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SUPPLEMENTARY INFORMATION

Solubility behaviour of random and gradient copolymers of di- and oligo(ethylene oxide) methacrylate in water: Effect of various additives

Maryam Bozorg , Birgit Hankiewicz and Volker Abetz

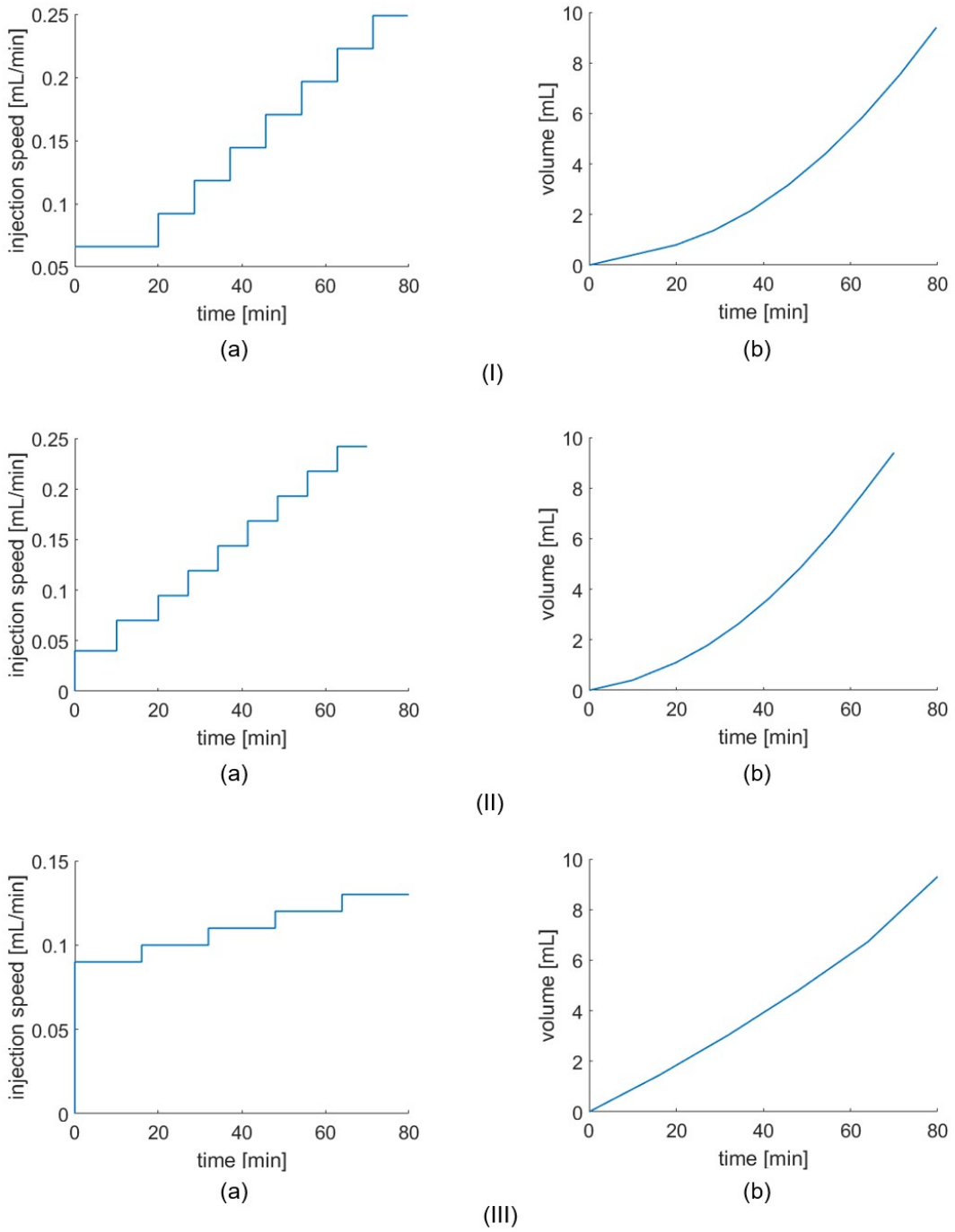

Figure S1 The injection program of OEOMA for different gradient copolymerization systems, as (a) injected speed vs. time and (b) injection volume vs. time for: (I) Injection program P1 resulting in gradient copolymer P1; (II) Injection program P2 resulting in gradient copolymer P2; (III) Injection program P3 resulting in gradient copolymer P3.

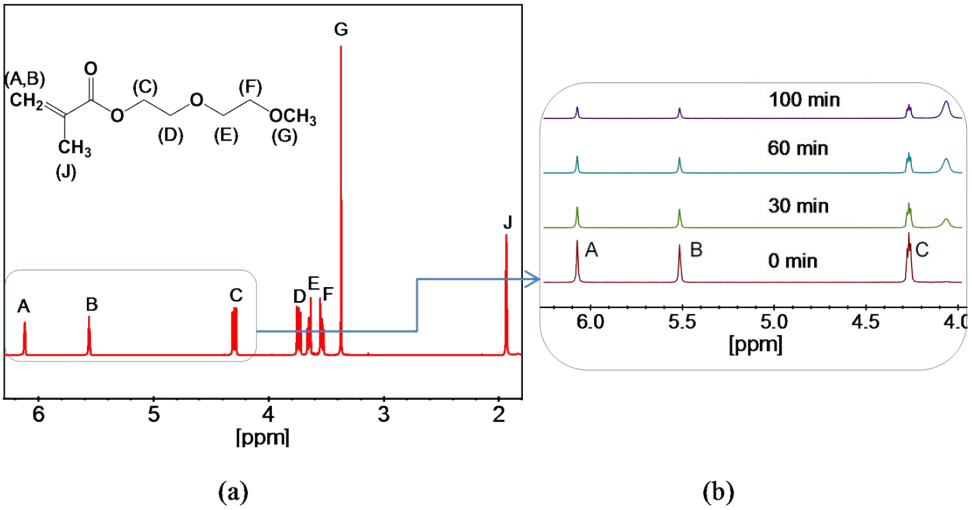

Figure S2 (a) The NMR spectrum of MEO_2MA; (b) The change of the NMR spectrum by time during the polymerization reaction. As the reaction goes on, the peaks at the region 5.45 - 6.12 ppm (A&B) tend to get smaller and eventually disappear. The peak at the region 3.9 - 4.4 ppm (C) which is corresponding to the esteric protons of the monomer gets replaced by the broad peak at the same region designated to the esteric protons of the polymer. The monomer conversion is calculated by comparing the integral of vinyl protons of the remaining monomers (A & B; 5.45 - 6.12 ppm) to the integration of the region C (3.9 - 4.4 ppm) which represents the protons next to the ester function of the homopolymer and the remaining monomer (1)(2). By time, the A&B peaks representing the monomer's double bond tend to disappear. Moreover, the sharp peak of C representing the esteric protons of monomer is replaced by a broad peak representing the esteric protons of the polymer.

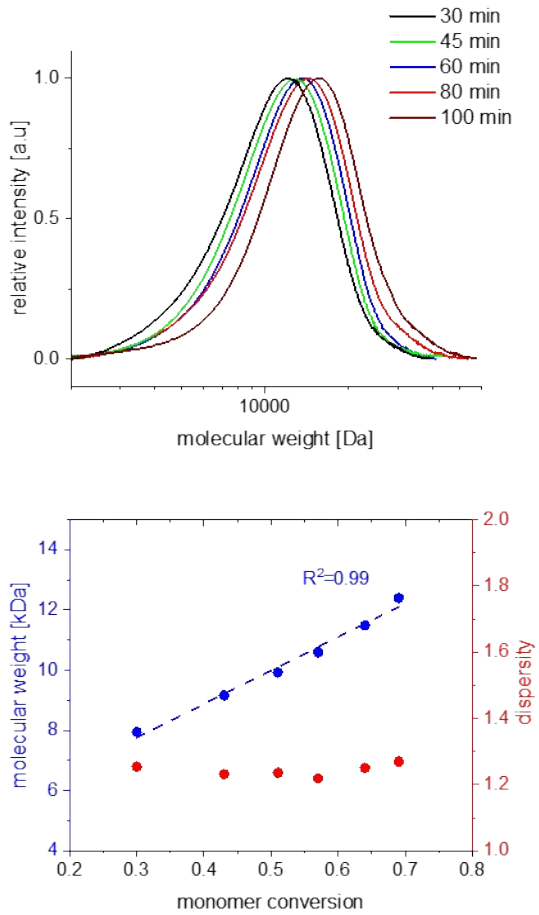

Figure S3 SEC results of MEO_2MA polymerization in anisole using PMDETA as a ligand (a). The change of molecular weight versus conversion at different time intervals (b). The SEC peaks are shifted to a higher molecular weight while the reaction is progressing. The molecular weight changes linearly as the conversion increases while the dispersity stays almost constant.

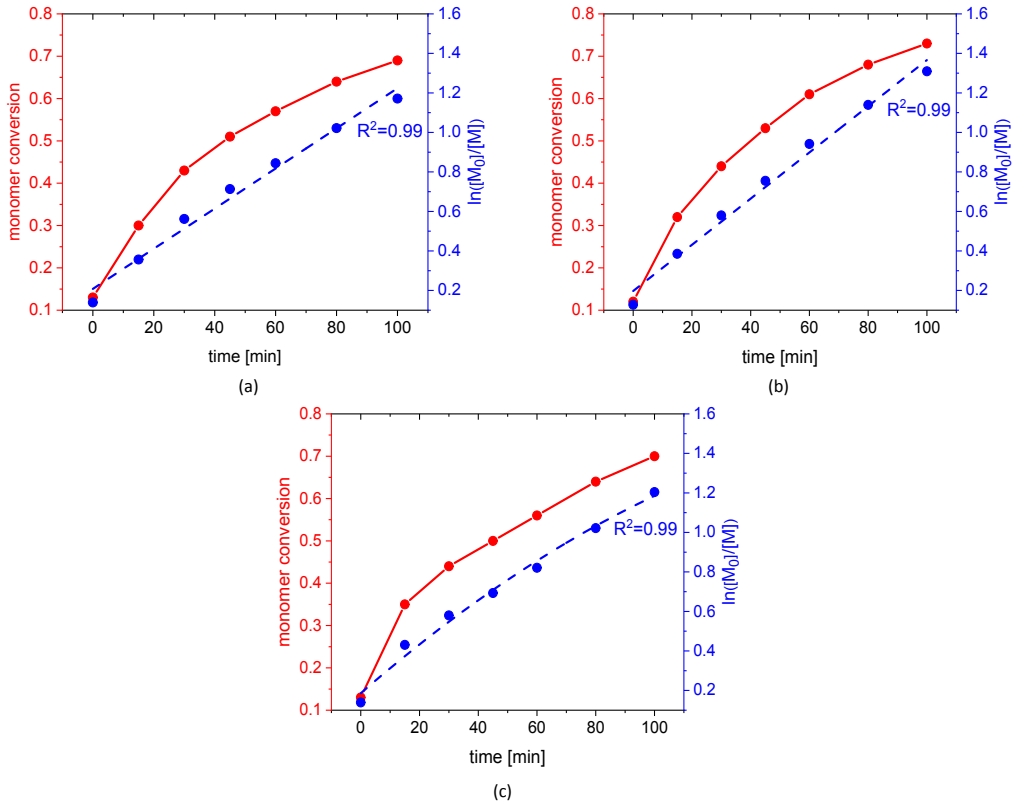

Figure S4 The monomer conversion versus reaction time and the semi-logarithmic plot of monomer conversion i.e. $\ln([M]_0/[M])$ versus reaction time for ATRP homopolymerization of MEO_2MA (a) and OEOMA (b) and ATRP random copolymerization of MEO_2MA and OEOM (c). All reactions were done with the reagent ratio of $[M]_0 : [I]_0 : [Cu^I]_0 : [L] = 100 : 1 : 0.5 : 1$ and the reaction time was 100 min. the monomer ratio for random copolymerization was MEO_2MA : OEOMA = 80 : 20.

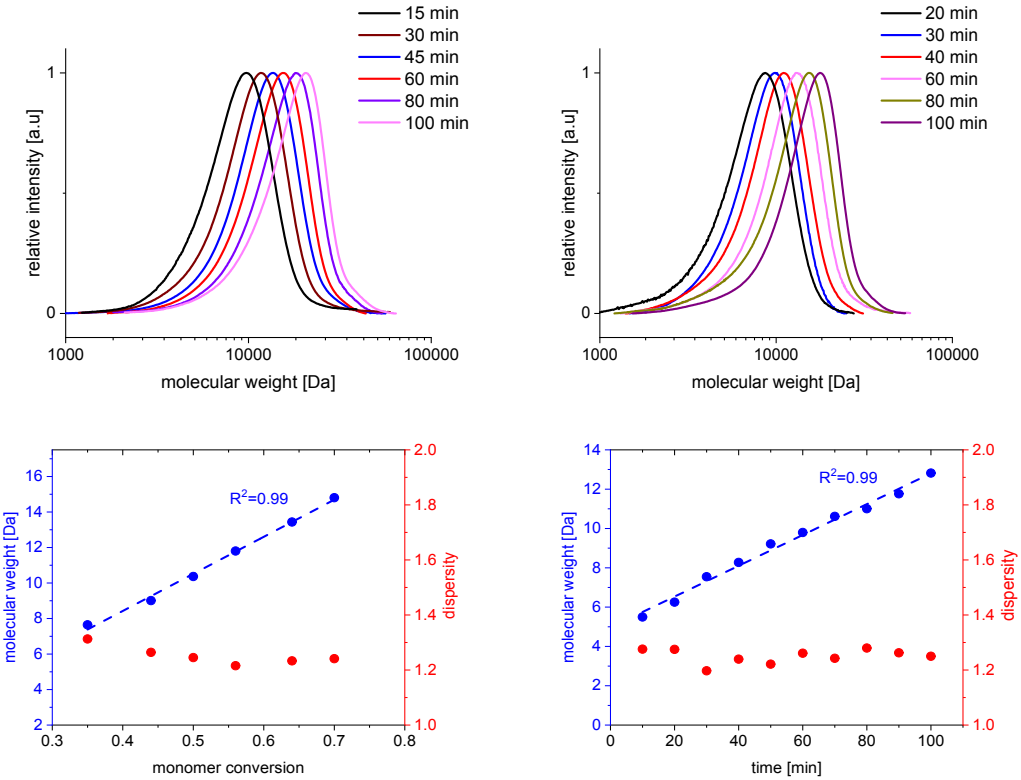

Figure S5 SEC results of MEO_2MA and OEOMA random (left) and gradient (right) copolymerization in anisole using PMDETA as a ligand. The upper graphs are the SEC traces at different time intervals. The lower graphs are the molecular weight growth and dispersity change vs. conversion. For both copolymers the SEC peaks are shifted to higher molecular weight while the reaction is progressing. The molecular weight changes linearly versus conversion while the dispersity stays almost constant. The molecular weight growth is slower for the gradient copolymerization due to the lower concentration of monomers during reaction.

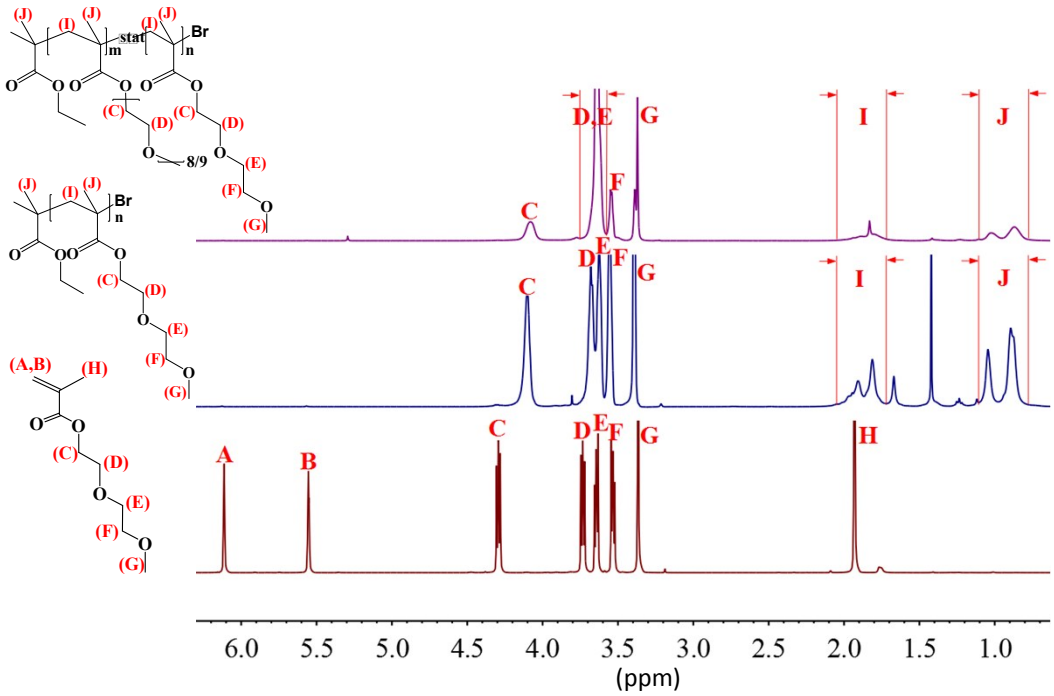

Figure S6 The ^{1}H NMR spectra of diethylene oxide methacrylate and its homopolymer as well as its copolymer with oligo ethylene oxide methacrylate.

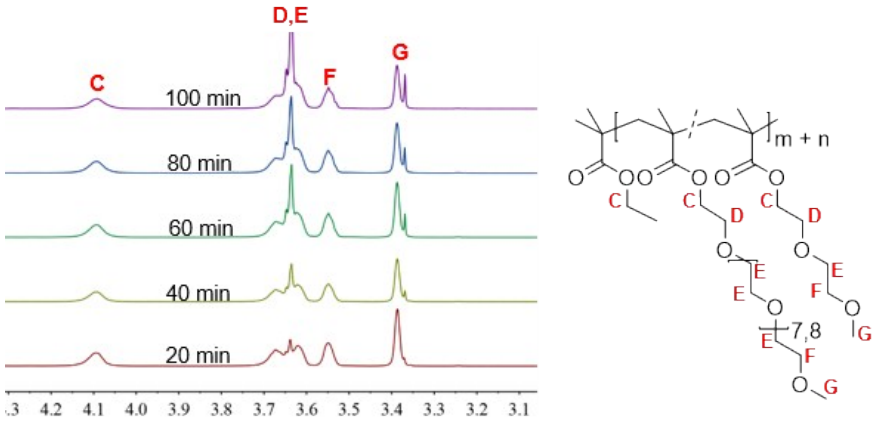

Figure S7 The zoomed-in 1H NMR spectra of the samples during the random copolymerization of MEO2MA and OEOMA. The change of the peaks in the range D, E shows how the copolymer composition is changing by time.

The signal between 3.9 and 4.2 ppm is associated with the first methylene group of the side chain and thereby two protons per repeating unit. The integration of the signal in the range of 3.9 - 4.4 ppm normalized to the integral in the range of 3.5 - 3.9 ppm thus yields the average number N of the remaining protons in the oligo(ethylene oxide) chains. For a composite of the two monomers $M(EO)_2MA$ (M) and $O(EO)_nMA$ (O), this results in the following expression:

$$A = N_M \times x + N_O \times y \quad (1)$$

wherein x and y are the molar fractions of M and O, respectively. As the sum of these fractions must be equal to one, eq 1 can be transformed to link either x or y to the integral A:

$$N_M \times (1 - y) + N_O \times y = A$$

$$\Leftrightarrow y = \frac{A - N_M}{N_O - N_M} \quad (2)$$

The values of N_j *(j = M, O)* are linked to the number n_j of ethylene oxide units by eq. (3), taking out the first two protons of each side chain.

$$N_j = 4 \times n_j - 2 \quad (3)$$

with $n_M = 2$ and $n_O = 9.08$. The latter was calculated from the molecular weight indicated from MEO_2MA's molecular weight (M_n = 500 g/mol). Combining eq. (2) and eq. (3) hence gives eq. (4), which was used to calculate the composition of the gradient copolymers (2).

$$y = \frac{A - 6}{34.32 - 6} = \frac{A - 6}{28.32} \quad (4)$$

In the following, the results of DLS measurements of gradient and random copolymers containing around 20 mol% OEOMA in aqueous solution is shown. The lower graphs show the normalized scattering intensity and the upper ones, the hydrodynamic radius. The dashed line shows the LCST. The type of additive as well as the additive concentration is mentioned on each graph. To make the comparison easier, for each additive the results for random and gradient copolymers are plotted after each other.
More than two-step aggregation is observed in the phase transition behavior of gradient and random copolymer in the presence of different salts indicating their high interaction with the polymer chain. In presence of kosmotropic salts, the second phase transition temperature is also decreasing by the increase of salt concentration. Three phase transition temperatures are observed in the case of strong kosmotropic cations.

The effect of anions

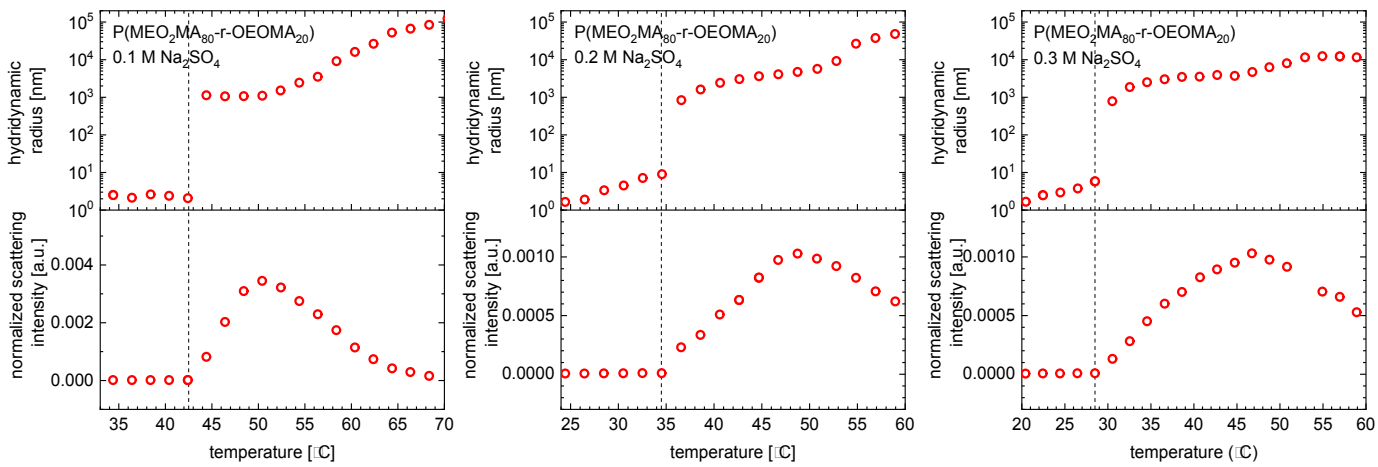

Figure S8 DLS measurements of the random copolymer $P(MEO_2MA_{81}\text{-r-}OEOMA_{19})$, M_n = 15.96 kDa, Đ = 1.17) in Na_2SO_4 aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

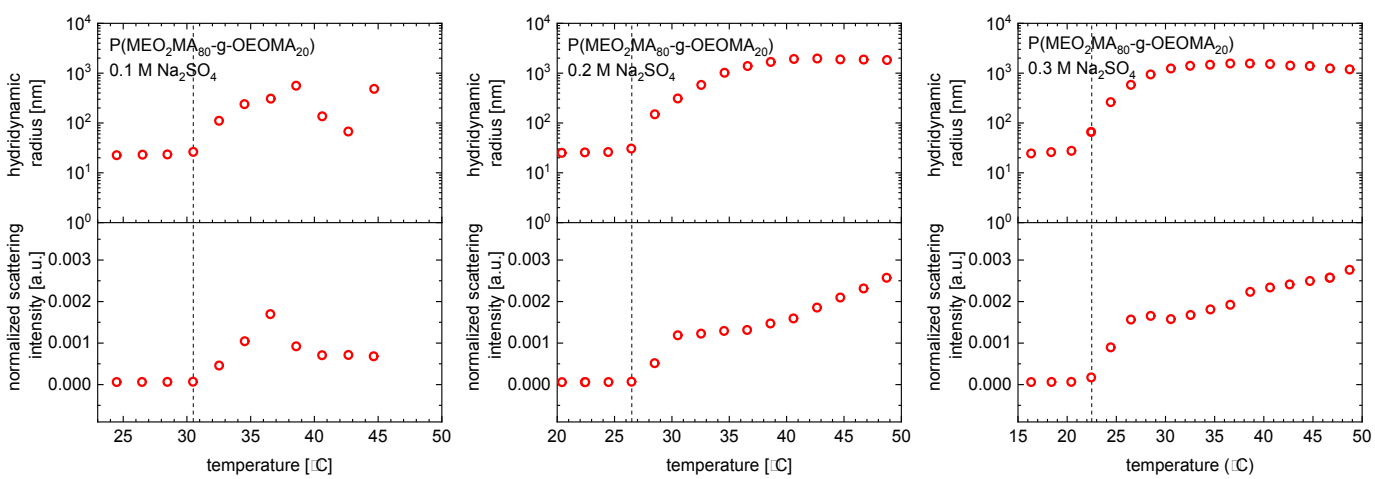

Figure S9 DLS measurements of the gradient copolymer $P(MEO_2MA_{80.5}\text{-g-}OEOMA_{19.5})$, M_n = 15.21 kDa, Đ = 1.24 (right) in Na_2SO_4 aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

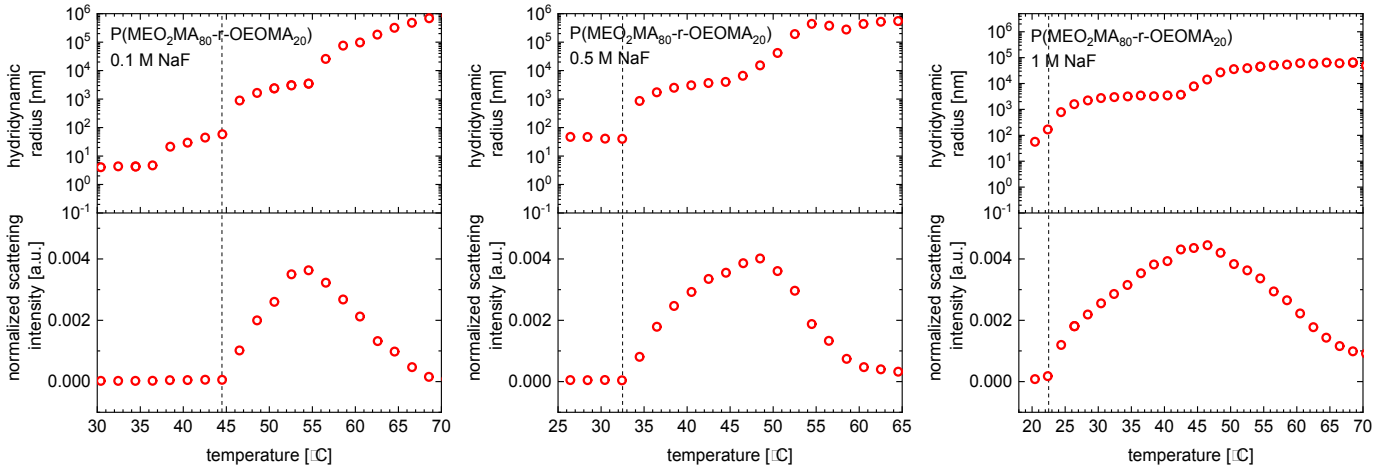

Figure S10 DLS measurements of the random copolymer P(MEO_2MA_{81}-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17) in NaF aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

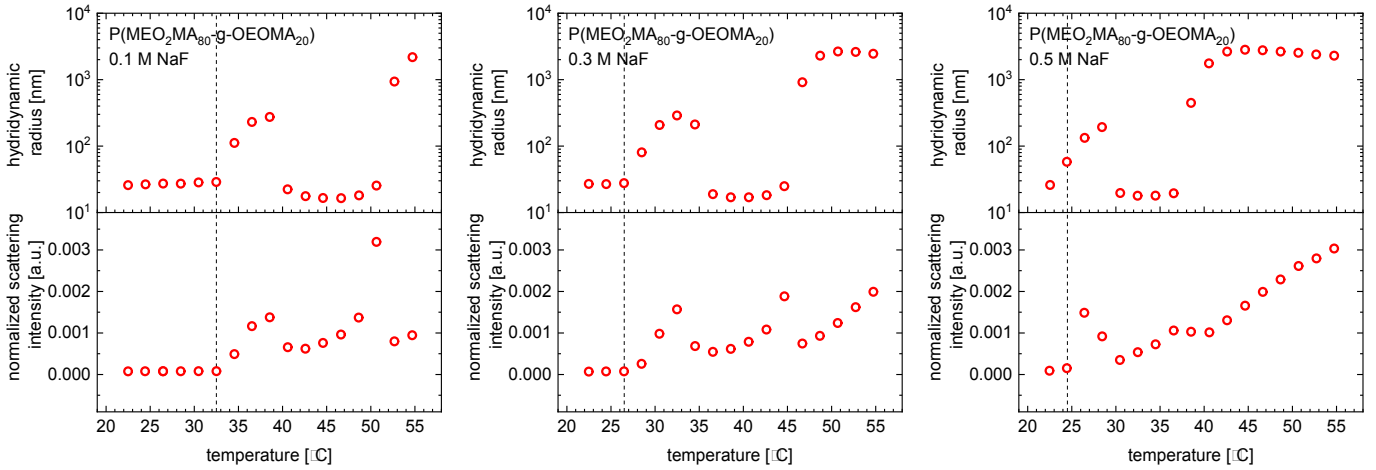

Figure S11 DLS measurements of the gradient copolymer P($MEO_2MA_{80.5}$-g-OEOMA19.5), M_n = 15.21 kDa, Đ = 1.24 (right) in NaF aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

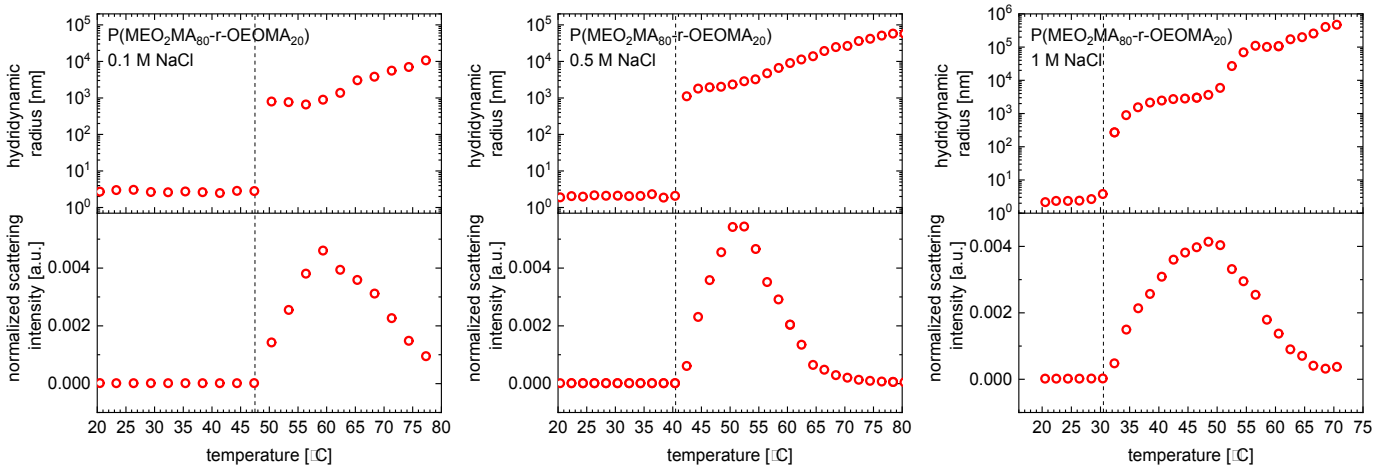

Figure S12 DLS measurements of the random copolymer P(MEO_2MA_{81}-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17) in NaCl aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

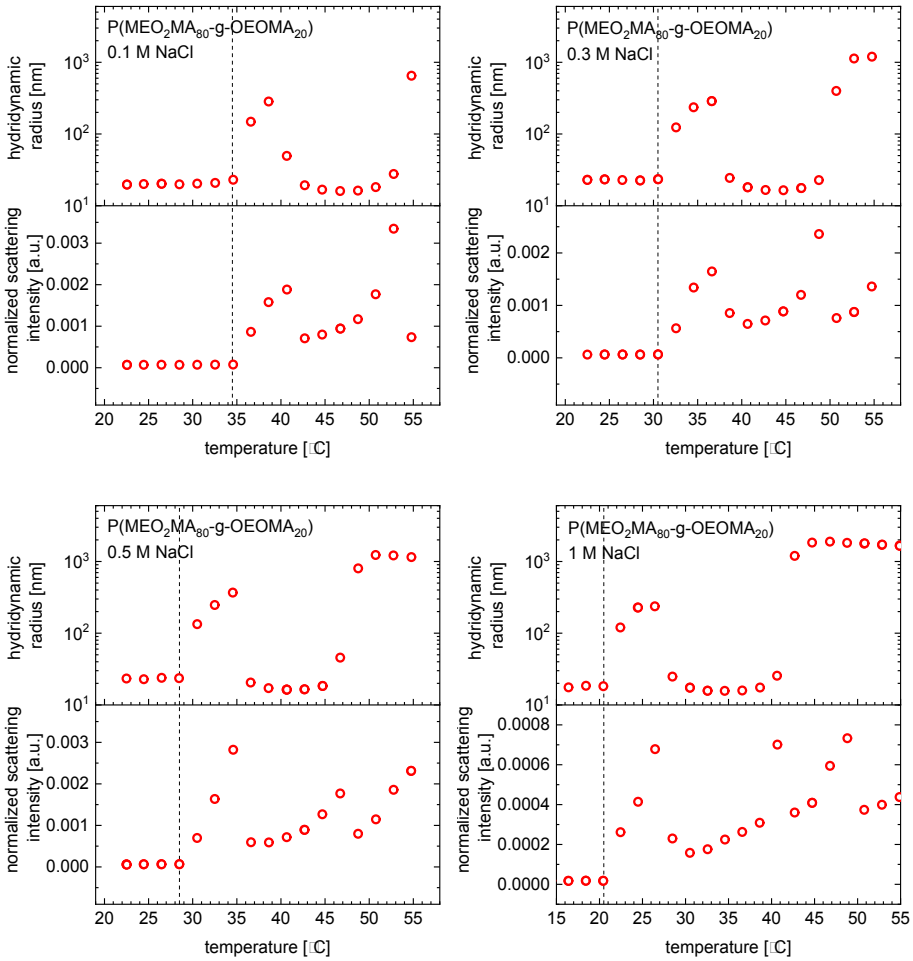

Figure S13 DLS measurements of the gradient copolymer P($MEO_2MA_{80.}$5-g-$OEOMA_{19.5}$), M_n = 15.21 kDa, Đ = 1.24 (right) in NaCl aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

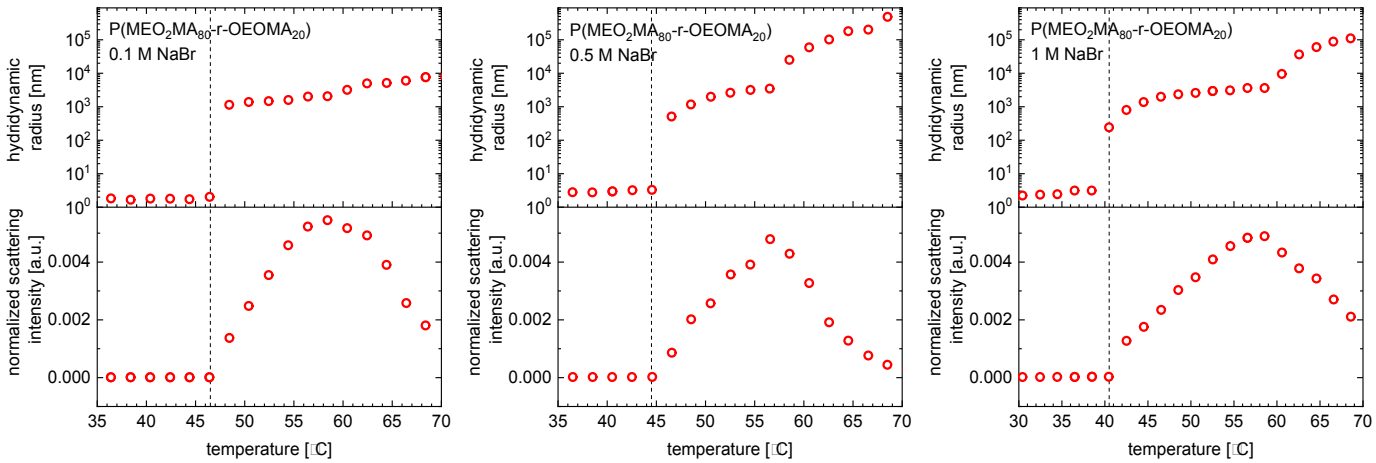

Figure S14 DLS measurements of the random copolymer P(MEO_2MA_{81}-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17) in NaBr aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

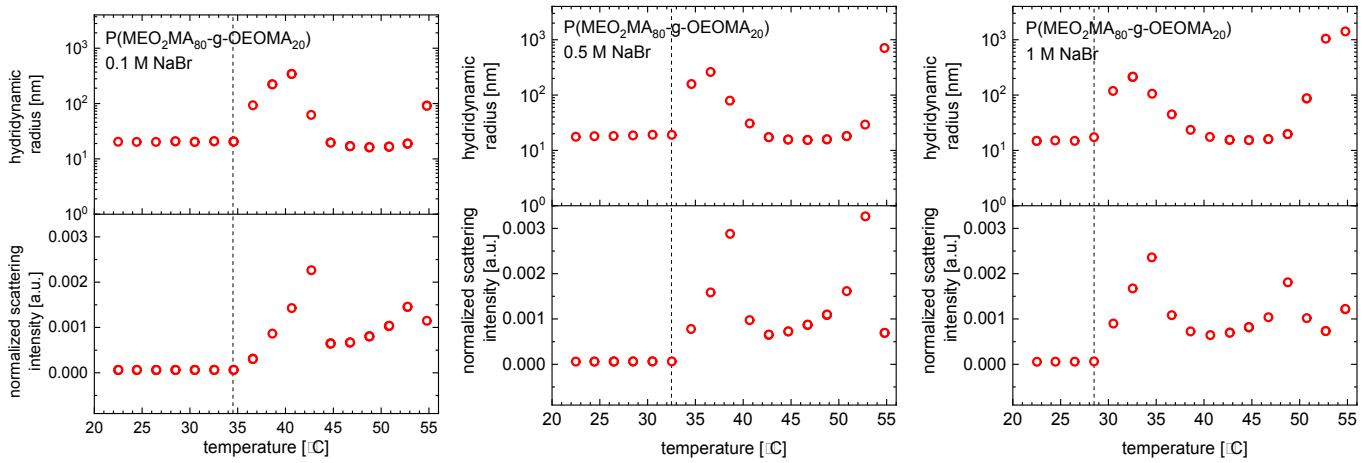

Figure S15 DLS measurements of the gradient copolymer P($MEO_2MA_{80.5}$-g-$OEOMA_{19.5}$), M_n = 15.21 kDa, Đ = 1.24 (right) in NaBr aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

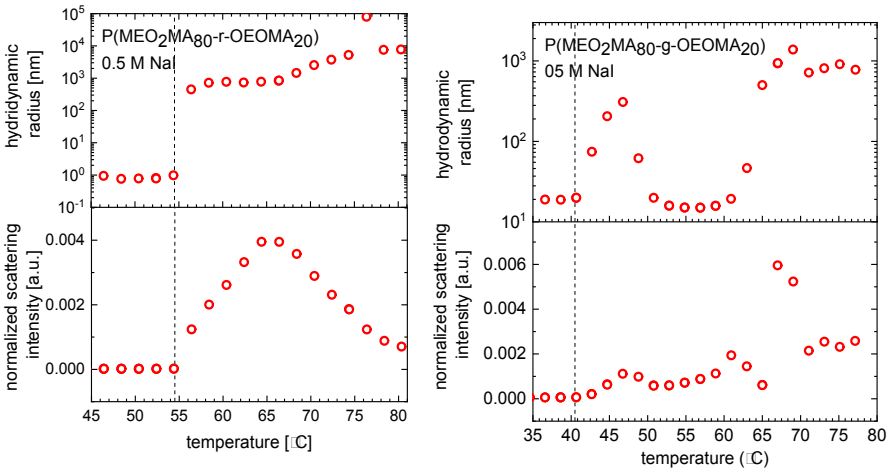

Figure S16 DLS measurements of the random copolymer P(MEO_2MA_{81}-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17 (left) and gradient copolymer P($MEO_2MA_{80.5}$-g-$OEOMA_{19.5}$), M_n = 15.21 kDa, Đ = 1.24 (right) in NaI aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST. It should be noted that the maximums of y scales for gradient copolymers are half of the one for random copolymer for better observation.

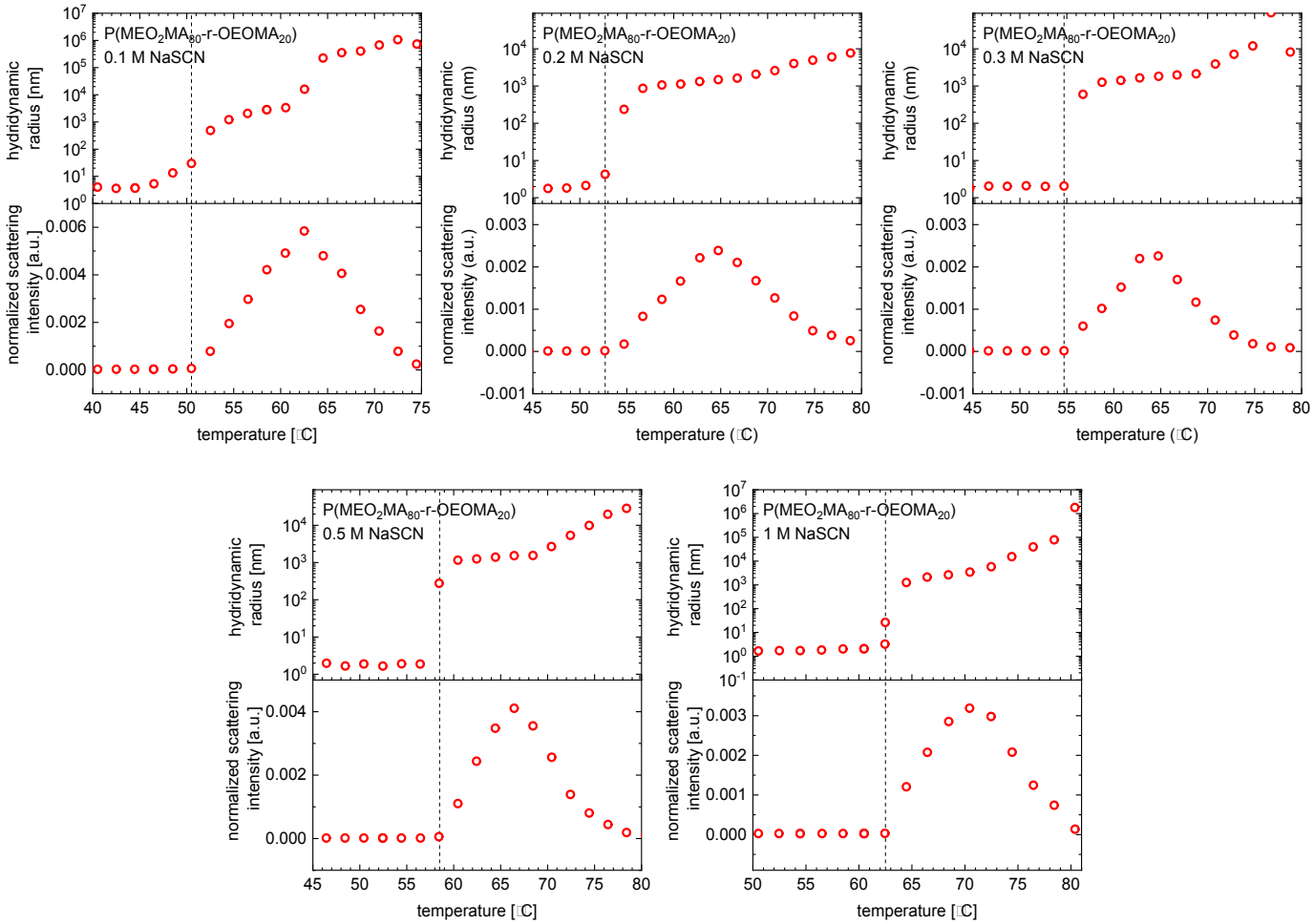

Figure S17 DLS measurements of the random copolymer P(MEO_2MA_{81}-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17) in NaSCN aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

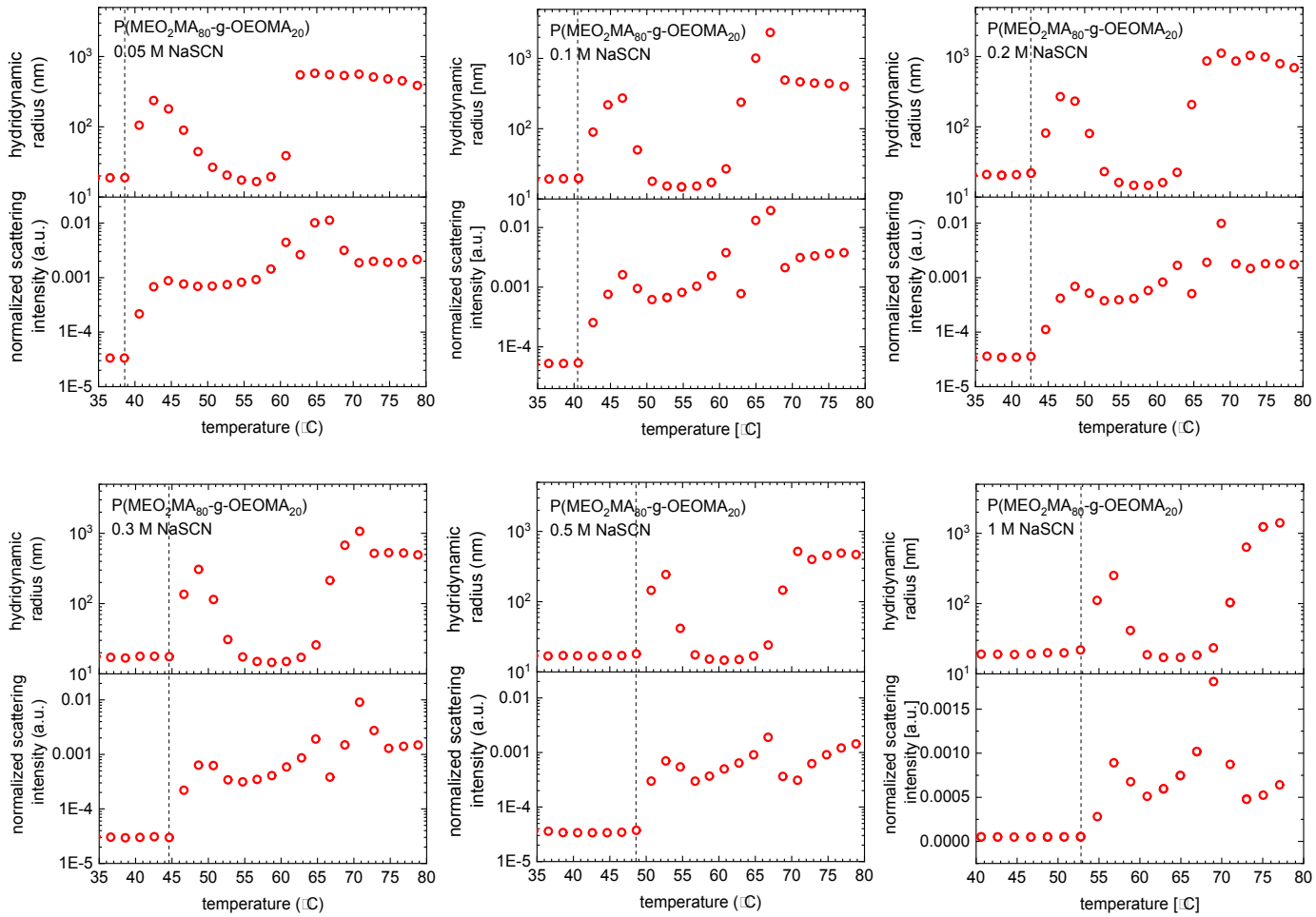

Figure S18 DLS measurements of the gradient copolymer P($MEO_2MA_{80.5}$-g-$OEOMA_{19.5}$), M_n = 15.21 kDa, Đ = 1.24 (right) in NaSCN aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

The effect of cations

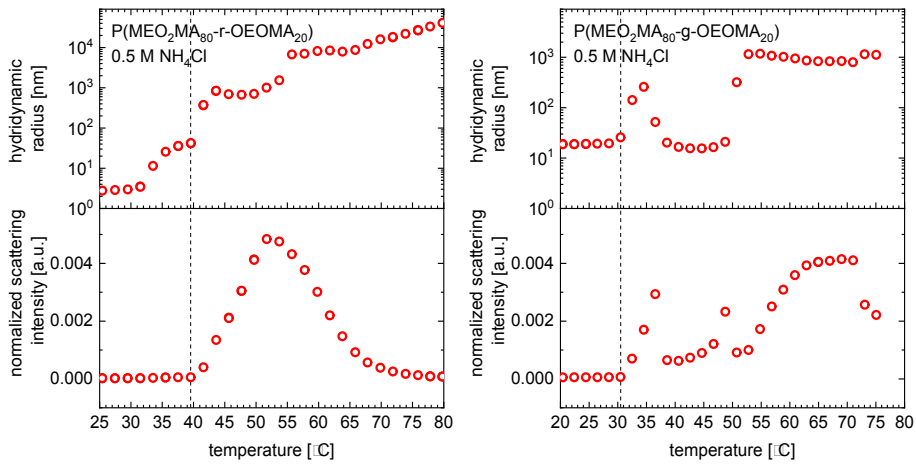

Figure S19 DLS measurements of the random copolymer P(MEO_2MA_{81}-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17 (left) and gradient copolymer P($MEO_2MA_{80.5}$-g-$OEOMA_{19.5}$), M_n = 15.21 kDa, Đ = 1.24 (right) in NH_4Cl aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST. It should be noted that the maxima of y scales for gradient copolymers are half of the one for random copolymer for better observation.

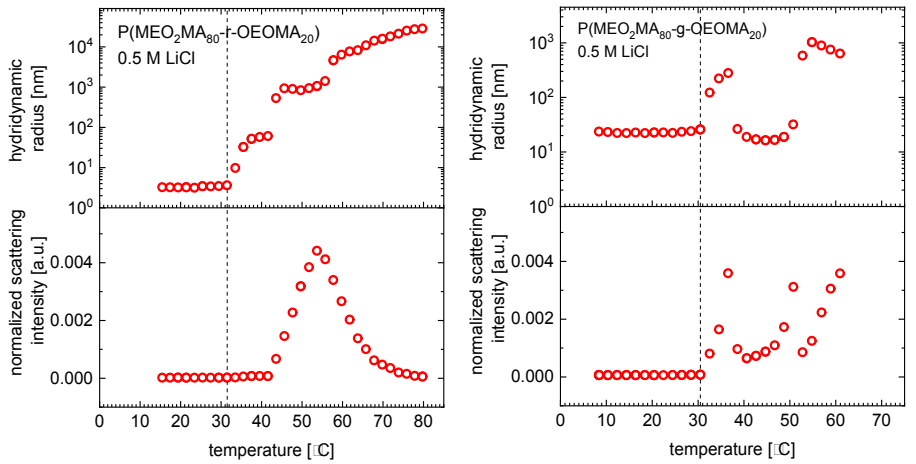

Figure S20 DLS measurements of the random copolymer P(MEO_2MA_{81}-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17 (left) and gradient copolymer P($MEO_2MA_{80.5}$-g-$OEOMA1_{9.5}$), M_n = 15.21 kDa, Đ = 1.24 (right) in LiCl aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST. It should be noted that the maxima of y scales for gradient copolymers are half of the one for random copolymer for better observation.

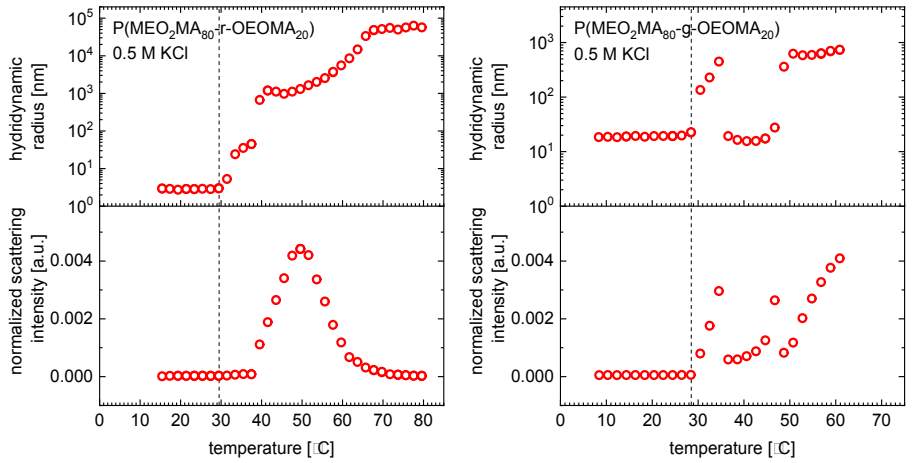

Figure S21 DLS measurements of the random copolymer P(MEO_2MA_{81}-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17 (left) and gradient copolymer P($MEO_2MA_{80.5}$-g-$OEOMA_{19.5}$), M_n = 15.21 kDa, Đ = 1.24 (right) in KCl aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST. It should be noted that the maxima of y scales for gradient copolymers are half of the one for random copolymer for better observation.

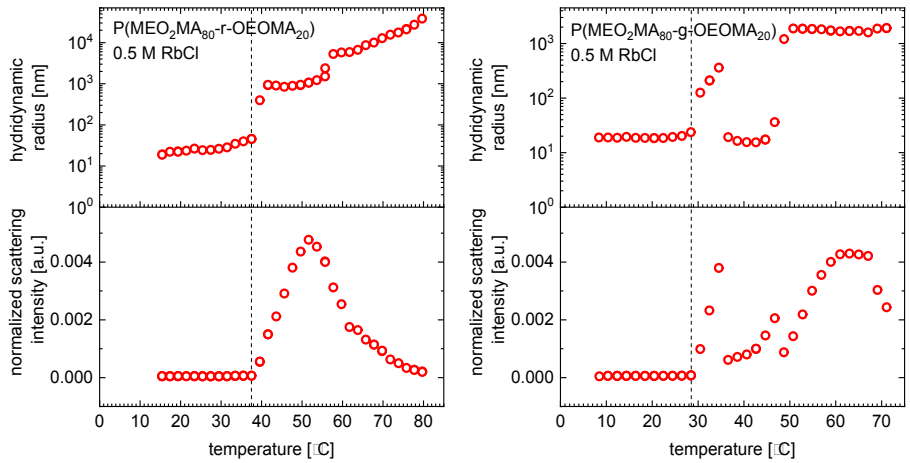

Figure S22 DLS measurements of the random copolymer P(MEO_2MA_{81}-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17 (left) and gradient copolymer P($MEO_2MA_{80.5}$-g-$OEOMA_{19.5}$), Mn = 15.21 kDa, Đ = 1.24 (right) in RbCl aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST. It should be noted that the maxima of y scales for gradient copolymers are half of the one for random copolymer for better observation.

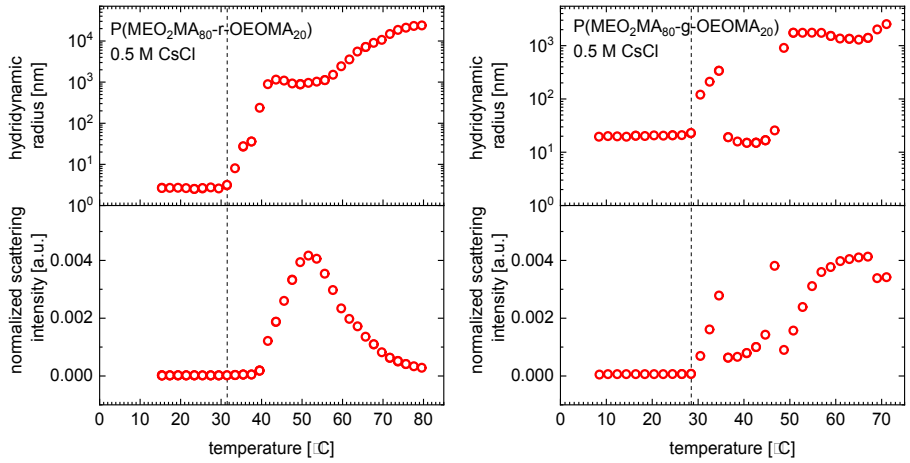

Figure S23 DLS measurements of the random copolymer P(MEO2MA81-r-OEOMA19), Mn = 15.96 kDa, Đ = 1.17 (left) and gradient copolymer P(MEO2MA80.5-g-OEOMA19.5), Mn = 15.21 kDa, Đ = 1.24 (right) in CsCl aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST. It should be noted that the maxima of y scales for gradient copolymers are half of the one for random copolymer for better observation.

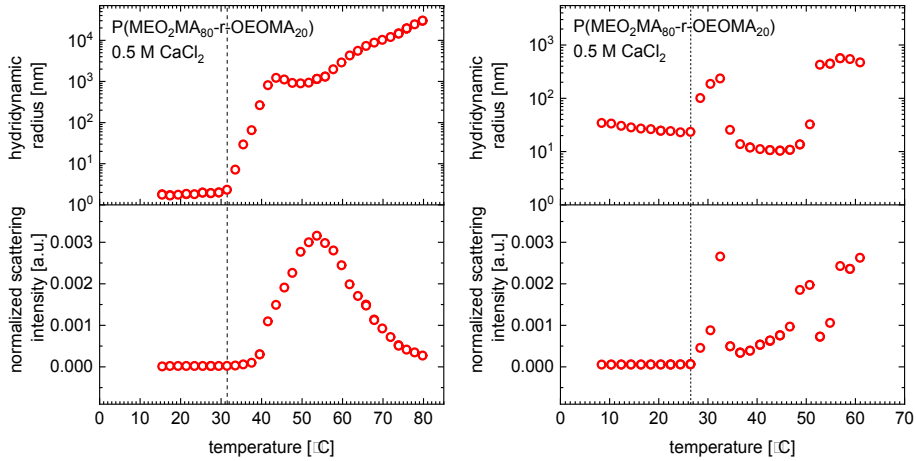

Figure S24 DLS measurements of the random copolymer P($MEO_2MA_8$1-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17 (left) and gradient copolymer P($MEO_2MA_{80.5}$-g-$OEOMA_{19.5}$), M_n = 15.21 kDa, Đ = 1.24 (right) in $CaCl_2$ aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST. It should be noted that the maxima of y scales for gradient copolymers are half of the one for random copolymer for better observation.

The effect of surfactants

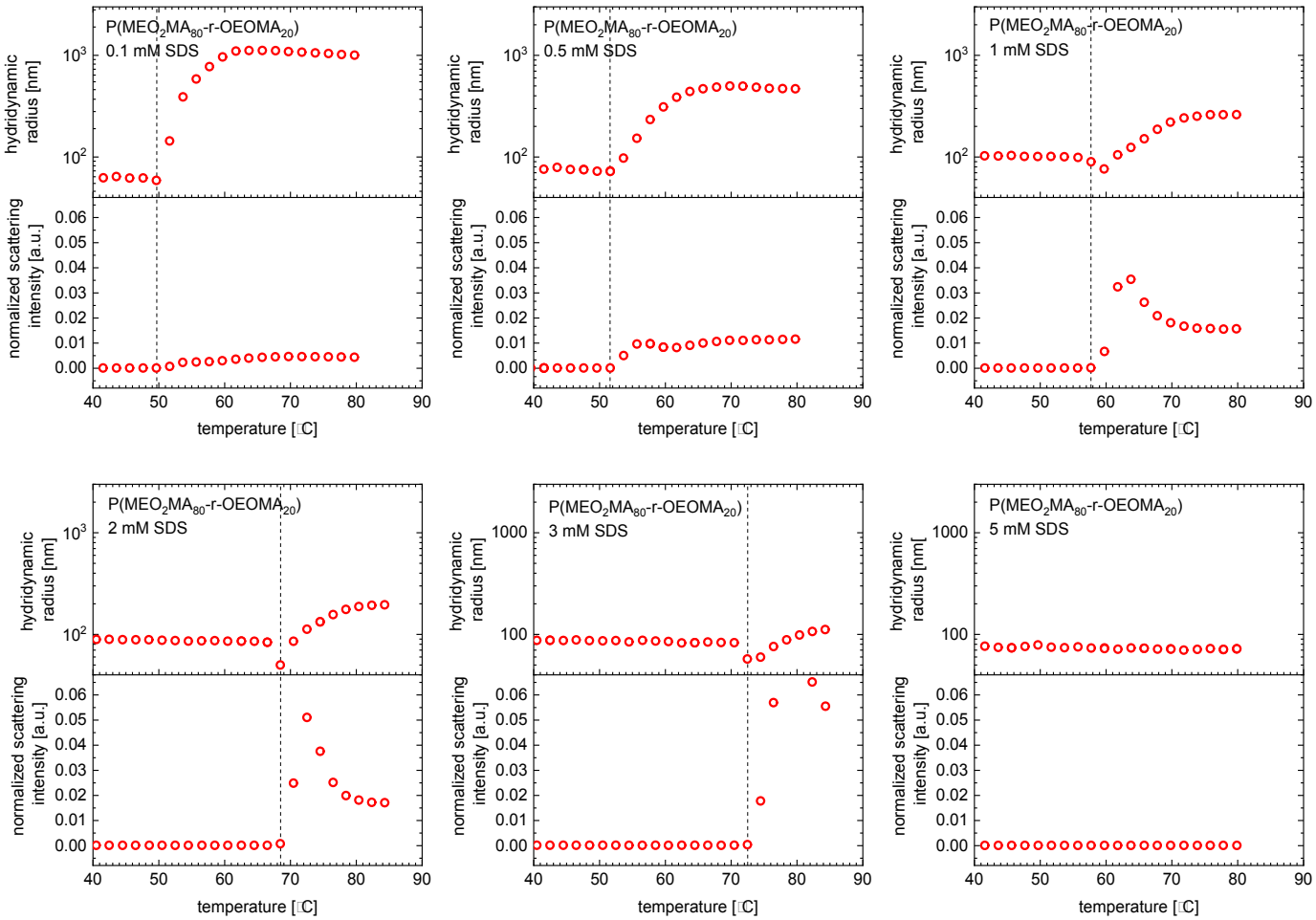

Figure S25 DLS measurements of the random copolymer P($MEO_2MA_8$1-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17) in SDS aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

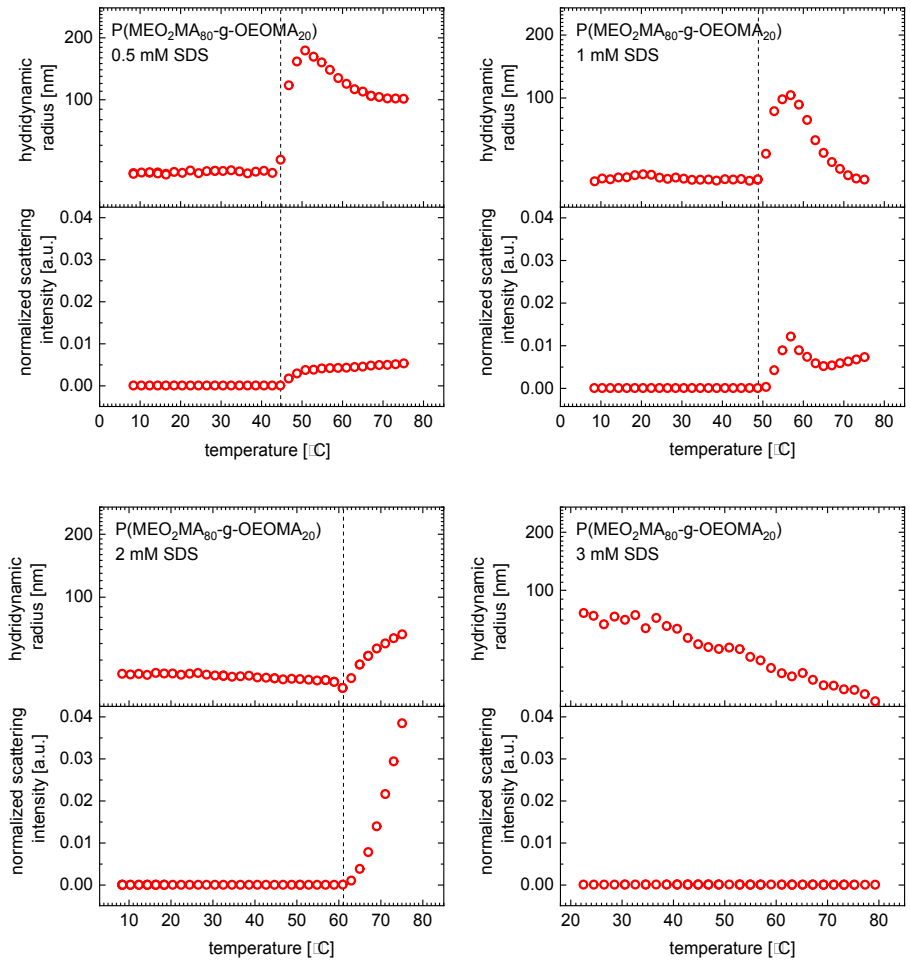

Figure S26 DLS measurements of the gradient copolymer $P(MEO_2MA_{80.5}\text{-g-}OEOMA_{19.5})$, M_n = 15.21 kDa, Đ = 1.24 in SDS aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

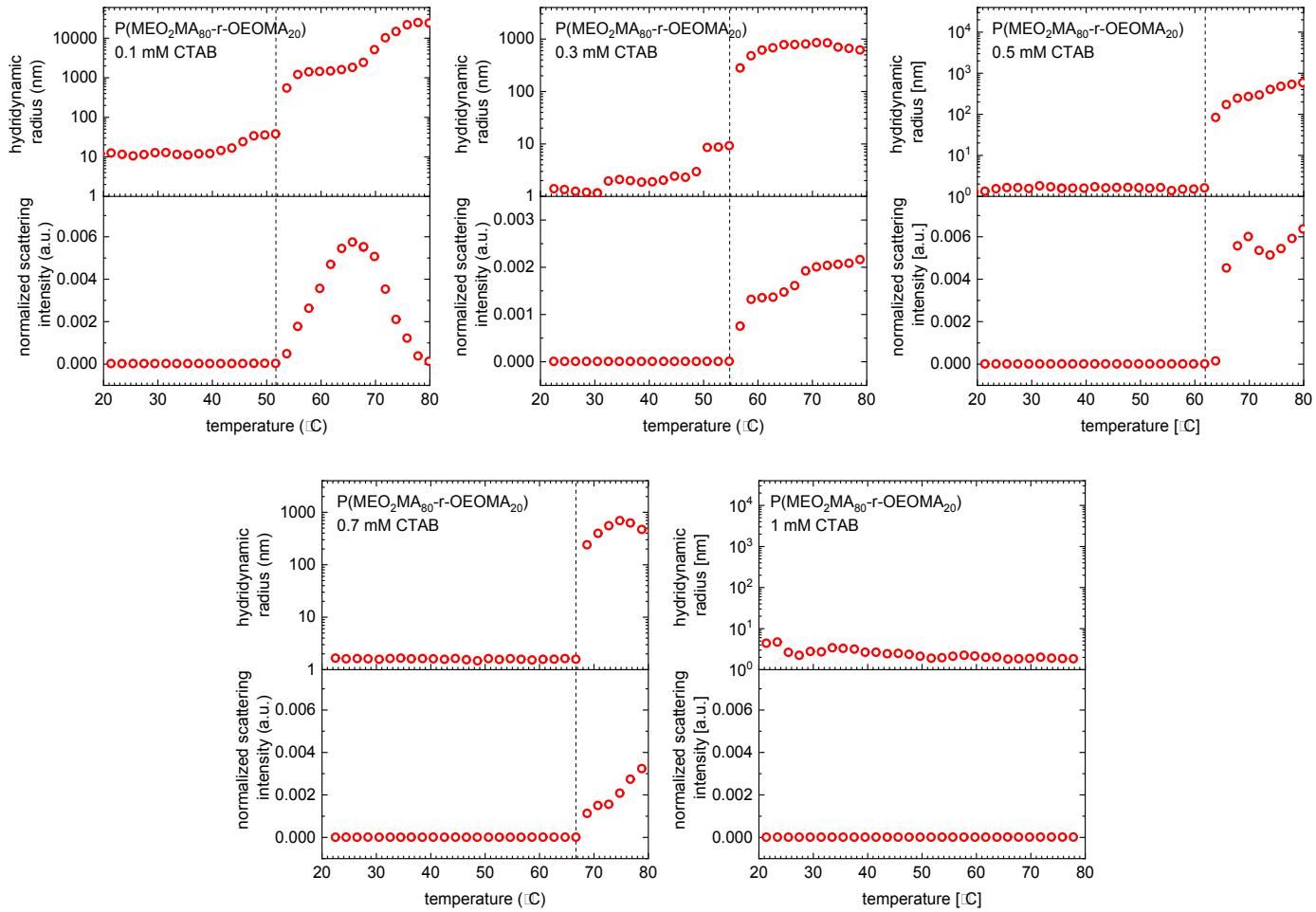

Figure S27 DLS measurements of the random copolymer P(MEO_2MA_{81}-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17) in SDS aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

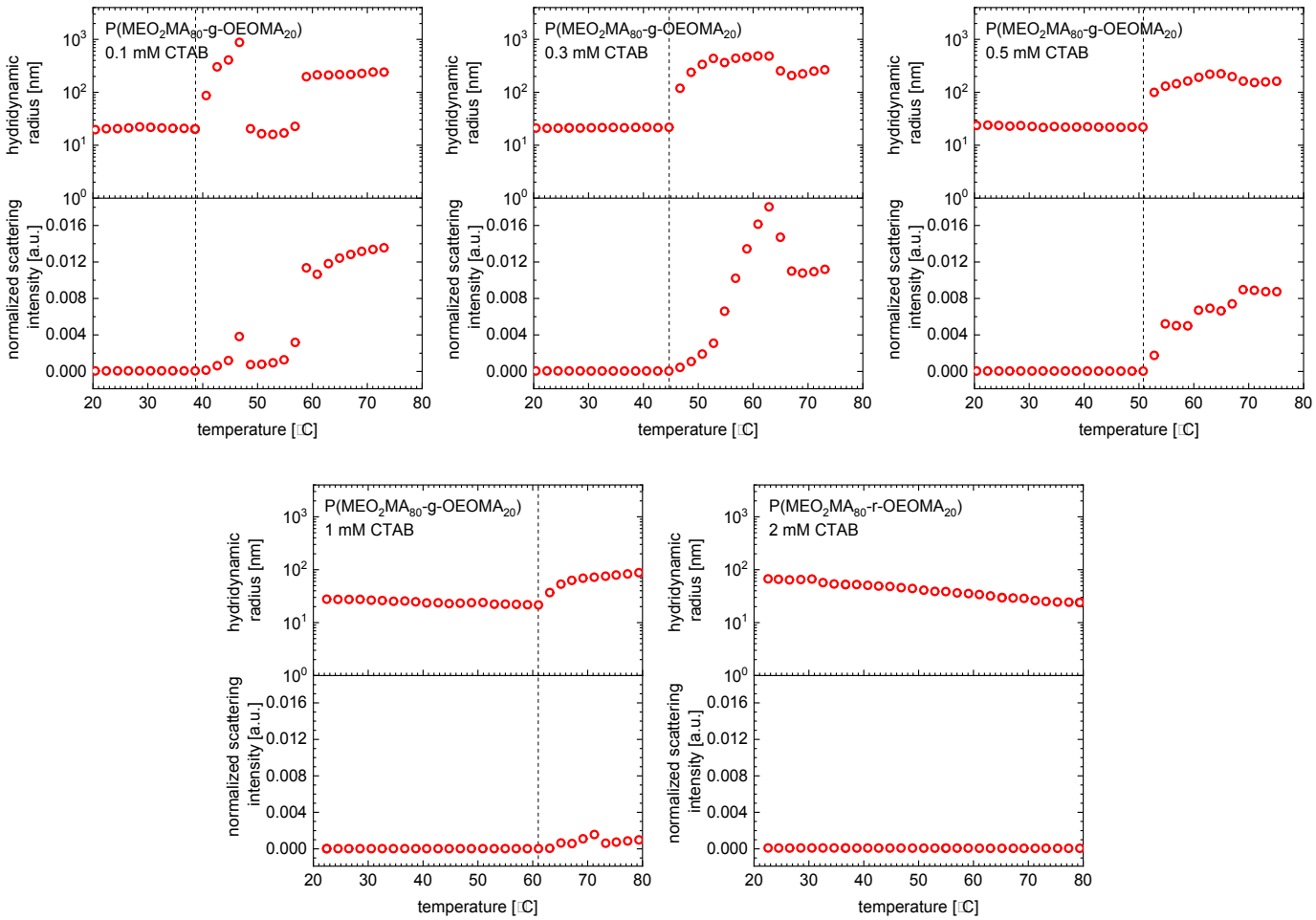

Figure S28 DLS measurements of the gradient copolymer P($MEO_2MA_{80.5}$-g-$OEOMA_{19.5}$), M_n = 15.21 kDa, Đ = 1.24 (right) in CTAB aqueous solution. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

The effect of ethanol

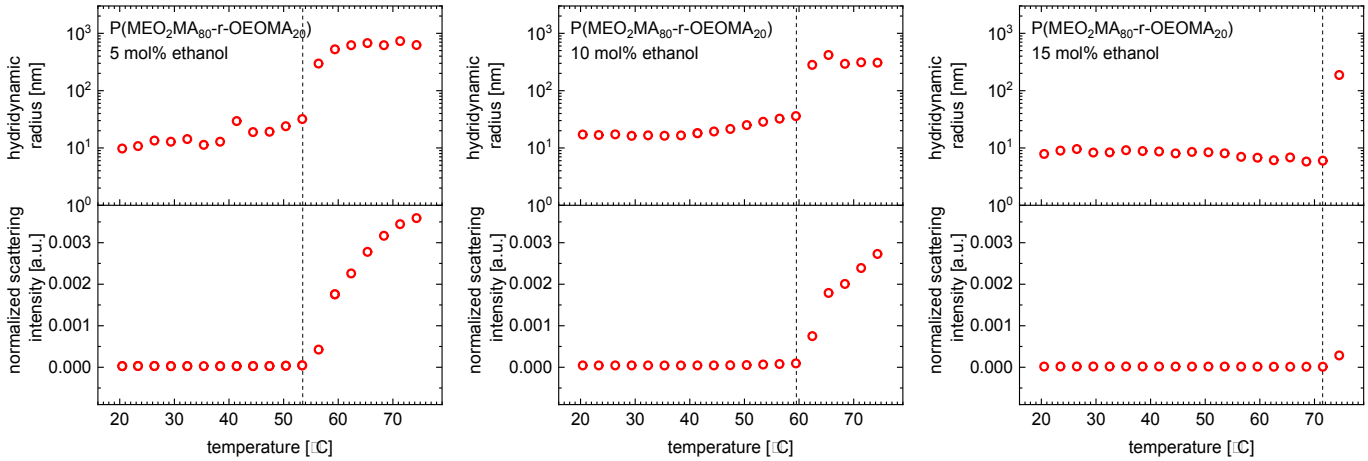

Figure S29 DLS measurements of the random copolymer P(MEO_2MA_{81}-r-$OEOMA_{19}$), M_n = 15.96 kDa, Đ = 1.17) in ethanol-water mixture. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

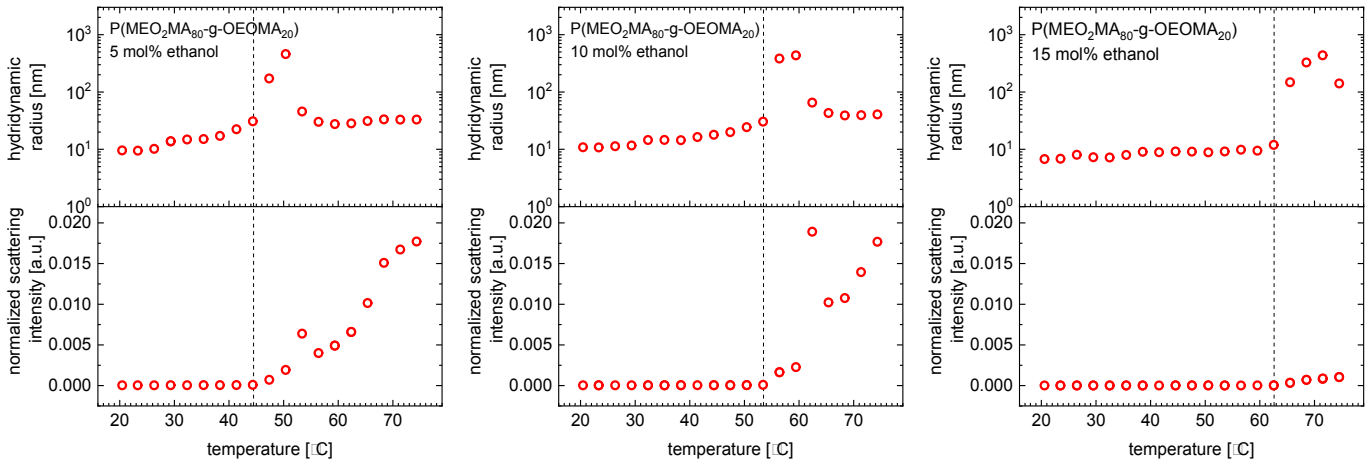

Figure S30 DLS measurements of the gradient copolymer P($MEO_2MA_{80.5}$-g-$OEOMA_{19.5}$), M_n = 15.21 kDa, Đ = 1.24 in ethanol-water mixture. The red points show the heating cycle and blue ones the cooling cycle. The vertical dashed lines point out the abrupt change in hydrodynamic radius (upper graph) and normalized scattering intensity (lower graph) and indicates the LCST.

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