

Supporting Information

Figure S1. SEC-traces after various extents of monomer conversion of copolymerizations of BA with various concentrations of **1.1** up to a reaction time of 155 min.

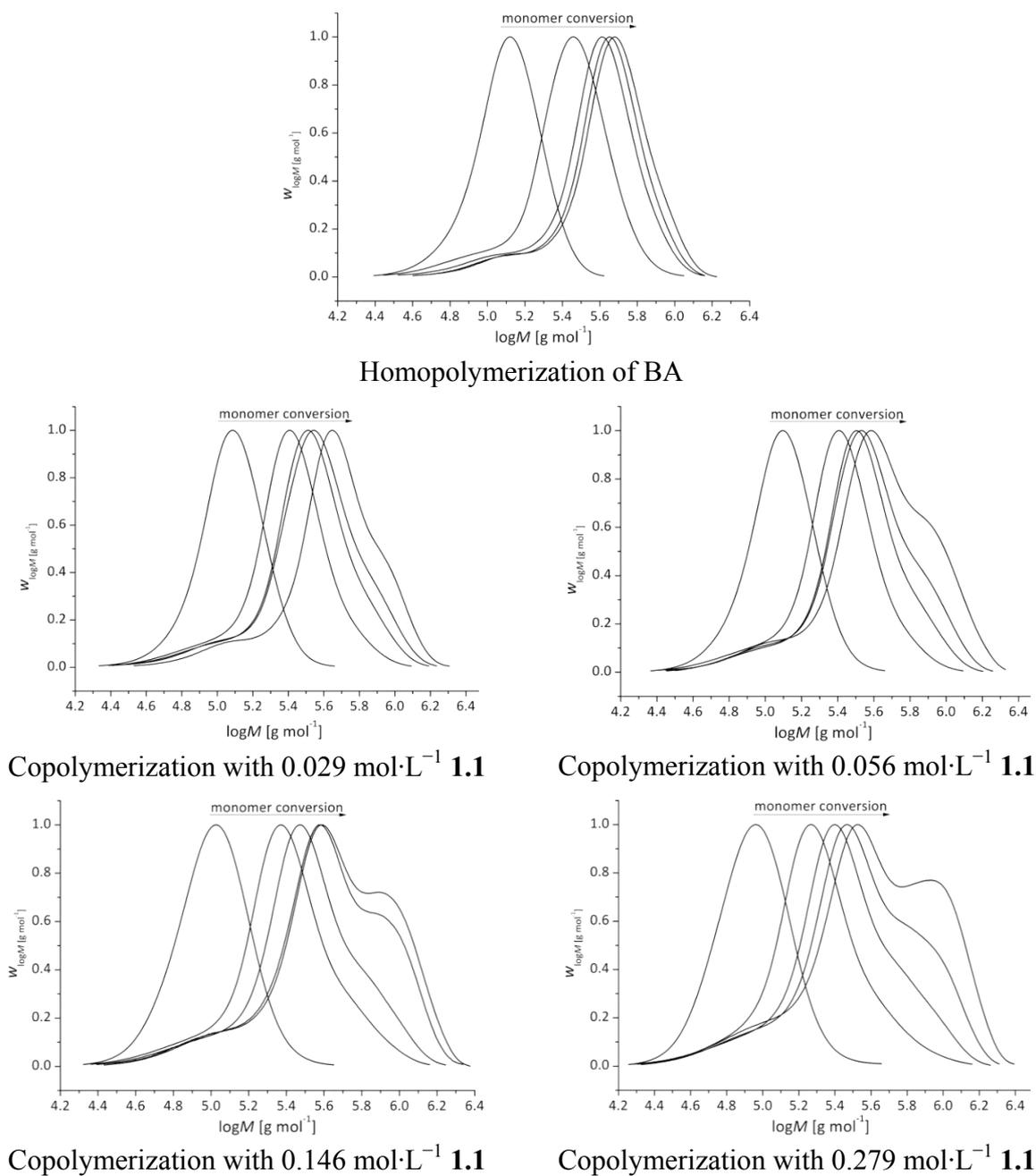


Figure S2. Corrected SEC-UV-traces of different copolymerizations of NIPAAm with **1.1** after various extents of monomer conversion up to a reaction time of 127 min.

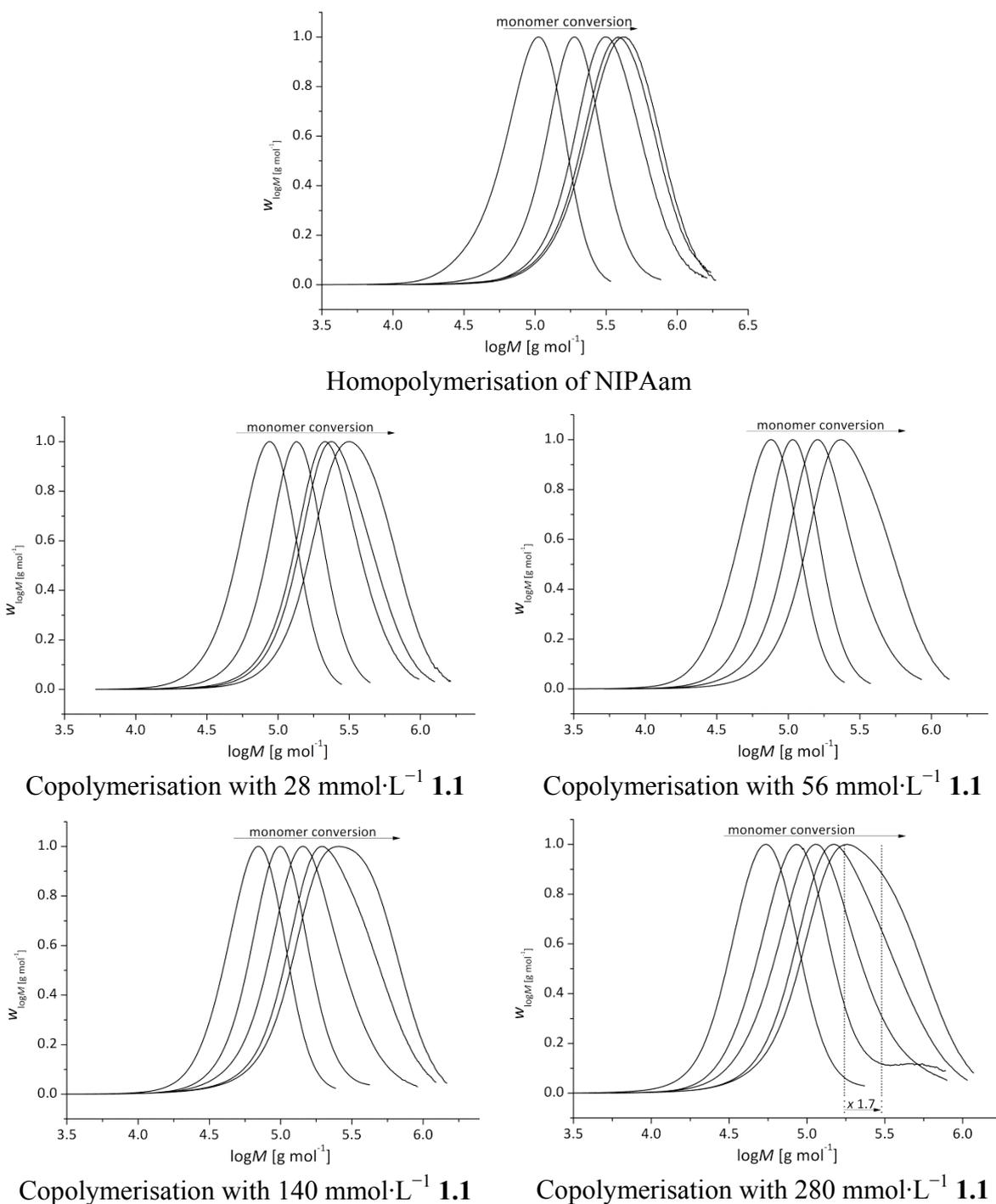
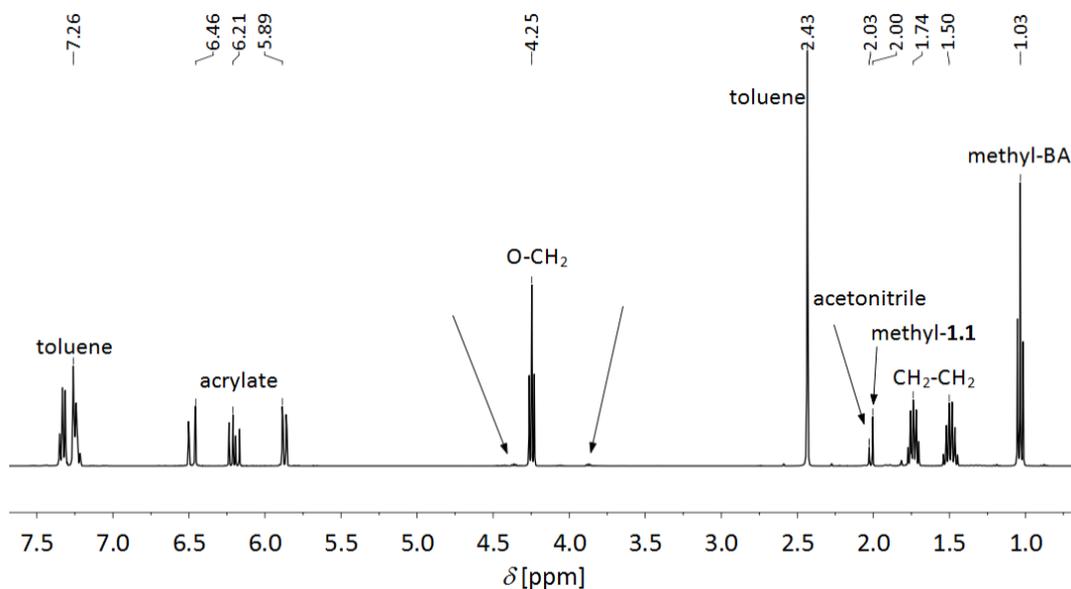


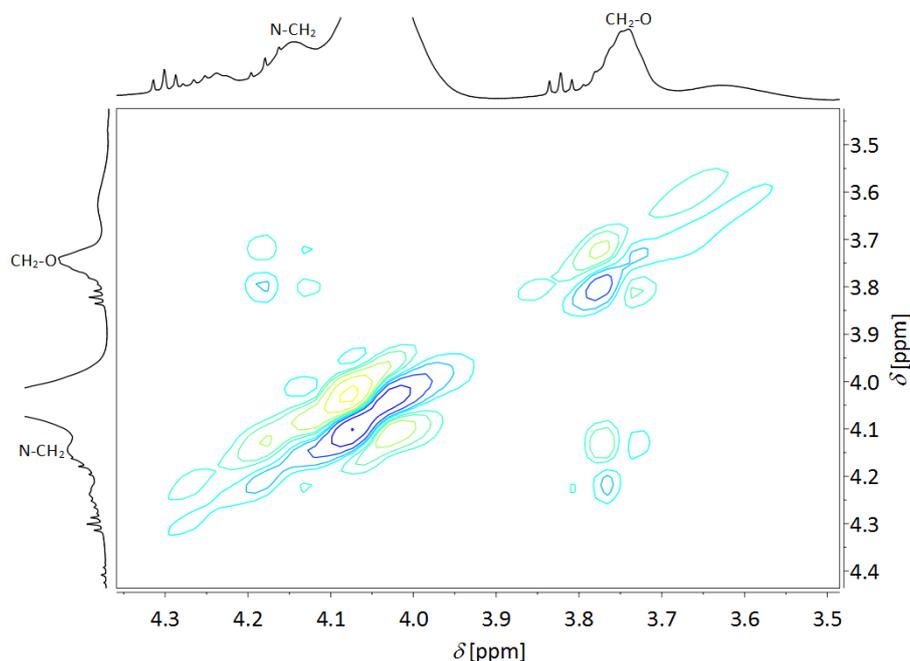
Figure S3. ^1H NMR spectrum of the polymerization mixture consisting of $c_{1.1} = 105 \text{ mmol}\cdot\text{L}^{-1}$, $c_{\text{AIBN}} = 0.85 \text{ mmol}\cdot\text{L}^{-1}$, $c_{\text{R62}} = 0.55 \text{ mmol}\cdot\text{L}^{-1}$, $c_{\text{BA}} = 351 \text{ mmol}\cdot\text{L}^{-1}$ in toluene recorded in CDCl_3 .



From left to right the different signals in Fig. S3 can be assigned to the compounds in the mixture: In the aromatic region above 7.00 ppm the multiplet of the solvent toluene is found which overlaps with the singlet of residual CHCl_3 at 7.26 ppm. From 6.46 to 5.89 ppm the signals of the acrylic unit, which is similar in BA and **1.1**, appear. The doublets of doublets caused by the terminal protons of the double bond are detected at 5.89 and 6.46 ppm, respectively. The quartet in between belongs to the proton next to the carbonyl group. At 4.25 ppm the CH_2 -group directly adjacent to the BA's ester group shows a triplet. Left and right from this signal, quintets of low intensity, marked by the black arrows, can be seen. These correspond to the protons of the ethyl bridge in **1.1** connecting the UV-sensitive and the monomeric units and have to be categorized. Further in the up field region of the spectrum the methyl group of the toluene can be found as well as the singlet of the DMI's methyl groups at 2.00 ppm and the singlet of the internal standard acetonitrile. The quintet at 1.74 ppm and the sextet at 1.48 ppm result from the protons of the $\text{CH}_2\text{-CH}_2$ -group in the butyl moiety of BA and the terminal methyl group of this rest causes a triplet at 1.03 ppm. As can be seen, neither the RAFT-agent nor the initiator can be identified as the concentrations of those compounds in the mixture are very small and have no influence on the measurement.

COSY spectra show the spin-spin-coupling of equal nuclei mediated through bonds and give therefore information about the direct interactions of connected groups. Such a H,H-COSY plot for a *p*(BA-*co*-**1.1**) sample is shown below (Figure S4).

Figure S4. Extract from the H,H-COSY spectrum of a poly(BA-co-1.1) sample recorded in CDCl₃. Only a partial spectrum, from 3.50 to 4.40 ppm, is shown as the other H,H-coupling processes are not relevant for the structure elucidation of 1.1's ethyl bridge.



Example for the Calculation of the Number of 1.1-units per Star Polymer Molecule:

$$I_{BA} = 1 = 3 \text{ protons} \rightarrow \frac{I_{BA}}{3 \text{ protons}} = \frac{1}{3 \text{ protons}} = 0.333\bar{3}$$

$$I_{1.1} = 0.0061 = 2 \text{ protons} \rightarrow \frac{I_{1.1}}{2 \text{ protons}} = \frac{0.069}{2 \text{ protons}} = 0.0345 \quad \text{S-1}$$

$$F_{1.1} = \frac{\frac{I_{1.1}}{2 \text{ protons}}}{\frac{I_{BA}}{3 \text{ protons}} + \frac{I_{1.1}}{2 \text{ protons}}} = \frac{0.0345}{0.368} = 0.094 \text{ mol \%}$$

$$F_{BA} = \frac{\frac{I_{BA}}{3 \text{ protons}}}{\frac{I_{BA}}{3 \text{ protons}} + \frac{I_{1.1}}{2 \text{ protons}}} = \frac{0.33}{0.368} = 0.906 \text{ mol \%} \quad \text{S-2}$$

$$F_{BA} \cdot M_{BA} = m_{BA} \rightarrow 0.906 \text{ mol \%} \times 128.17 \text{ g} \cdot \text{mol}^{-1} = 116.15 \text{ g}$$

$$F_{1.1} \cdot M_{1.1} = m_{1.1} \rightarrow 0.094 \text{ mol \%} \times 223.23 \text{ g} \cdot \text{mol}^{-1} = 20.94 \text{ g}$$

$$m_{BA} + m_{1.1} = m_{100 \text{ wt \%}} \rightarrow 116.15 \text{ g} + 20.94 \text{ g} = 137.09 \text{ g} \equiv 100 \text{ wt \%}$$

$$m_{BA} \equiv 84.73 \text{ wt \%}$$

$$m_{1.1} \equiv 15.27 \text{ wt \%} \quad \text{S-3}$$

$$\frac{(M_n^{\text{UV-1.52}} - M_{R62})}{N_A} = w_{\text{star}} \rightarrow \frac{(121,000 \text{ g} \cdot \text{mol}^{-1} - 1,864 \text{ g} \cdot \text{mol}^{-1})}{6.022 \times 10^{23} \text{ mol}^{-1}} = 1.97 \times 10^{-19} \text{ g}$$

$$15.27 \text{ wt \%} \equiv 3.01 \times 10^{-20} \text{ g}$$

$$\frac{M_{1.1}}{N_A} = w_{1.1} \rightarrow \frac{223.23 \text{ g} \cdot \text{mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 3.71 \times 10^{-22} \text{ g} \quad \text{S-4}$$

$$\text{number of 1.1-units} = \frac{3.01 \times 10^{-20} \text{ g}}{3.71 \times 10^{-22} \text{ g}} \approx 81 \quad \text{S-5}$$

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