

Supporting Information

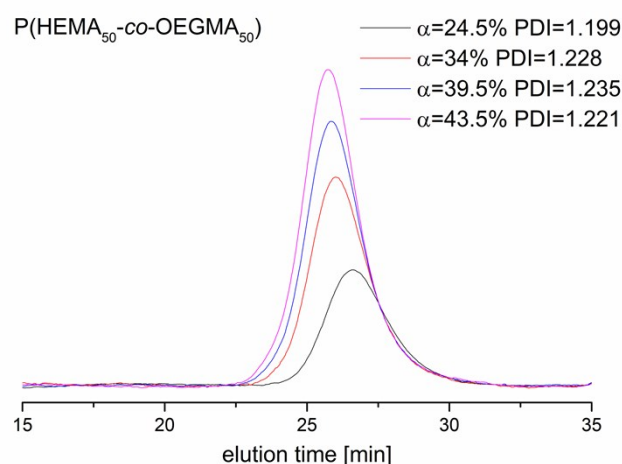
Thermoresponsive P(HEMA-*co*-OEGMA) copolymers: Synthesis, characteristics and solution behavior

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Figure S1 presents the chromatograms of P(HEMA₅₀-*co*-OEGMA₅₀) at different monomers



conversion.

Figure S1. Chromatograms of P(HEMA₅₀-*co*-OEGMA₅₀) at different conversion.

Table S1 shows dn/dc values in DMF calculated for P(HEMA-*co*-OEGMA) copolymers. The dn/dc were calculated as in the article ¹ for previously determined copolymer composition. The molar mass and mass distributions of the copolymers were obtained using these dn/dc values.

Table S1. Calculated dn/dc values in DMF of P(HEMA-*co*-OEGMA) copolymers with different composition and homopolymers of HEMA and OEGMA.

Polymer	dn/dc in DMF [mL/g]
P(OEGMA)	0.053 ^a
P(HEMA ₃₀ - <i>co</i> -OEGMA ₇₀)	0.057
P(HEMA ₄₀ - <i>co</i> -OEGMA ₆₀)	0.058
P(HEMA ₅₀ - <i>co</i> -OEGMA ₅₀)	0.060
P(HEMA ₆₀ - <i>co</i> -OEGMA ₄₀)	0.062
P(HEMA ₇₀ - <i>co</i> -OEGMA ₃₀)	0.064
P(HEMA ₈₀ - <i>co</i> -OEGMA ₂₀)	0.068
P(HEMA ₉₀ - <i>co</i> -OEGMA ₁₀)	0.071
P(HEMA)	0.076 ^b

^a Taken from ²

^b Taken from ³

In order to know the microstructure of obtained copolymers the kinetic studies were performed. The amounts of monomers used in copolymerization reaction in kinetics studies were shown in Table S2.

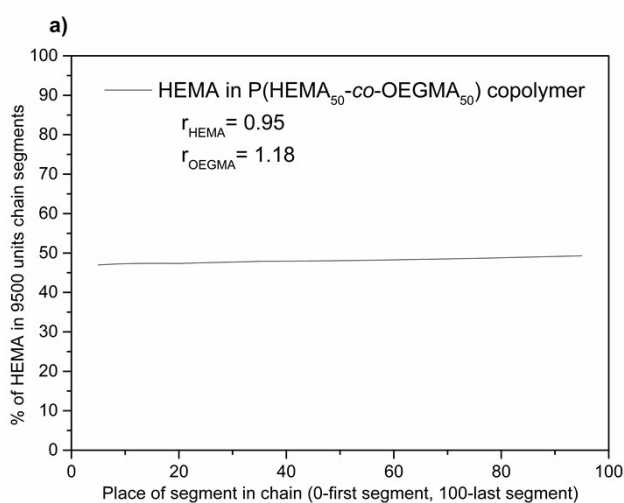
Table

S2.

HEMA in feed [mol %]	OEGMA in feed [mol %]	amount of HEMA	amount of OEGMA
90	10	1.1956 g (0.009187 mol)	0.3044 g (0.001015 mol)
80	20	0.9516 g (0.007312 mol)	0.5484 g (0.001828 mol)
50	50	0.4538 g (0.003487 mol)	1.0462 g (0.003487 mol)
30	70	0.2352 g (0.001807 mol)	1.2648 g (0.004216 mol)
10	90	0.0685 g (0.000526 mol)	1.4315 g (0.004772 mol)

Amounts of monomers used in copolymerization reactions in kinetics studies.

The distribution of the HEMA units along P(HEMA-*co*-OEGMA) chains obtained by Monte Carlo simulation are shown in Figure S2. The graphic representation of P(HEMA₅₀-*co*-OEGMA₅₀) polymer chain with yellow bars for OEGMA units and black bars for HEMA units is shown in Figure S2b.



b)



Figure S2. a) Distribution of HEMA in P(HEMA₅₀-*co*-OEGMA₅₀) chain **b)** graphical representation of HEMA (black bar) and OEGMA (yellow bar) distribution in P(HEMA₅₀-*co*-OEGMA₅₀) chain.

Plots of transmittance versus temperature for aqueous solutions of P(HEMA-*co*-OEGMA)s at concentration 1 g/L in heating (black square) and cooling cycle (red circle) (Figure S3).

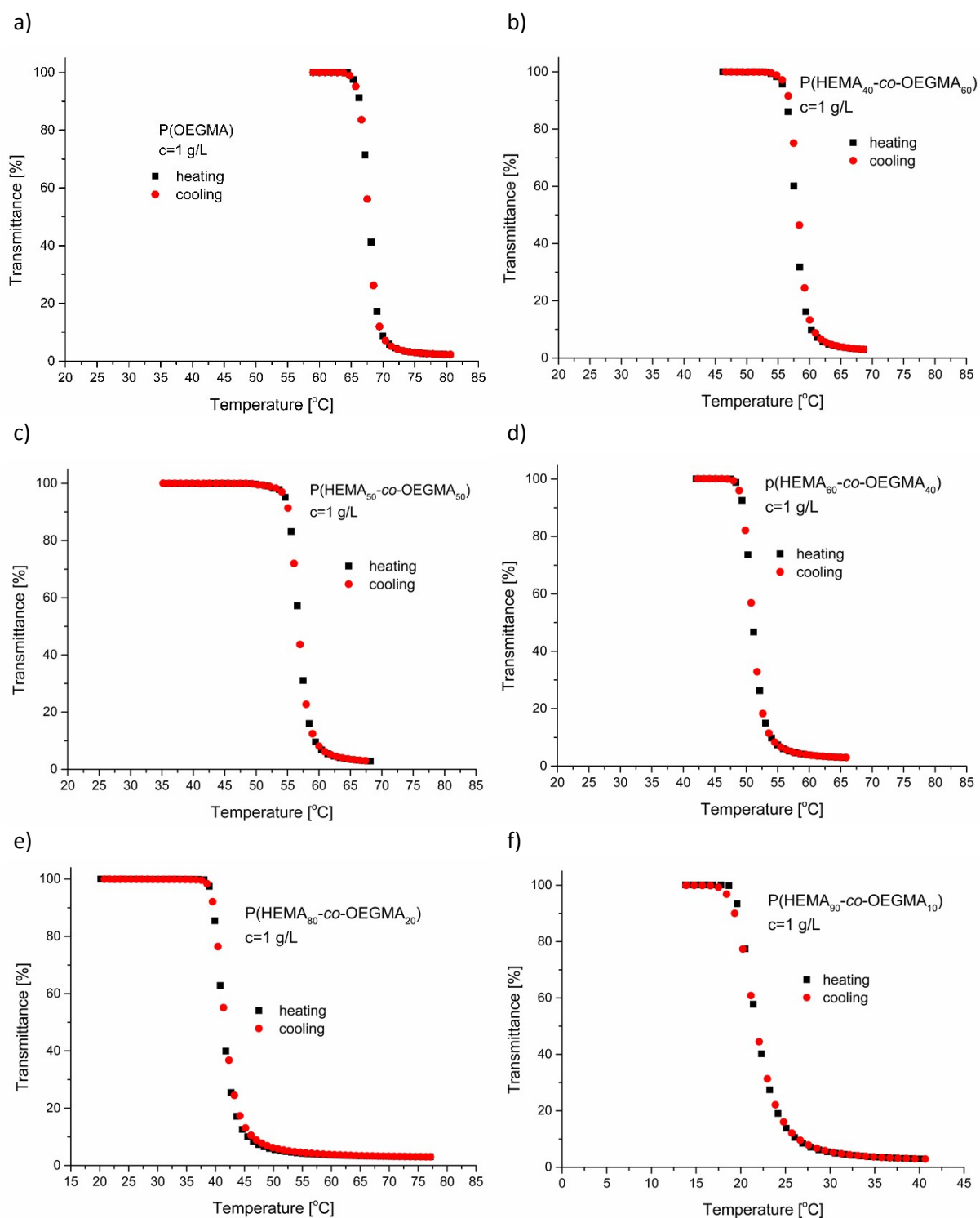


Figure S3. Transmittance versus temperature of polymer water solutions at concentration $c=1$ g/L. **a)** P(OEGMA), **b)** P(HEMA₄₀-co-OEGMA₆₀), **c)** P(HEMA₅₀-co-OEGMA₅₀), **d)** P(HEMA₆₀-co-OEGMA₄₀), **e)** P(HEMA₈₀-co-OEGMA₂₀), **f)** P(HEMA₉₀-co-OEGMA₁₀).

Figure S4 presents transmittance versus temperature dependences for P(HEMA-co-OEGMA) solutions at concentration 1 g/L in PBS. The heating (black square) and cooling cycle (red circle) are shown. There are significant differences between heating and cooling cycle. The

polymers precipitated during heating in presence of kosmotropic salts. After measure precipitated polymer in the form of gel on the bottom of the cuvette was observed. The resulting gels of P(HEMA₈₀-*co*-OEGMA₂₀) and P(HEMA₉₀-*co*-OEGMA₁₀) dissolved slowly at 4°C. Precipitated polymers with lower HEMA content dissolved as a result of mixing water solutions in room temperature.

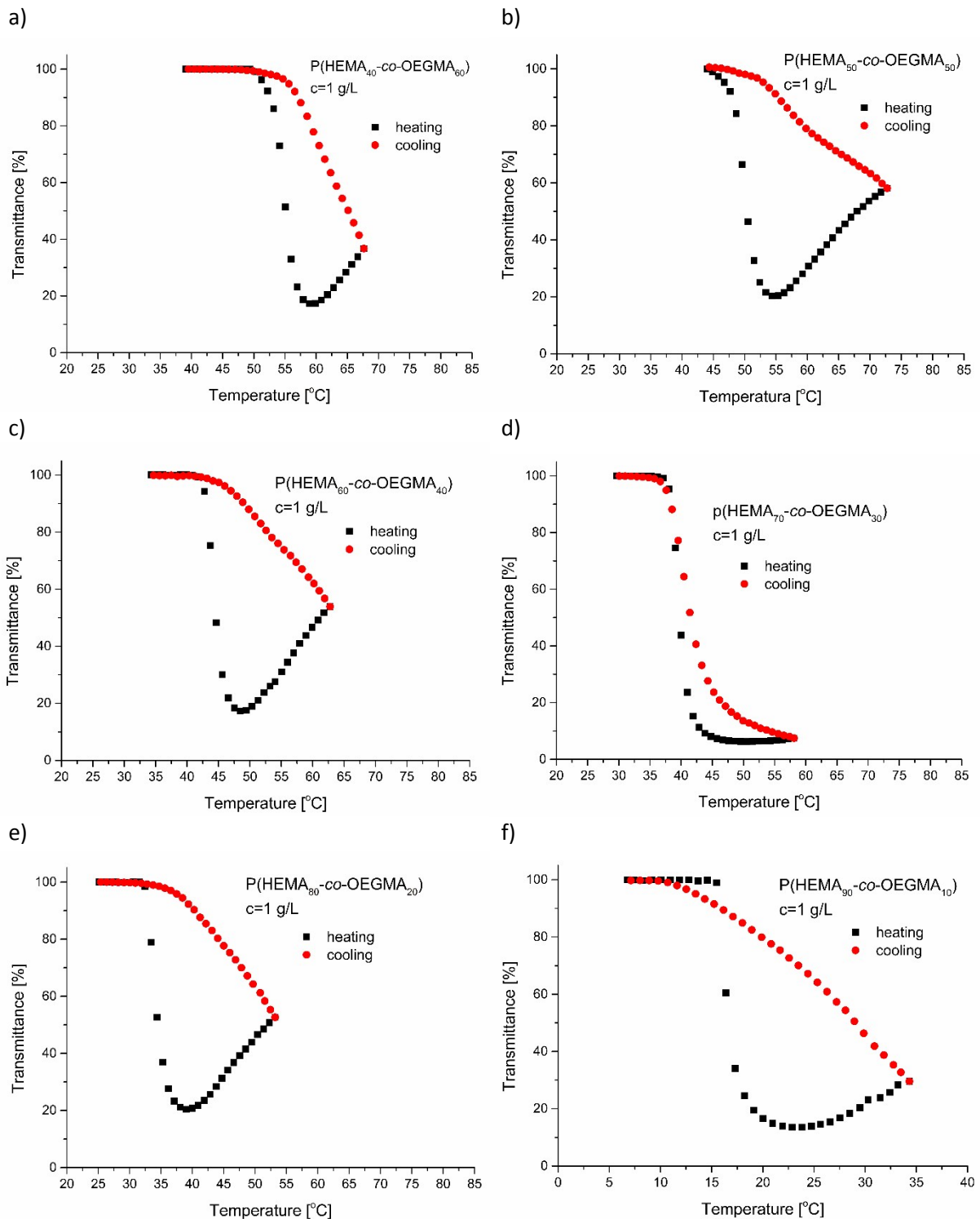


Figure S4. Transmittance versus temperature of polymer PBS solutions at concentration $c=1$ g/L. **a)** P(HEMA₄₀-*co*-OEGMA₆₀), **b)** P(HEMA₅₀-*co*-OEGMA₅₀), **c)** P(HEMA₆₀-*co*-OEGMA₄₀), **d)** P(HEMA₇₀-*co*-OEGMA₃₀), **e)** P(HEMA₈₀-*co*-OEGMA₂₀), **f)** P(HEMA₉₀-*co*-OEGMA₁₀).

T_{cp} values for P(HEMA-*co*-OEGMA)s at concentration 1 g/L, 0.5 g/L and 0.25 g/L in water and in PBS are shown in Table S3.

Polymer	HEMA [% mol]	T_{cp}			
		H ₂ O			PBS
		$c=1$ g/L	$c=0.5$ g/L	$c=0.25$ g/L	$c=1$ g/L
P(OEGMA)	-	68	69.5	72	61.5
P(HEMA ₃₀ - <i>co</i> -OEGMA ₇₀)	30.5	61	63	66.5	54.5
P(HEMA ₄₀ - <i>co</i> -OEGMA ₆₀)	37.5	58	61	62	54.5
P(HEMA ₅₀ - <i>co</i> -OEGMA ₅₀)	48.1	57	60	65	50
P(HEMA ₆₀ - <i>co</i> -OEGMA ₄₀)	61	51	53.5	57	44
P(HEMA ₇₀ - <i>co</i> -OEGMA ₃₀)	68.6	47	49	53	39.5
P(HEMA ₈₀ - <i>co</i> -OEGMA ₂₀)	79.7	41	45	50	34
P(HEMA ₉₀ - <i>co</i> -OEGMA ₁₀)	90.1	21.5	25.5	32.5	16.5

Table S3. The cloud point temperatures of P(HEMA-*co*-OEGMA) solutions in water and PBS.

References:

- (1) Coto, B.; Escola, J. M.; Suárez, I.; Caballero, M. J. Determination of Dn/dc Values for Ethylene-propylene Copolymers. *Polym. Test.* **2007**, *26* (5), 568–575. <https://doi.org/https://doi.org/10.1016/j.polymertesting.2007.02.001>.
- (2) Trzebicka, B., Szweda, D., Rangelov, S., Kowalczyk, A., Mendrek, B., Utrata-Wesołek, A. and Dworak, A. (Co)polymers of Oligo(ethylene Glycol) Methacrylates—temperature-induced Aggregation in Aqueous Solution. *J. Polym. Sci. Part A Polym. Chem.* **2013**, *51* (3), 614–623. <https://doi.org/10.1002/pola.26410>.

- (3) Brandrup, J.; Immergut, E. H.; Grulke, E. A.; Abe, A.; Bloch, D. R. *Polymer Handbook*; Wiley New York, 1999; Vol. 89.