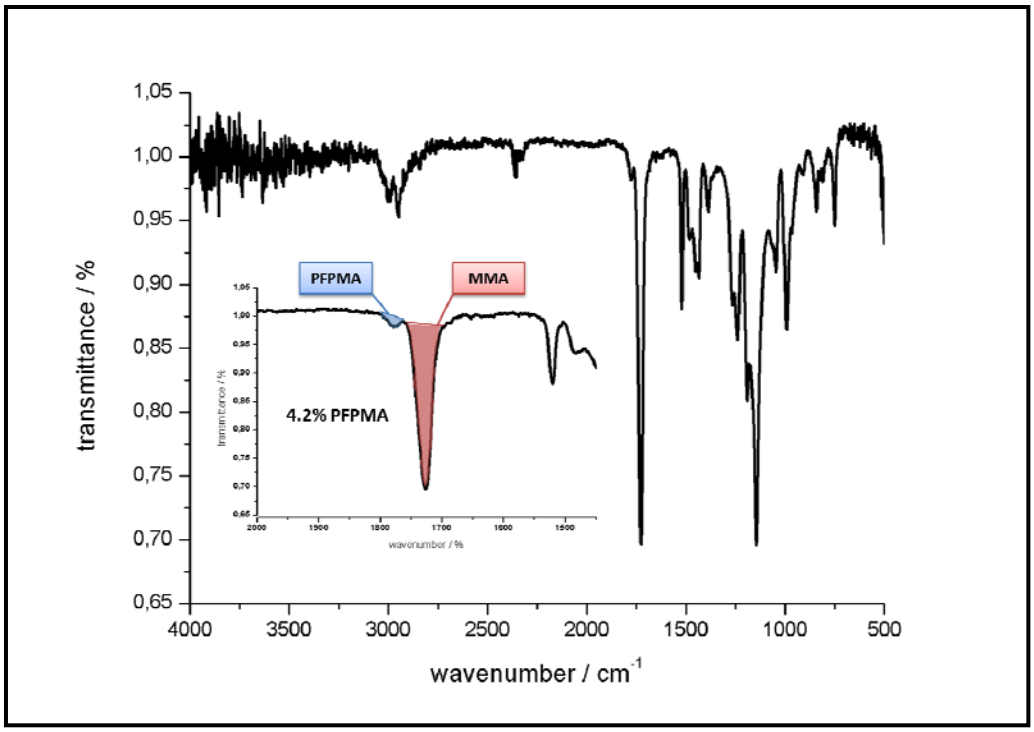
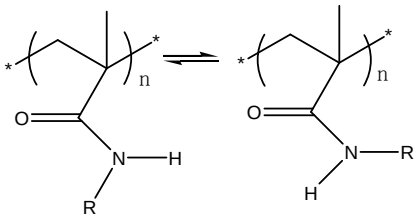



**figure S 4: FT-IR spectra of the statistical copolymer P(MMA-co-PFPMA), including the integration of the corresponding functional groups.**

*Estimation of the acrylamide content in the copolymers P2-P6*

In order to estimate the content of the acrylamide moieties, the corresponding signals in the $^1$H-NMR spectra were integrated. The resulting acrylamide contents are listed in Table S1 and calculation methodologies are included after this Table.

All spectra and the signals that were used for the calculations are shown below in Figure S5. It was unexpectedly observed that the signal for the proton from the NH group for P4 with the benzyl acrylamide comonomer is split, possibly resulting from the two different conformations of acrylamide:




The equilibrium of the two conformations most commonly results in one broad averaged peak as reported for PNIPAM.[2] Apparently the benzyl side chains slow down the interconversion of the two acrylamide conformations leading to two separate signals.

**Table S 1: Acrylamide contents in PMMA copolymer**

| Copolymer | P2 | P3 | P4 | P5 | P6 |
|---|---|---|---|---|---|
| Acrylamide content (AA%) | 5.8 % | 5.7 % | 8.1 % | 4.4 % | 6.7 % |

The acrylamide contents (AA%) for P2-P5 were calculated based on $^1$H NMR data using the following equation:

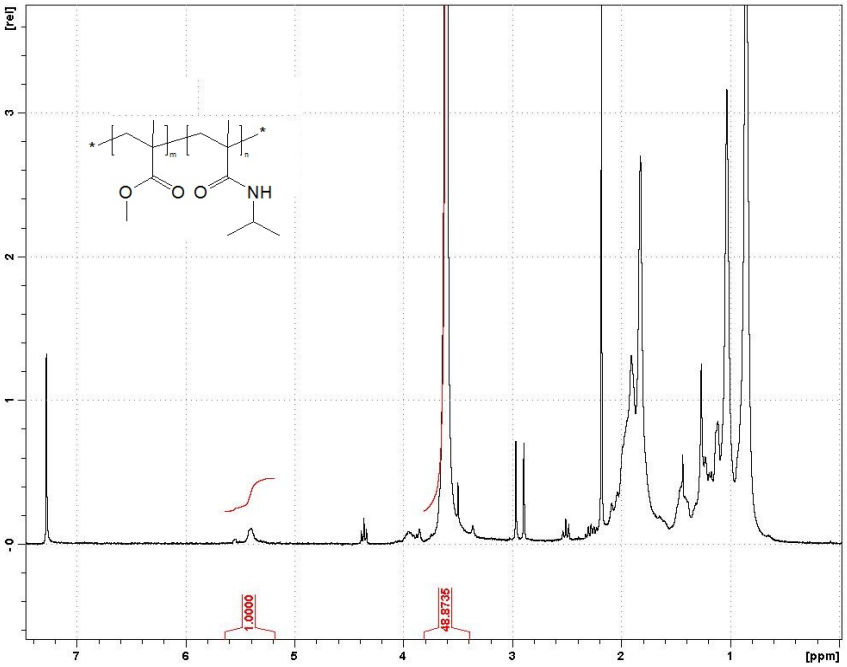
$$AA\% = \frac{I_{NH}}{I_{NH} + I_{CH_3}/3}$$

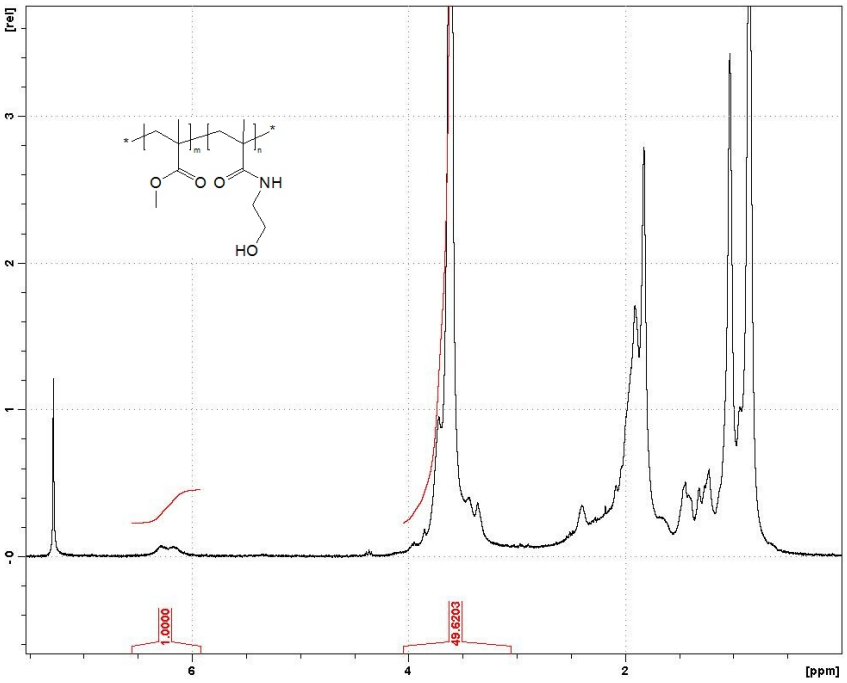
where $I_{NH}$ is the integration of proton from NH group and
$I_{CH_3}$ is the integration of $OCH_3$ group

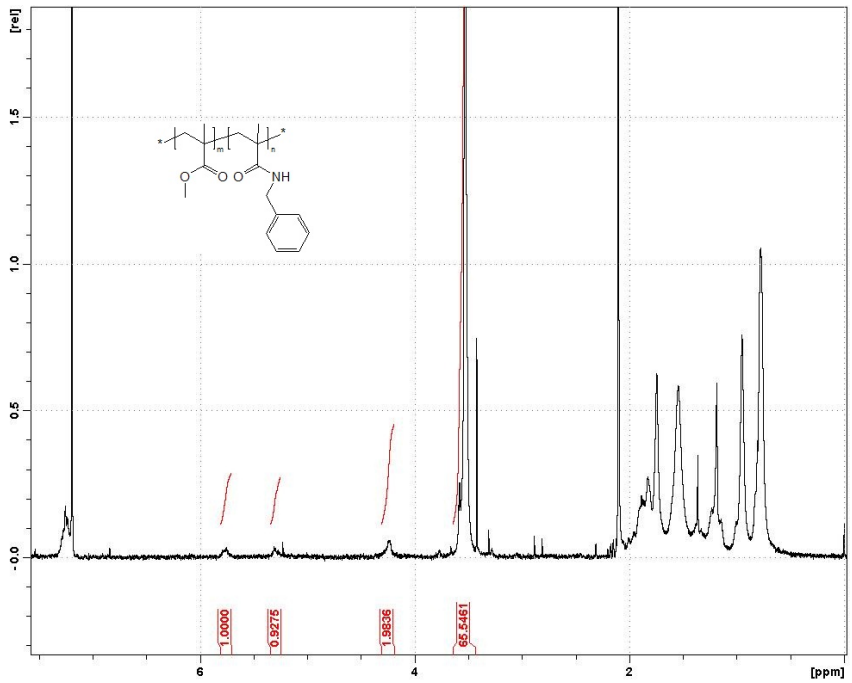
AA% of P6 was calculated by:

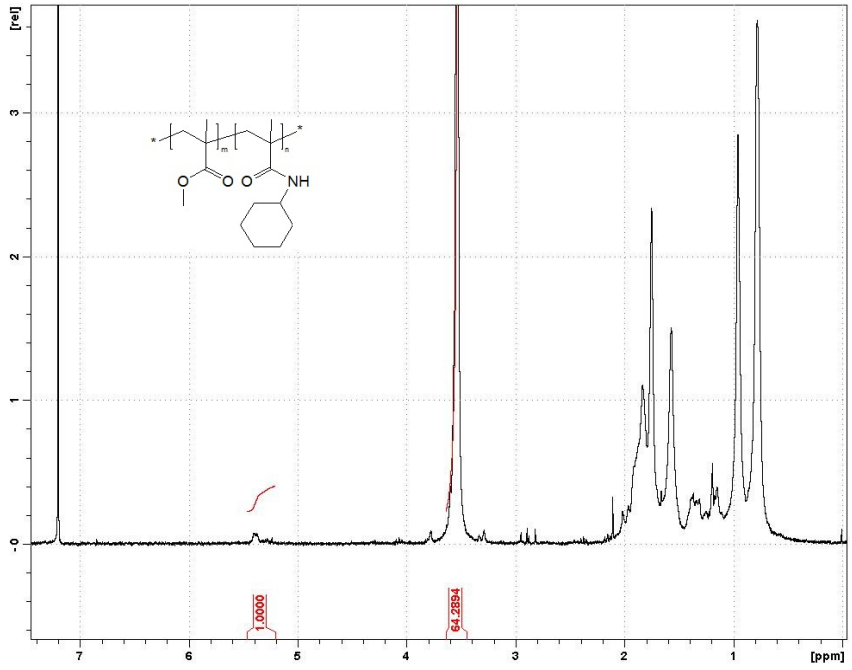
$$AA\% = \frac{I_{CH_2}/2}{I_{CH_2}/2 + I_{CH_3}/3}$$

where $I_{CH_2}$ is the integration of 2 protons from methylene group ($CH_2$-$NH_2$ )





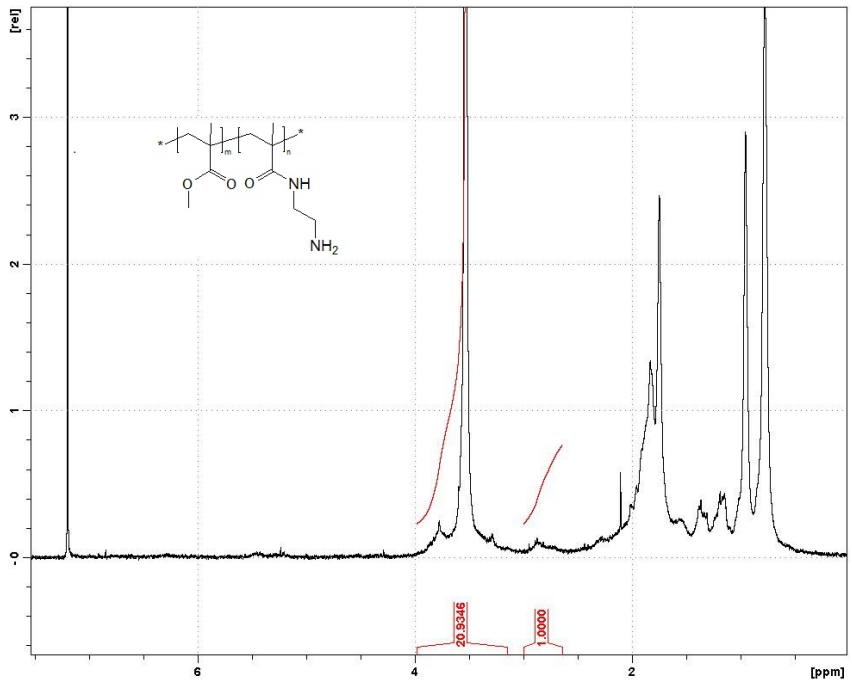



**Figure S 5: H NMR spectra (recorded with a delay time D1 of 60 s) of the PMMA copolymers, P2-P6, including the integration of the corresponding functional groups that were used to calculate the composition of the copolymers.**

References

1 K. Nilles and P. Theato, Journal of Polymer Science Part A: Polymer Chemistry, 2010, 48, 3683-3692.

2 S Wallyn, M Lammens, R K. O'reilly, F du Prez, *Journal of Polymer Science Part A: Polymer Chemistry*, 2011, 49, 2878–2885.