

Supplementary Material

Table S1. The conditions under which the chain extensions of PNIPAM-Cl with styrene via ARGET ATRP were conducted; number-averaged molecular masses (M_n) of copolymers and macroinitiator determined from SEC analyses; estimated number of styrene mers in copolymers' chains.

| Sample | Time [h] | [I]/[M]/[CuCl ₂]/[L]/[Sn(EH) ₂] ^a | M_n | M_n | Estimated number of mers ^c |
|---------|----------|---|---------------------|--------------------------------|---------------------------------------|
| | | | PNIPA M^b [Da] | copolymer ^b [Da] | |
| PNPSI | 23 | 1 : 200 : 0.002 : 0.1 : 0.4 | 4100 | 4700 | 6 |
| PNPSII | 24 | 1 : 200 : 0.005 : 0.1 : 0.48 | 4100 | 4200 | 1 |
| PNPSIII | 93 | 1 : 200 : 0.005 : 0.85 : 0.08 | 4100 | 4400 | 3 |
| PNPSIV | 79 | 1 : 200 : 0.03 : 0.08 : 0.15 | 3300 | 3900 | 6 |
| PNPSV | 54 | 1 : 200 : 0.3 : 0.3 : 0.3 | 3300 | 4100 | 8 |
| PNPSVI | 64 | 1 : 200 : 0.3 : 0.3 : 0.5 | 3900 | 4600 | 7 |
| PNPSVII | 96 | 1 : 200 : 0.3 : 0.3 : 1.5 | 3500 | 3700 | 2 |

^a I = PNIPAM-Cl molecules terminated by chlorine (macroinitiator), M = styrene (monomer), L = Me₆TREN (ligand); ^b from SEC in 1% (w/v) LiBr/DMF, ^c calculated as the difference between number-average molecular masses of copolymer and PNIPAM-Cl used in the chain extension.

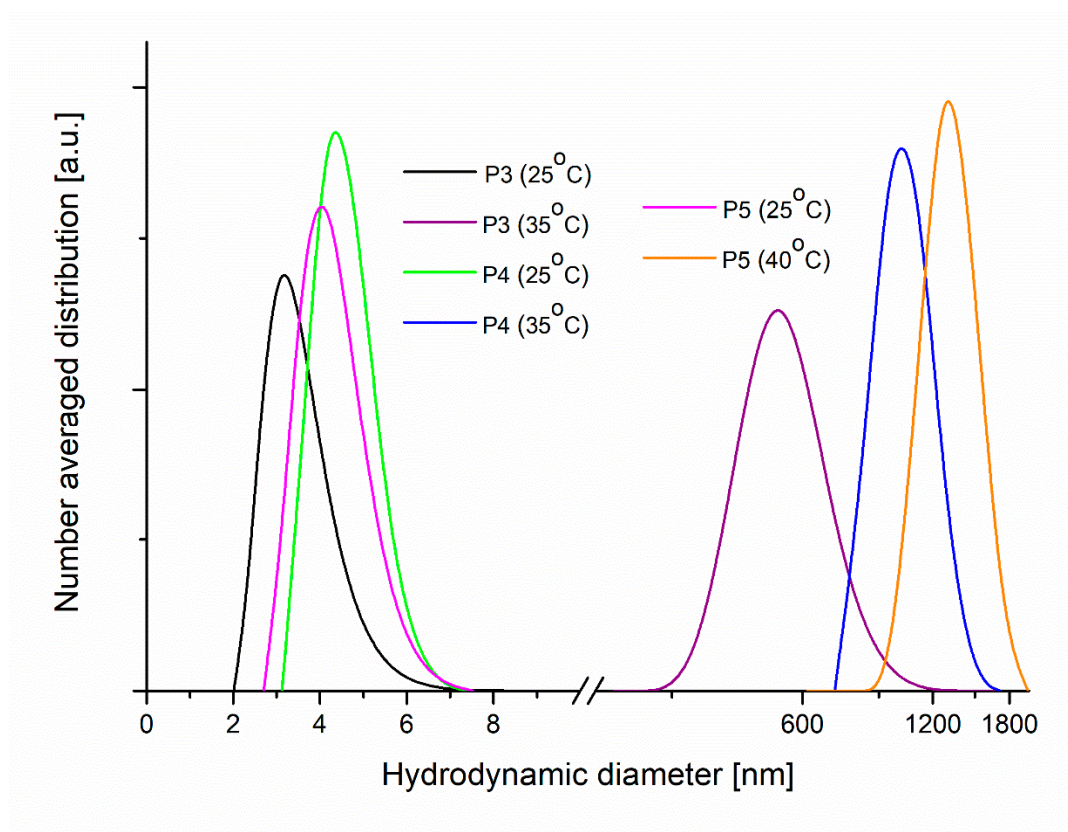


Figure S1. The number averaged hydrodynamic diameter distribution in aqueous solutions (1.5% w/w) of homopolymers (description of the samples in Table 1 in main document) at 25, 35 and 40 °C from DLS measurements. For P5 the changes in the size of particles at 35°C have not be observed in comparison with the sizes which observed at 25°C.

Table S2. Results of SEC analyses (with THF as eluent) for the prepared homopolymers before and after removal of terminal chlorine atoms as well as after esterification by using α -bromoisobutyryl bromide.

| PNIPAM-Cl | | After Dehalogenation (PNIPAM-H) | | After Esterification (PNIPAM-Br) | |
|------------|------|---------------------------------|------|----------------------------------|------|
| M_n [Da] | PDI | M_n [Da] | PDI | M_n [Da] | PDI |
| 1500 | 1.53 | 2000 | 1.48 | 2200 | 1.49 |
| 3400 | 1.28 | 4000 | 1.15 | 4000 | 1.15 |
| 4100 | 1.41 | 5200 | 1.34 | 5400 | 1.30 |
| 5600 | 1.36 | 6100 | 1.30 | 6000 | 1.30 |

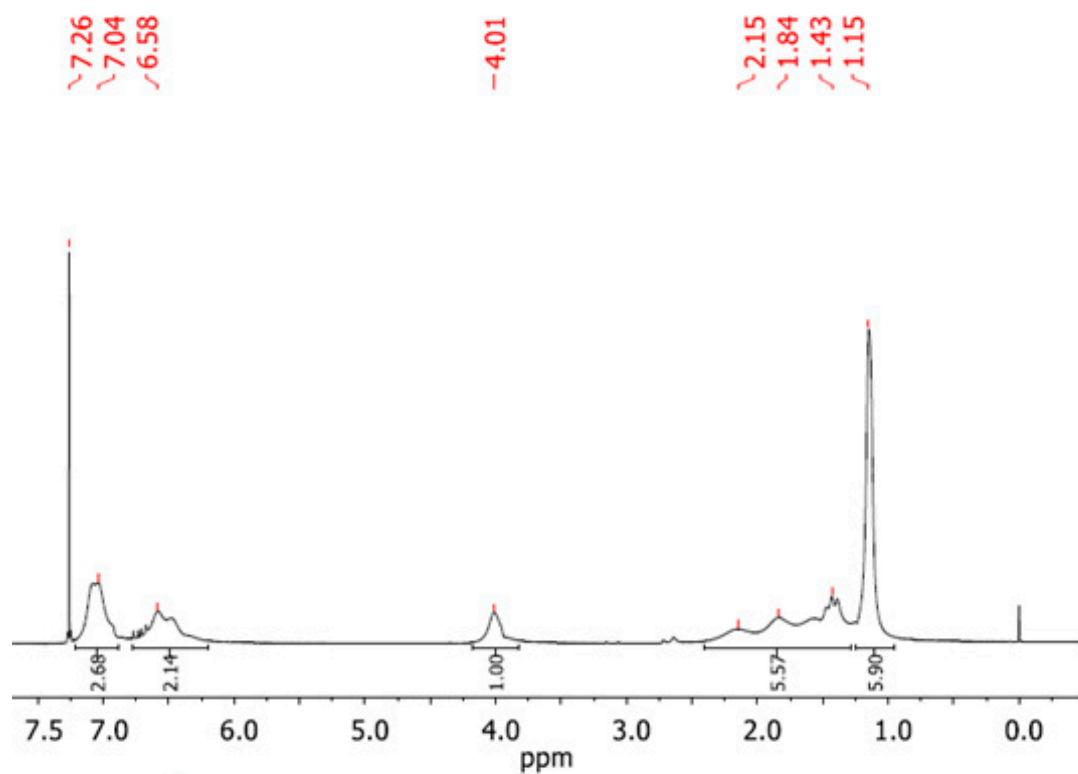


Figure S2. The 300 MHz ^1H NMR spectrum of diblock copolymer PNIPAM-*b*-PS (recorded for the sample denoted as PNPS3 in Table 3) in CDCl_3 .



Figure S3. The photo of aqueous solution of the synthesized diblock copolymer PNIPAM-*b*-PS (a solution of sample PNPS3). As the molecule of PNPS3 is amphiphilic characteristic foam appears as a result of surface tension decreasing.

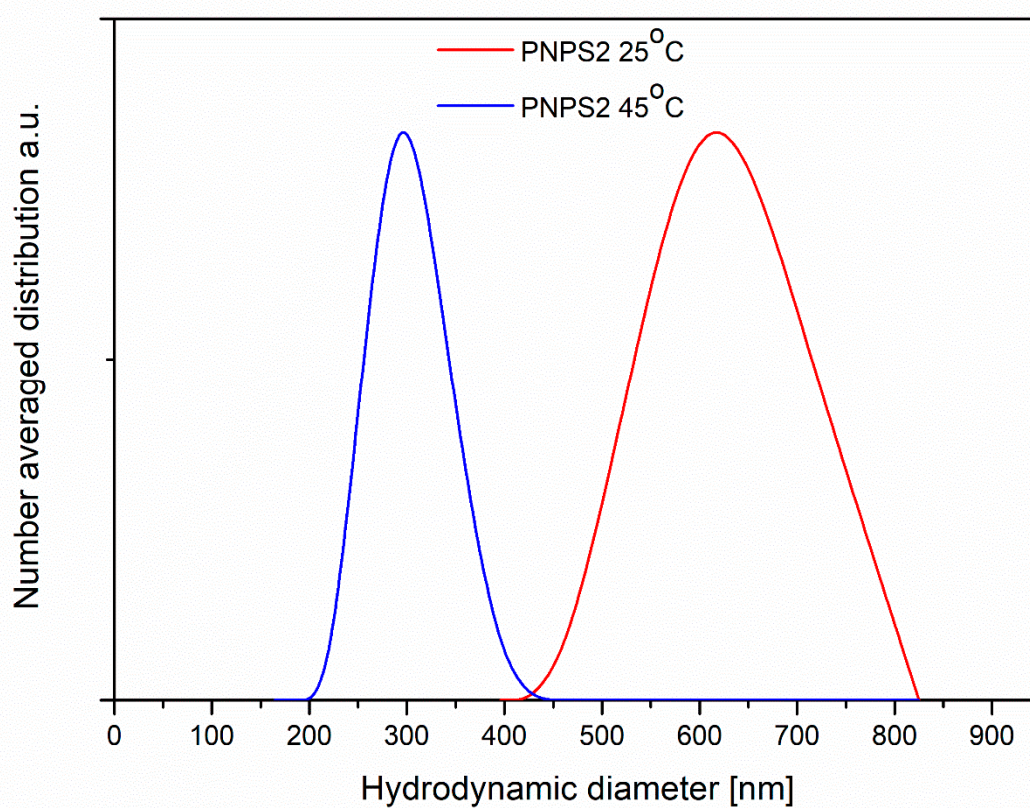


Figure S4. The number averaged hydrodynamic diameter distribution in aqueous solutions of PNPS2 at 25 and 45°C from DLS measurements.

Table S3. conditions under which of the chain extensions of PNIPAM-Br with styrene *via* ATRP were conducted; number-averaged molecular masses (M_n) of copolymers and macroinitiator determined from SEC analyses.

| Sample | Time [h] | Temp. [°C] | [I]/[M]/[CuBr]/[L] ^a | M_n PNIPAM ^b [Da] | M_n copolymer ^b [Da] |
|-------------|----------|------------|---------------------------------|--------------------------------|-----------------------------------|
| PNPS(200)21 | 21 | 90 | 1 : 200 : 2 : 2 | 11753 | 17950 |

^a I = PNIPAM-Br (macroinitiator), M = styrene (monomer), L = bpy (ligand); ^b from SEC in 1% (w/v) LiBr/DMF.

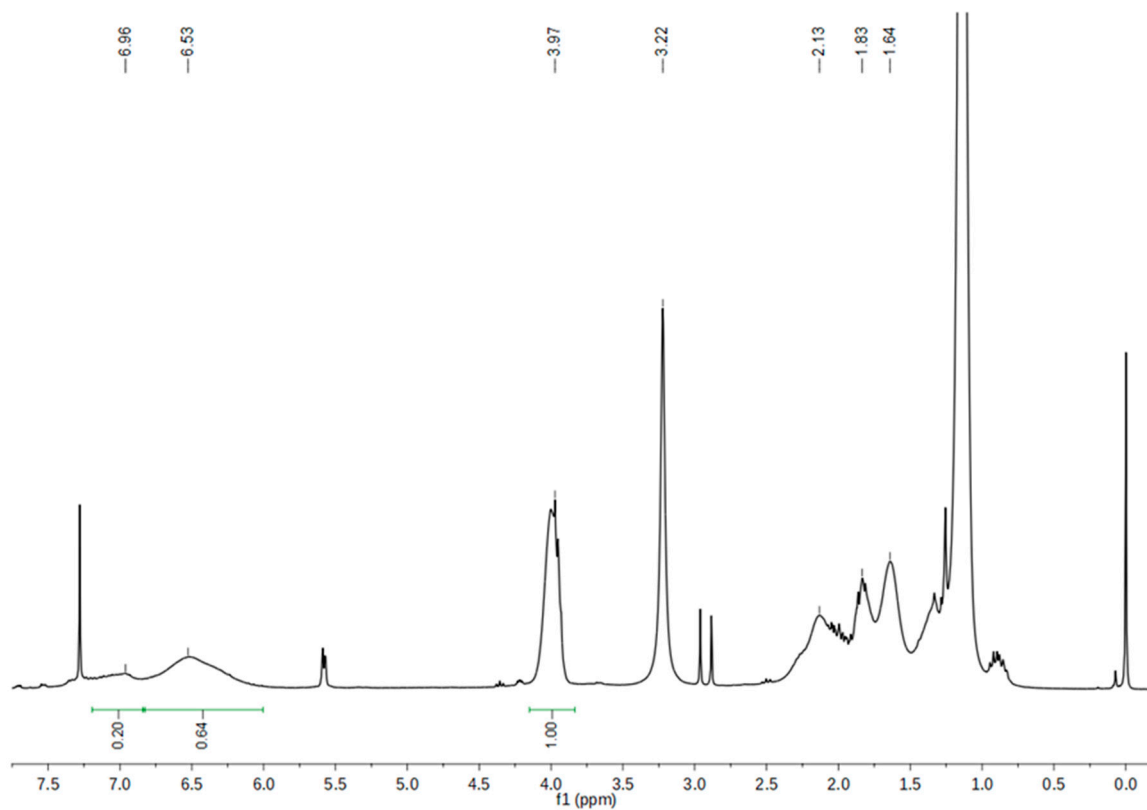


Figure S5. ¹H NMR spectrum of copolymer PNPS(200)21 synthesized via ATRP under conditions reported in Table S3.