

Supporting Information

Thermoresponsive behaviour of poly(*N,N*-diethylacrylamide) in aqueous two-phase systems

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Polymer Synthesis:

RAFT-polymerisation of PDEA_{40k}

Destabilised DEA (4.0 g, 31.5 mmol, 788 eq.), EMP (9.0 mg, 0.04 mmol, 1.0 eq.), and DMF (4 mL) were mixed in a vial containing a stirring bar and sealed with a septum. The solution was bubbled with nitrogen for 30 min and the polymerisation was initiated using two visible light LEDs 20 cm apart (50 W Bridgelux BXRA-50C5300; $\lambda > 410\text{nm}$, connected to a self-made circuit and cooling system). The polymerisation was stopped after 24 h. Subsequently, the polymer was dialysed against deionised water (Spectra/Por 3500 Da) for 3 days. Finally, the sample was freeze-dried and a slightly yellow solid (2.17 g, $M_n = 40000 \text{ g}\cdot\text{mol}^{-1}$, $D = 1.26$) was obtained.

Polymer analysis:

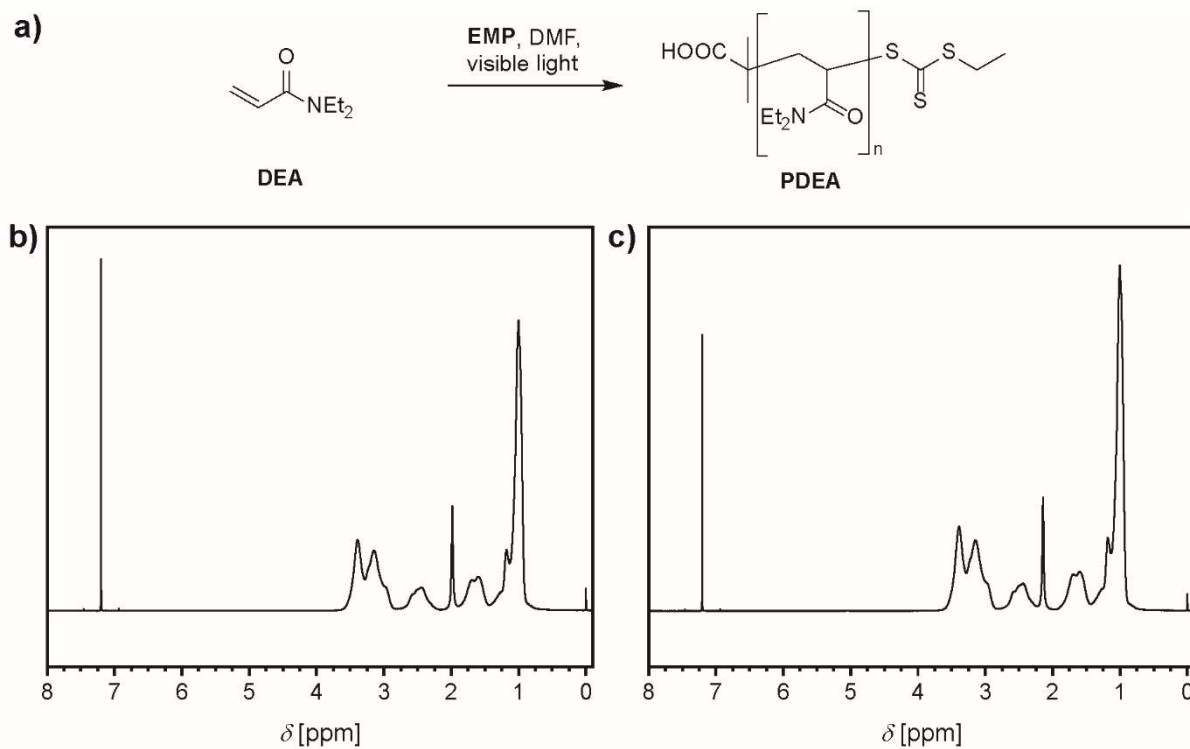


Figure S1. a) Reaction scheme of the photo induced RAFT-polymerisation of *N,N*-diethylacrylamide (DEA), b) $^1\text{H-NMR}$ of PDEA_{55k} in CDCl_3 and c) $^1\text{H-NMR}$ of PDEA_{40k} in CDCl_3 .

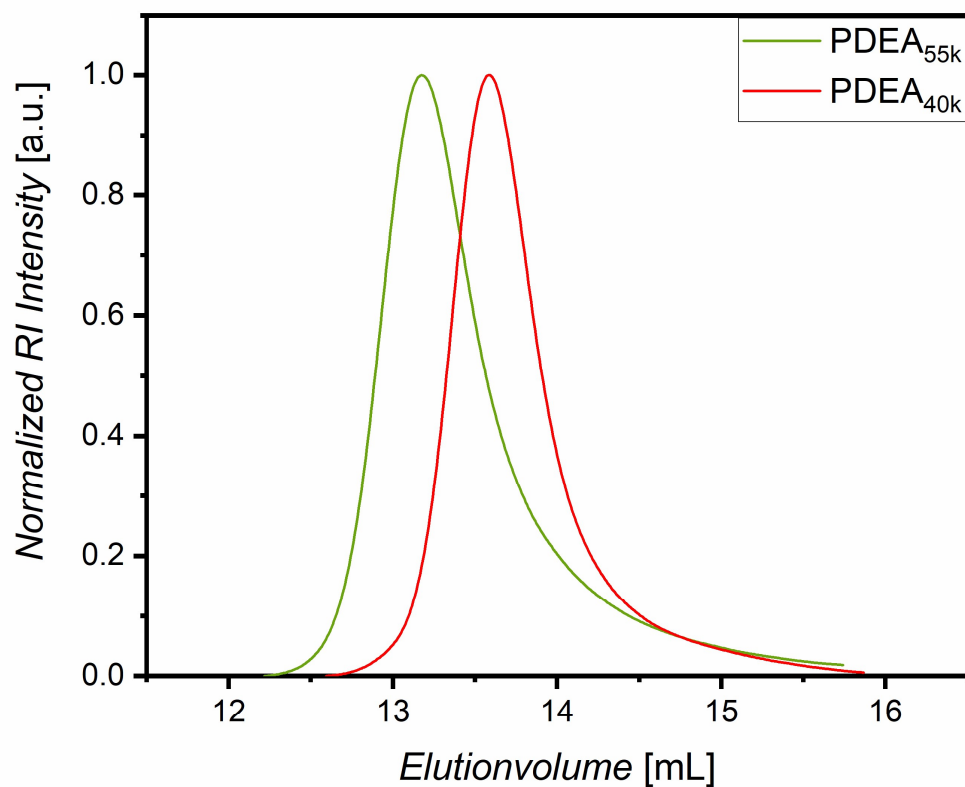


Figure S2. Results of SEC of PDEA samples in THF against PS standards.

Table S1. Analytical results for PDEA polymers.

Polymer	[DEA]/[EMP]	Conversion ^a	$M_{n, \text{theory}} \text{ (g}\cdot\text{mol}^{-1}\text{)}$	$M_{n, \text{SEC}} \text{ (g}\cdot\text{mol}^{-1}\text{)}$ ^b	\bar{D}^b
PDMA _{40k}	788	60%	60100	40000	1.26
PDEA _{55k}	1575	81%	162200	54800	1.30

a) measured via ¹H NMR

b) measured in THF against PS standards

ATPS formation:

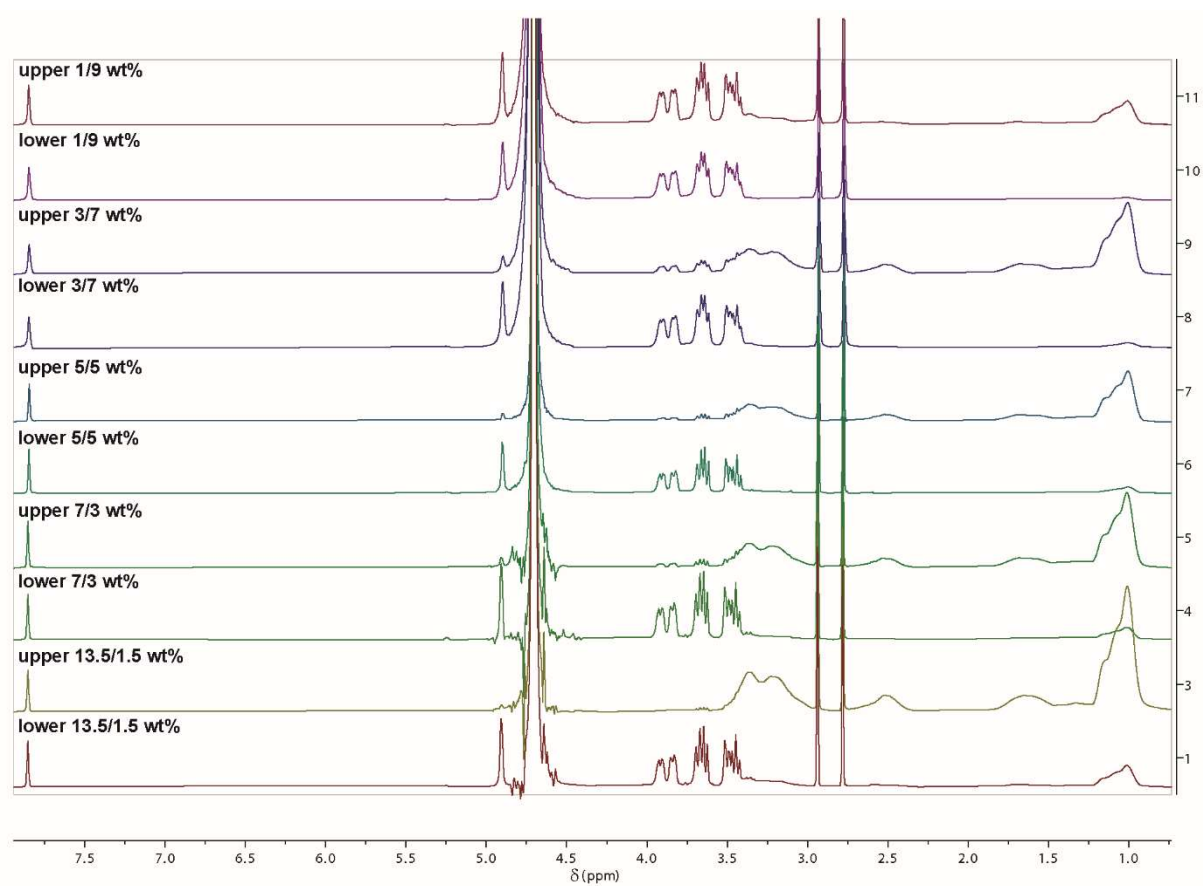


Figure S3. ¹H-NMR in D₂O of the PDEA_{55k}/Dex ATPS using DMF as internal standard: 1/9 wt%, 3/7 wt%, 5/5 wt%, 7/3wt% and 13.5/1.5 wt% from top to bottom.

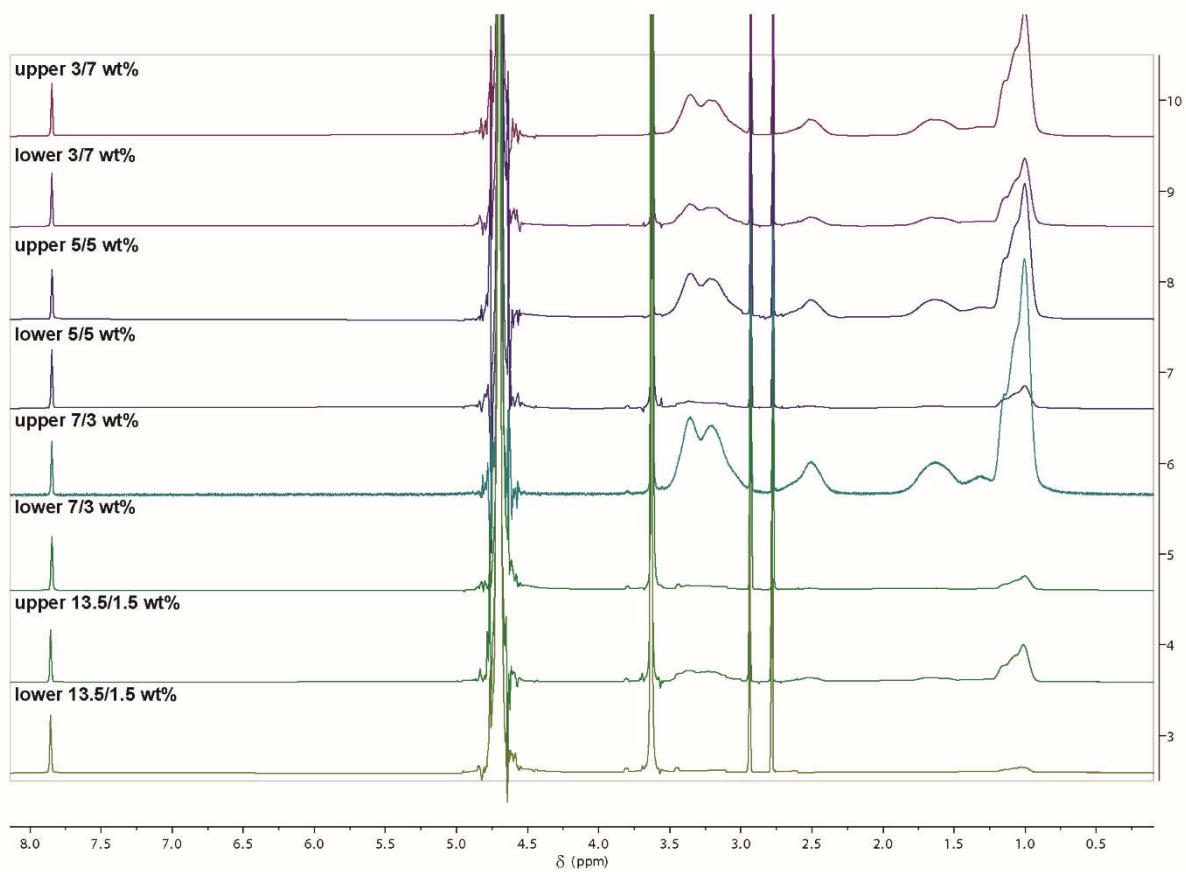


Figure S4. $^1\text{H-NMR}$ in D_2O of the PDEA_{55k}/PEG ATPS using DMF as internal standard: 3/7 wt%, 5/5 wt%, 7/3wt% and 13.5/1.5 wt% from top to bottom.

$$P_X = \frac{c_{XL1}}{c_{XL2}}$$

Equation S1. For the calculation of the partition coefficient for a polymer X in the ATPS with P_X -partition coefficient, c_{XL1} -concentration of the polymer in the upper phase (L1) and c_{XL2} -concentration of the polymer in the lower phase (L2).

$$F_{X,L_x} = \frac{c_{XL1}}{c_{XL1} + c_{XL2}}$$

Equation S2. For the calculation of mole fractions for a polymer X in the A3PS with F_{X,L_x} -mole fraction, c_{XL1} -concentration of the polymer in the upper phase (L1) and c_{XL2} -concentration of the polymer in the middle phase (L2).

Table S2. Partition coefficients for PDEA_{55k}/Dex systems measured via ¹H NMR.

[PDEA _{55k}]/[Dex] (wt%/wt%)	$P_{PDEA,upper}$	$P_{PDEA,lower}$	$P_{Dex,upper}$	$P_{Dex,lower}$
1/9	5.19	0.19	0.74	1.35
	(±0.294)	(±0.011)	(±0.042)	(±0.076)
3/7	25.25	0.04	0.23	4.39
	(±1.428)	(±0.002)	(±0.013)	(±0.248)
5/5	9.45	0.11	0.30	3.38
	(±0.535)	(±0.006)	(±0.017)	(±0.191)
7/3	4.36	0.23	0.14	7.28
	(±0.247)	(±0.013)	(±0.008)	(±0.412)
13.5/1.5	2.90	0.35	0.15	6.52
	(±0.164)	(±0.020)	(±0.009)	(±0.369)

Table S3. Mole fractions for PDEA_{55k}/Dex systems measured via ¹H NMR.

[PDEA _{55k}]/[Dex] (wt%/wt%)	$F_{\text{PDEA,upper}}$	$F_{\text{PDEA,lower}}$	$F_{\text{Dex,upper}}$	$F_{\text{Dex,lower}}$
1/9	0.84	0.16	0.43	0.57
	(±0.047)	(±0.009)	(±0.024)	(±0.032)
3/7	0.96	0.04	0.19	0.81
	(±0.054)	(±0.002)	(±0.011)	(±0.046)
5/5	0.90	0.10	0.23	0.77
	(±0.051)	(±0.005)	(±0.013)	(±0.044)
7/3	0.81	0.19	0.12	0.88
	(±0.046)	(±0.011)	(±0.007)	(±0.050)
13.5/1.5	0.74	0.26	0.13	0.87
	(±0.042)	(±0.015)	(±0.008)	(±0.049)

Table S4. Partition coefficients for PDEA_{55k}/PEG systems measured via ¹H NMR.

[PDEA _{55k}]/[PEG] (wt%/wt%)	$P_{\text{PDEA,upper}}$	$P_{\text{PDEA,lower}}$	$P_{\text{PEG,upper}}$	$P_{\text{PEG,lower}}$
3/7	0.16	6.07	1.16	0.86
	(±0.009)	(±0.343)	(±0.132)	(±0.097)
5/5	0.18	5.41	3.93	0.25
	(±0.010)	(±0.306)	(±0.445)	(±0.029)
7/3	0.14	7.00	3.87	0.26
	(±0.008)	(±0.396)	(±0.437)	(±0.029)
13.5/1.5	0.51	1.94	2.32	0.43
	(±0.029)	(±0.110)	(±0.263)	(±0.049)

Table S5. Mole fractions for PDEA_{55k}/PEG systems measured via ¹H NMR.

[PDEA _{55k}]/[PEG] (wt%/wt%)	$F_{\text{PDEA,upper}}$	$F_{\text{PDEA,lower}}$	$F_{\text{PEG,upper}}$	$F_{\text{PEG,lower}}$
3/7	0.14 (±0.008)	0.86 (±0.049)	0.54 (±0.061)	0.46 (±0.052)
5/5	0.16 (±0.009)	0.84 (±0.048)	0.80 (±0.090)	0.20 (±0.023)
7/3	0.12 (±0.007)	0.88 (±0.049)	0.79 (±0.090)	0.21 (±0.023)
13.5/1.5	0.34 (±0.019)	0.66 (±0.037)	0.70 (±0.079)	0.30 (±0.034)

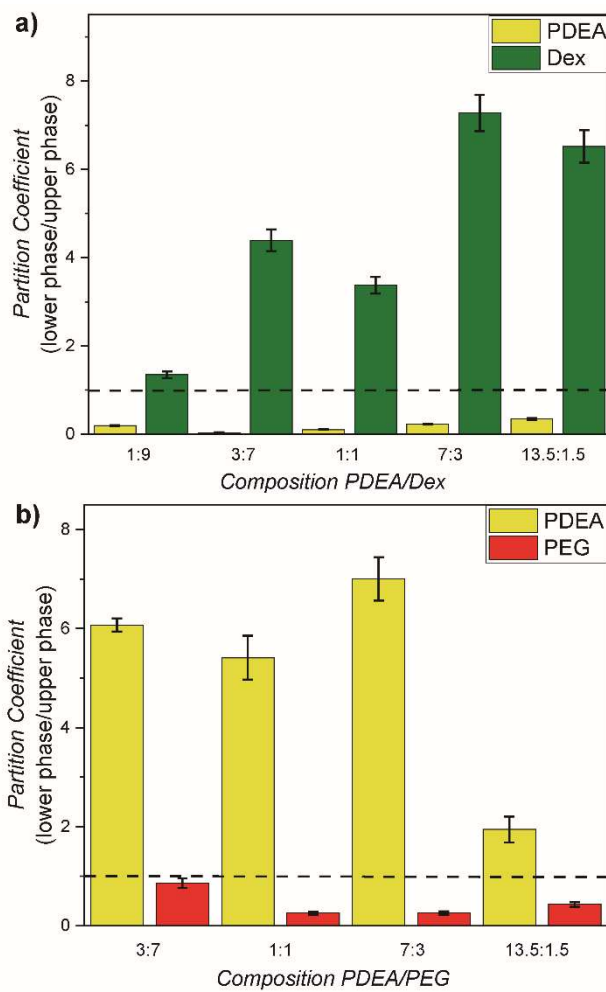


Figure S5. Partition coefficients after phase separation (lower phase/upper phase), detected *via* ^1H -NMR in D_2O using DMF as internal standard: a) PDEA_{55k} and Dex; b) PDEA_{55k} and PEG.

Thermoresponse:

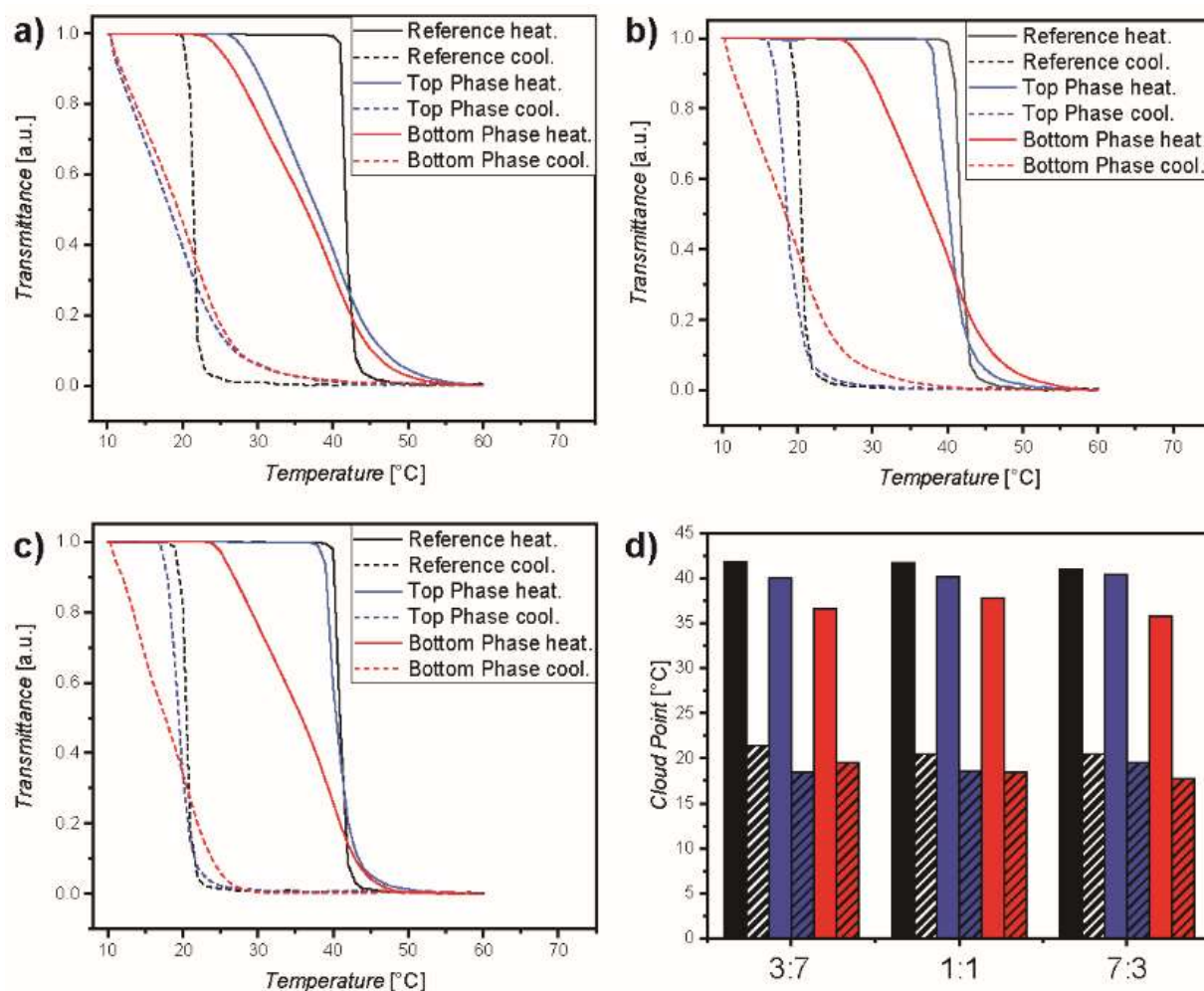


Figure S6. Thermoresponse of PDEA_{55k}/Dex ATPS (heating rate 2 °C min⁻¹): a) turbidimetry results of PDEA_{55k}/Dex 3 wt%/7 wt% (reference PDEA_{55k} in water at 3 wt%), b) turbidimetry results of PDEA_{55k}/Dex 5 wt%/5 wt% (reference PDEA_{55k} in water at 5 wt%), c) turbidimetry results of PDEA_{55k}/Dex 7 wt%/3 wt% (reference PDEA_{55k} in water at 7 wt%) and d) cloud points for various compositions of PDEA_{55k}/Dex ATPS (solid: heating, shaded: cooling; black: reference at the respective concentration in water, blue: top phase, red: bottom phase).

Table S6. Cloud points for the systems PDEA_{40k}/Dex and PDEA_{55k}/Dex (reference measured at the same concentration as in ATPS, heating rate 2 °C min⁻¹).

[PDEA _{40k}]/[Dex] (wt%/wt%)	$T_{c,reference\ heat.}$ [°C]	$T_{c,reference\ cool.}$ [°C]	$T_{c,upper\ heat.}$ [°C]	$T_{c,upper\ cool.}$ [°C]	$T_{c,lower\ heat.}$ [°C]	$T_{c,upper\ cool.}$ [°C]
3/7	40.9	21.4	34.8	18.8	36.9	18.1
5/5	41.2	20.5	40.5	23.7	35.5	17.4
7/3	41.5	21.4	38.7	22.7	37.7	20.8
[PDEA _{55k}]/[Dex] (wt%/wt%)	$T_{c,reference\ heat.}$ [°C]	$T_{c,reference\ cool.}$ [°C]	$T_{c,upper\ heat.}$ [°C]	$T_{c,upper\ cool.}$ [°C]	$T_{c,lower\ heat.}$ [°C]	$T_{c,upper\ cool.}$ [°C]
3/7	41.8	21.4	40.0	18.4	36.6	19.5
5/5	41.7	20.5	40.2	18.6	37.8	18.4
7/3	41.0	20.5	40.4	19.5	35.8	17.7

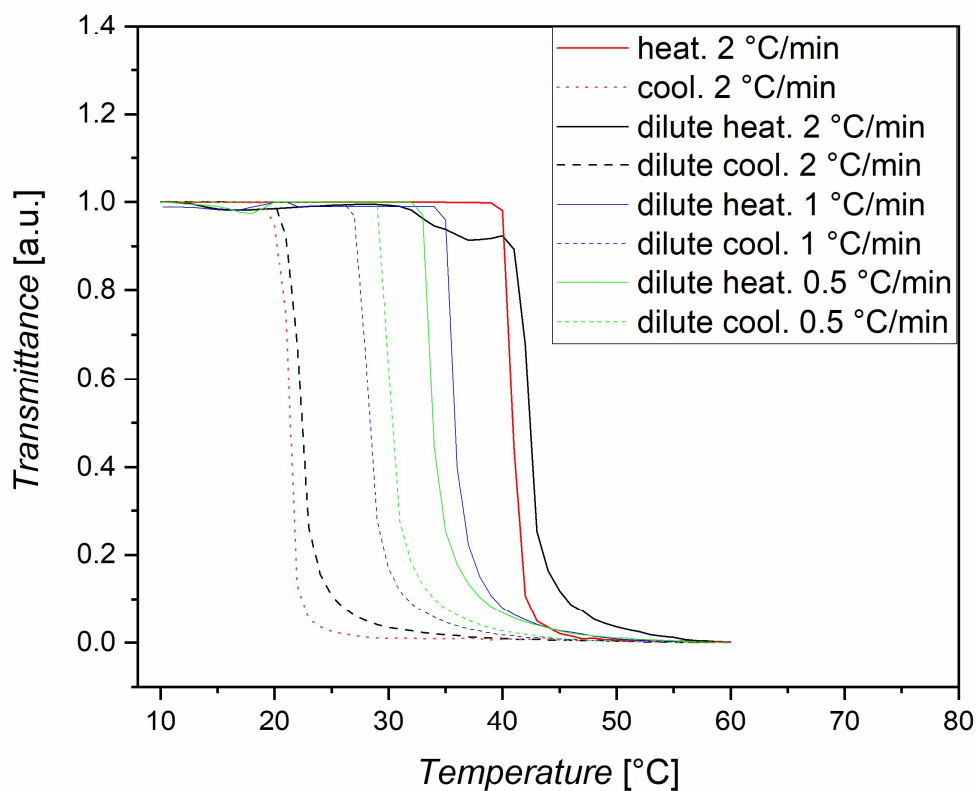


Figure S7. Thermoresponse of PDEA_{40k} in water (solid curves heating, dashed curves cooling) at a concentration of 0.5 wt% with heating rate of 2 °C min⁻¹ (black curves), 0.5 wt% with heating rate of 1 °C min⁻¹ (blue curves), 0.5 wt% with heating rate of 0.5 °C min⁻¹ (green curves) and 3 wt% with heating rate of 2 °C min⁻¹ (red curves).

Analysis of A3PS:

$$P_{X,L1-L2} = \frac{c_{XL1}}{c_{XL2}} \quad P_{X,L2-L3} = \frac{c_{XL2}}{c_{XL3}} \quad P_{X,L1-L3} = \frac{c_{XL1}}{c_{XL3}}$$

Equation S3. For the calculation of the partition coefficient for a polymer X in the A3PS with $P_{X,Lx-Ly}$ -partition coefficient, c_{XL1} -concentration of the polymer in the upper phase (L1), c_{XL2} -concentration of the polymer in the middle phase (L2) and c_{XL3} -concentration of the polymer in the lower phase (L3).

$$F_{X,Lx} = \frac{c_{XL1}}{c_{XL1} + c_{XL2} + c_{XL3}}$$

Equation S4. For the calculation of mole fractions for a polymer X in the A3PS with $F_{X,Lx}$ -mole fraction, c_{XL1} -concentration of the polymer in the upper phase (L1), c_{XL2} -concentration of the polymer in the middle phase (L2) and c_{XL3} -concentration of the polymer in the lower phase (L3).

Table S7. Partition coefficients for PDEA_{40k}/Dex/PEG (5/5/5 wt%) system measured via ¹H NMR.

$P_{\text{PDEA,upper-middle}}$	0.23 (± 0.013)
$P_{\text{PDEA,middle-lower}}$	8.07 (± 0.457)
$P_{\text{PDEA,upper-lower}}$	1.87 (± 0.106)
$P_{\text{Dex,upper-middle}}$	0.14 (± 0.005)
$P_{\text{Dex,middle-lower}}$	1.04 (± 0.042)
$P_{\text{Dex,upper-lower}}$	0.14 (± 0.008)
$P_{\text{PEG,upper-middle}}$	4.97 (± 0.281)
$P_{\text{PEG,middle-lower}}$	0.20 (± 0.011)
$P_{\text{PEG,upper-lower}}$	8.14 (± 0.461)

Table S8. Mole fractions for PDEA_{40k}/Dex/PEG (5/5/5 wt%) system measured via ¹H NMR.

$F_{\text{PDEA,upper}}$	0.17 (± 0.010)
$F_{\text{PDEA,middle}}$	0.74 (± 0.042)
$F_{\text{PDEA,lower}}$	0.09 (± 0.005)
$F_{\text{Dex,upper}}$	0.07 (± 0.003)
$F_{\text{Dex,middle}}$	0.48 (± 0.027)
$F_{\text{Dex,lower}}$	0.46 (± 0.026)
$F_{\text{PEG,upper}}$	0.76 (± 0.043)
$F_{\text{PEG,middle}}$	0.15 (± 0.009)
$F_{\text{PEG,lower}}$	0.09 (± 0.005)

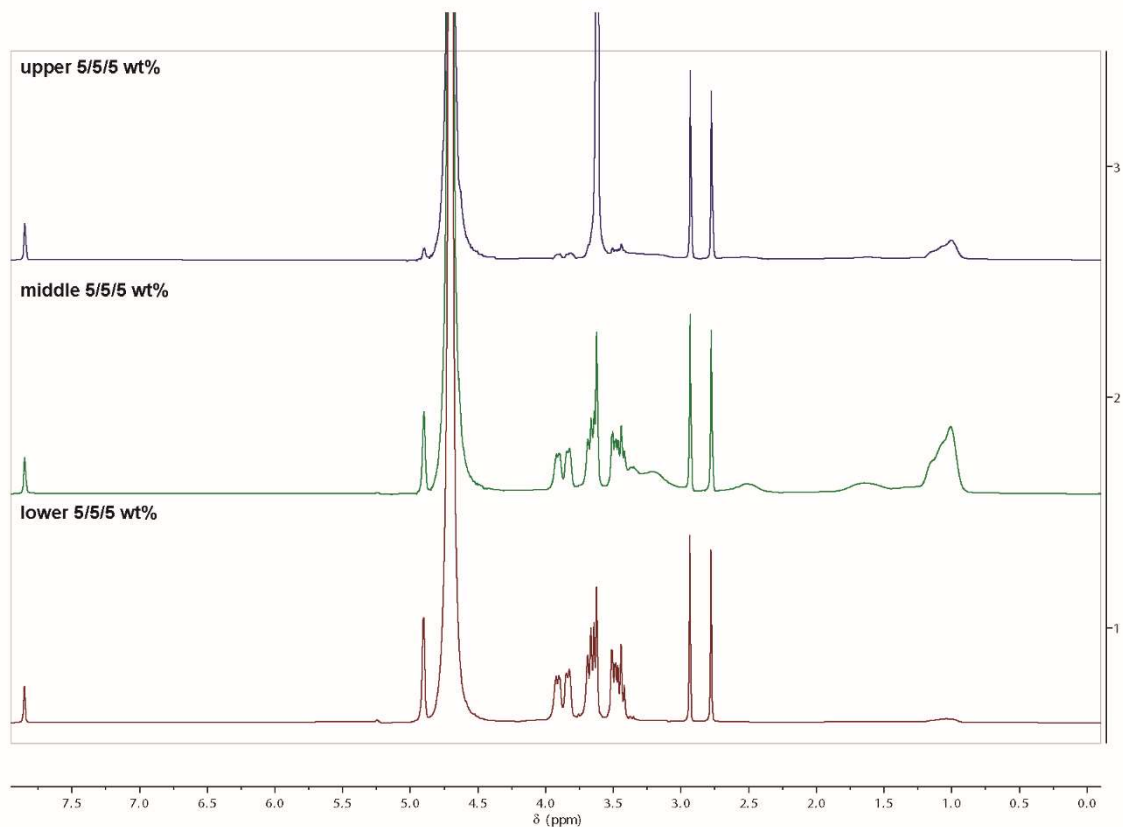


Figure S8. ^1H -NMR in D_2O of the $\text{PDEA}_{55\text{k}}/\text{Dex}/\text{PEG}$ A3PS using DMF as internal standard (5/5/5 wt%).

Table S9. Cloud points for the system $\text{PDEA}_{40\text{k}}/\text{Dex}/\text{PEG}$ (5/5/5 wt%) (reference measured at the same concentration as in A3PS, heating rate $2\text{ }^\circ\text{C min}^{-1}$).

$T_{\text{c,ref. heat.}}$	$T_{\text{c,ref. cool.}}$	$T_{\text{c,upper heat.}}$	$T_{\text{c,upper cool.}}$	$T_{\text{c,middle heat.}}$	$T_{\text{c,middle cool.}}$	$T_{\text{c,lower heat.}}$	$T_{\text{c,upper cool.}}$
[$^\circ\text{C}$]	[$^\circ\text{C}$]	[$^\circ\text{C}$]	[$^\circ\text{C}$]	[$^\circ\text{C}$]	[$^\circ\text{C}$]	[$^\circ\text{C}$]	[$^\circ\text{C}$]
41.3	20.5	26.6	13.4	27.9	16.8	45.4	26.1