

Electronic Supplementary Information

Thermo-Responsive Cellulose-Based Architectures: Tailoring LCST Using Poly(Ethylene Glycol) Methacrylates

Christian Porsch, Susanne Hansson, Niklas Nordgren, and Eva Malmström*

KTH Royal Institute of Technology, School of Chemical Engineering, Dept. of Fibre and Polymer Technology, SE-100 44 Stockholm, Sweden

ESI.1. Calculation of the degree of substitution (DS) for the initiating moieties on HPC.

The wt% of Br was obtained from ICP-SMS analysis. The molecular weight of the repeating unit (M_{RU}) was calculated from the molar weight of the propoxy units calculated from the molar substitution (MS) of propoxy units on HPC, obtained from NMR, and the anhydroglucose group molecular weight. M_{ini} is the molecular weight of the initiating unit and M_{Br} is the total molecular weight of the bromine/s in the initiating group. M_H is the molecular weight of a proton.

$$\%Br = \frac{DS \times M_{Br}}{M_{ini} \times DS + M_{RU} - M_H \times DS}$$

which can be rewritten as :

$$DS = \frac{\%Br \times M_{RU}}{M_{Br} - \%Br \times (M_{ini} - M_H)}$$

with the values of 2 – bromoisobutyrate group inserted :

$$HPC - I_{0.6} : DS = \frac{0.114 \times (162 + (2.9 \times 57))}{79.9 - 0.114 \times (149.9 - 1.01)} \approx 0.6$$

$$HPC - I_{1.4} : DS = \frac{0.201 \times (162 + (2.9 \times 57))}{79.9 - 0.201 \times (149.9 - 1.01)} \approx 1.4$$

ESI.2. Preparation of Phosphate buffer saline (PBS).

2 L of PBS was prepared according to the following procedure: NaCl (16 g, 0.27 mol), KCl (0.4 g, 5.4 mmol), Na₂HPO₄·7 H₂O (2.7 g, 10.1 mmol), and KH₂PO₄ (0.48 g, 3.5 mmol) was dissolved in 1600 ml distilled water. pH was adjusted to 7.4 using HCl (2M) and the volume was adjusted to 2 L using additional distilled water.

ESI.3. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF)

MALDI-TOF analyses were conducted on a Bruker UltraFlex MALDI-TOF mass spectrometer with a SCOUT-MTP ion source (Bruker Daltonics) equipped with a nitrogen laser (337 nm), a gridless ion source, and a reflector. THF solutions of either 9-nitroanthracene and trifluoroacetic acid sodium salt, 2,5-dihydroxybenzoic acid, or galvinoxyl free radical were used as matrices (all purchased from Aldrich).

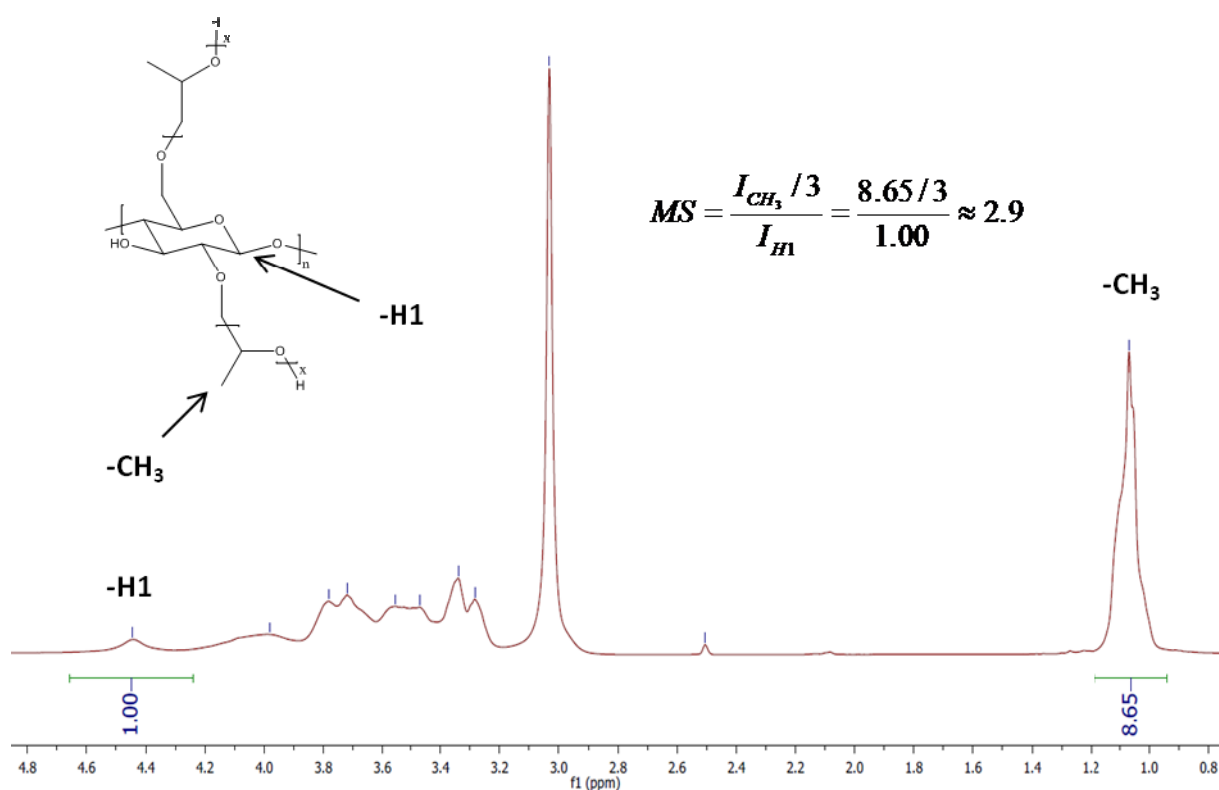


Fig. ESI.1. ¹H-NMR of HPC in DMSO-d₆ recorded at 95 °C. The molar substitution of propoxy groups was calculated from the spectrum.

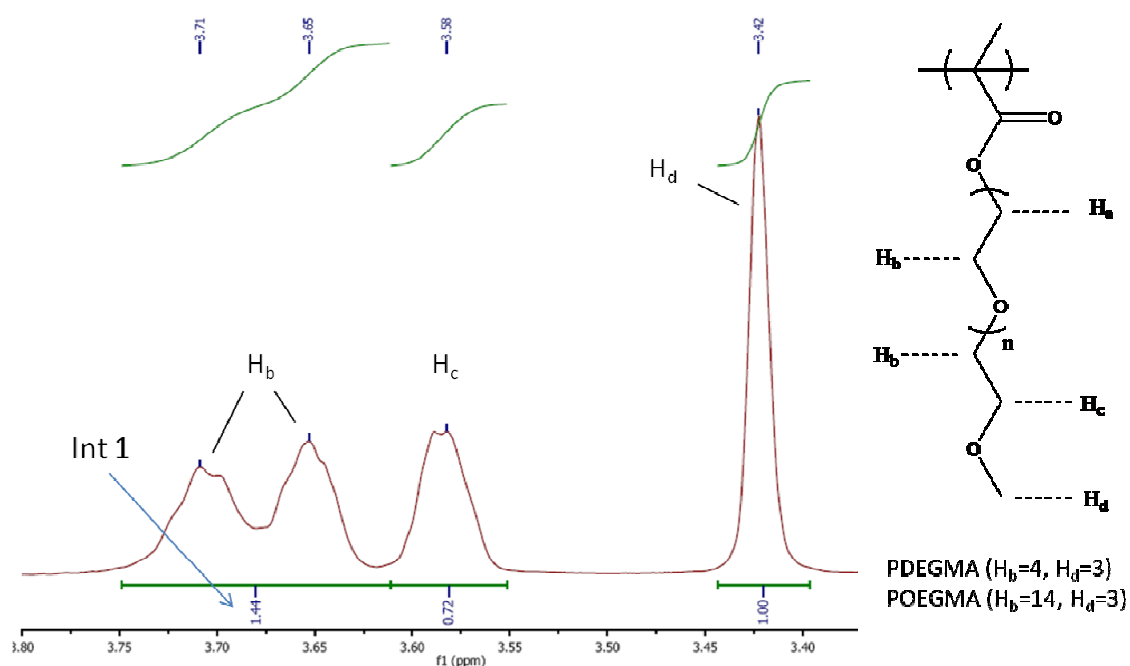


Fig. ESI.2. ¹H-NMR PDEGMA in CDCl₃ focusing in the region used to calculate the polymer composition. The compositions of the copolymers were calculated as described above.

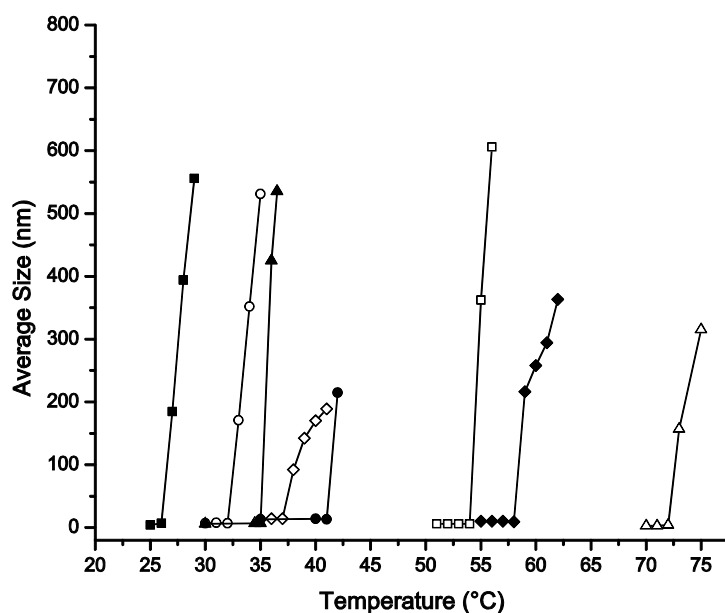


Fig. ESI.3. Average size as a function of temperature of the linear homo- and copolymers in the present study. The increase in size corresponds to molecular aggregation at LCST, due to collapse of the polymer chains PDEGMA (■), P(OEGMA₁₅-co-DEGMA₈₅) (○), P(OEGMA₁₉-co-DEGMA₈₁) (▲), P(OEGMA₂₇-co-DEGMA₇₃) (◇), P(OEGMA₃₇-co-DEGMA₆₃) (●), P(OEGMA₅₄-co-DEGMA₄₆) (□), P(OEGMA₇₃-co-DEGMA₂₇) (◆), POEGMA (Δ).

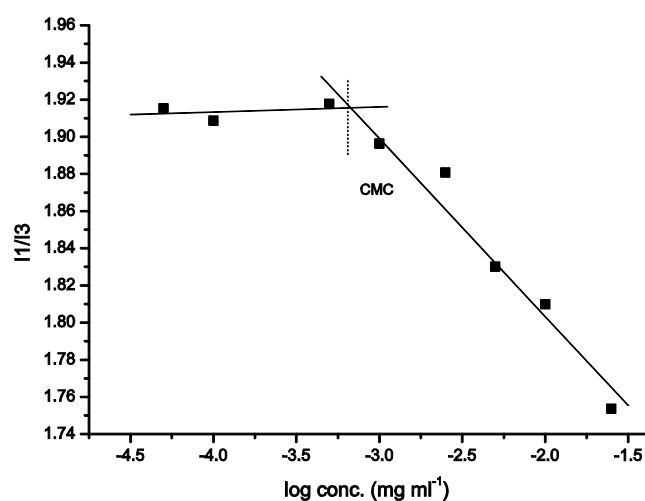


Fig. ESI.4. Change in the fluorescence characteristics of pyrene as a function of HPC_{0.6}-g-PDEGMA concentration.

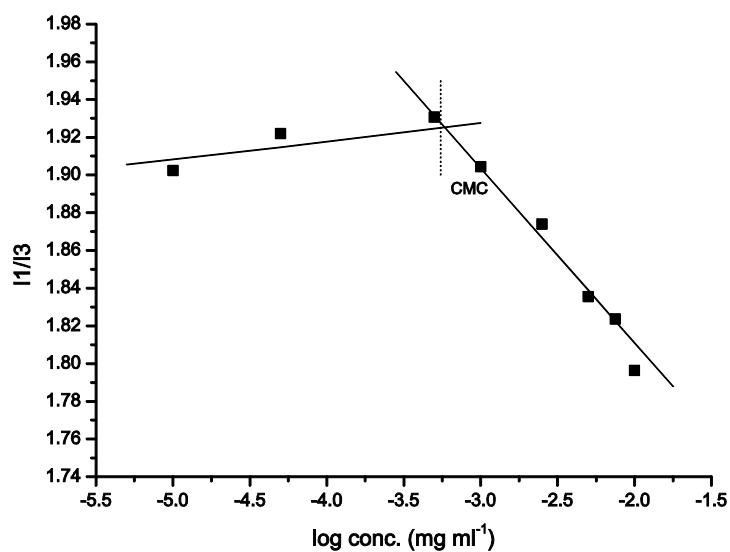


Fig. ESI.5. Change in the fluorescence characteristics of pyrene as a function of $\text{HPC}_{0.6}\text{-}g\text{-P(OEGMA}_{52}\text{-co-DEGMA}_{48})$ concentration.

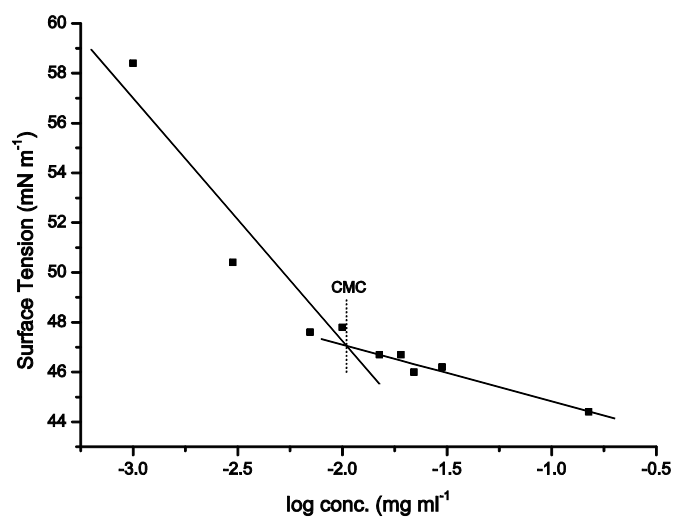


Fig. ESI.6. Change in surface tension as a function of concentration of $\text{HPC}_{0.6}\text{-}g\text{-PDEGMA}$ solutions.

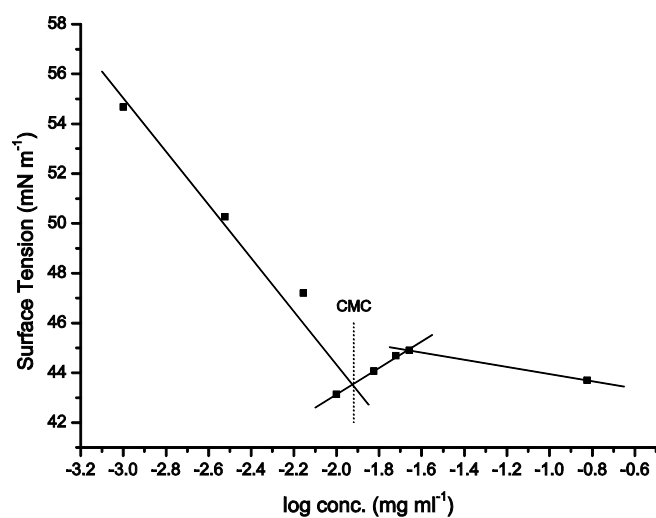


Fig. ESI.7. Change in surface tension as a function of concentration of HPC_{0.6}-g-P(OEGMA₅₂-co-DEGMA₄₈) solutions.

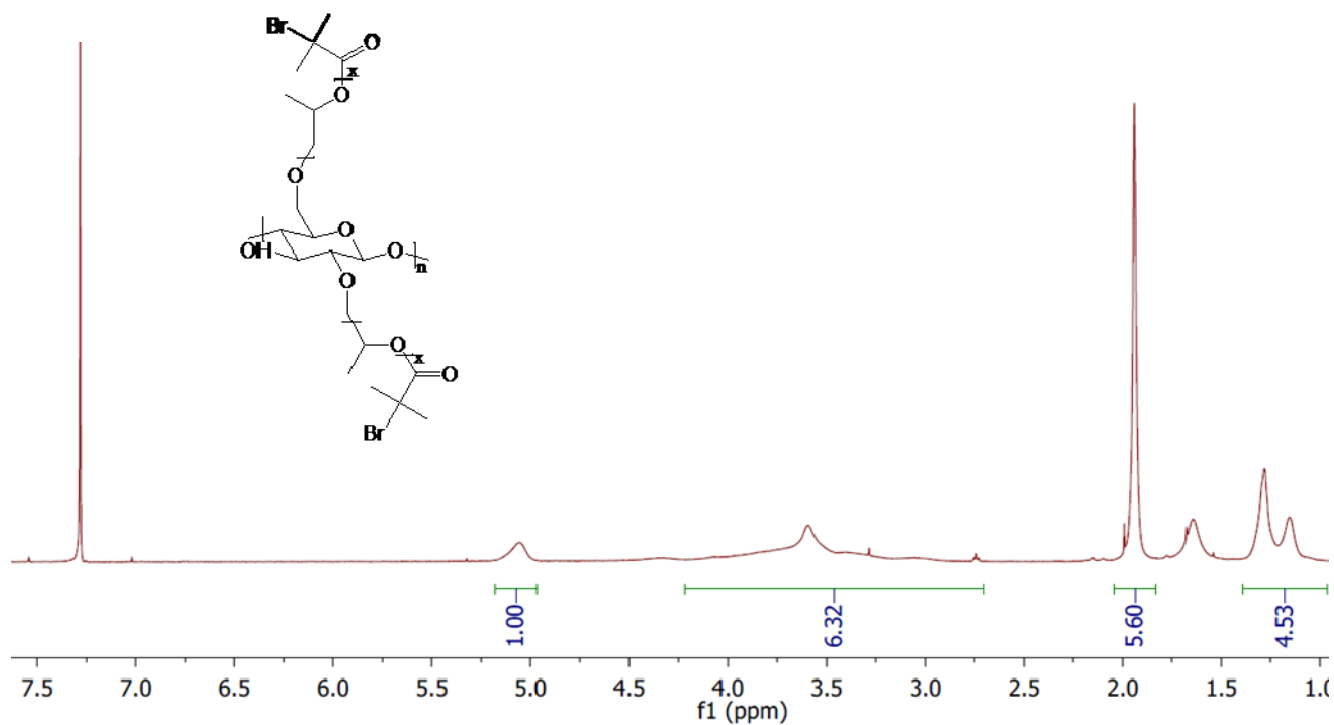


Fig. ESI.8. ¹H-NMR of HPC-I_{1.4} in CDCl₃. ¹H-NMR (CDCl₃): δ 1.16 (br), 1.28 (br), 1.94 (s), 2.70-4.20 (br), 3.60 (value of sharpest peak inside broad peak), 4.35 (br), 5.05 (br) ppm.

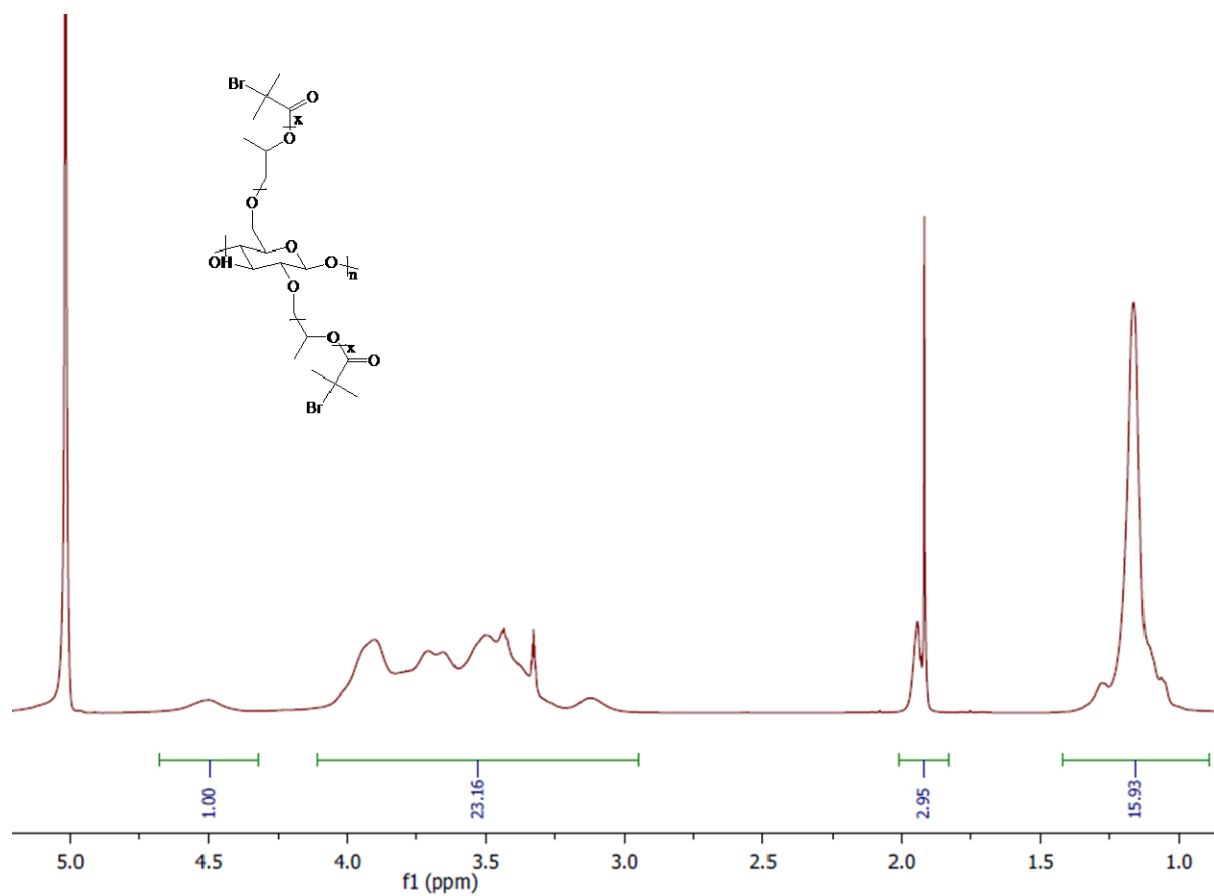


Fig. ESI.9. ¹H-NMR of HPC-I_{0.6} in MeOD. ¹H-NMR (MeOD): δ 1.16 (br), 1.93 (s), 3.00-4.10 (br), 4.50 (br), 4.99 (s) ppm.

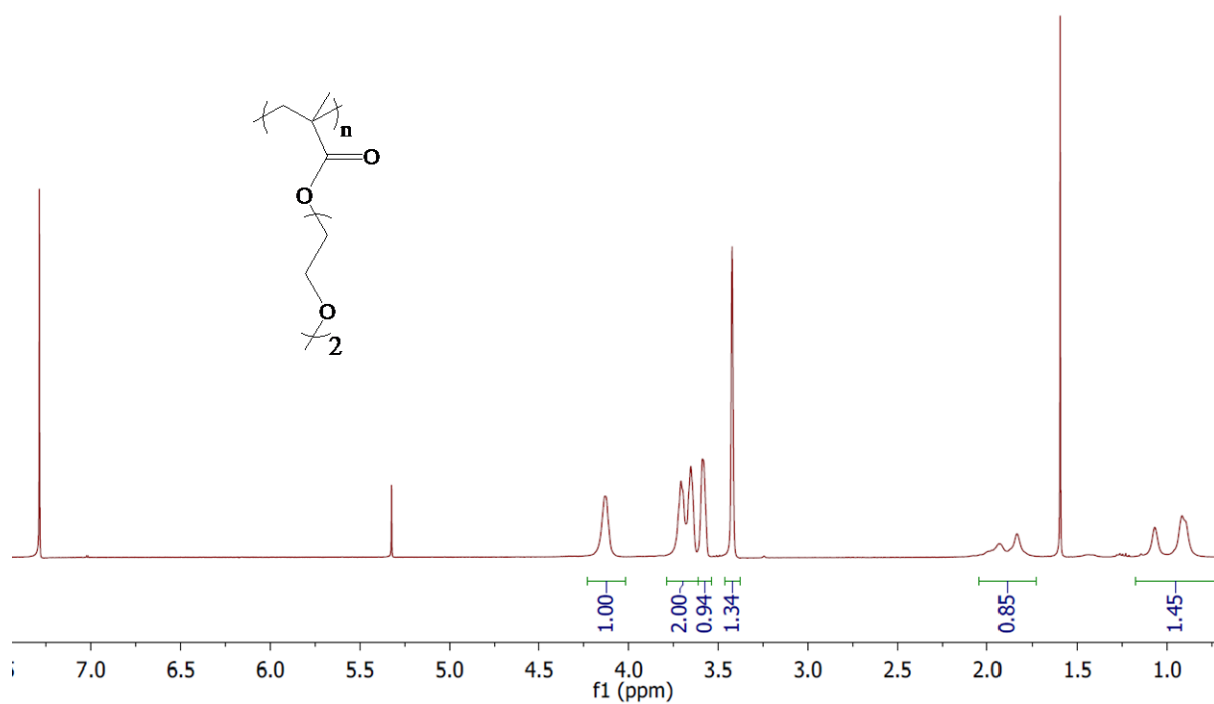


Fig. ESI.10. $^1\text{H-NMR}$ of PDEGMA in CDCl_3 . $^1\text{H-NMR}$ (CDCl_3): δ 0.91 (br), 1.06 (br), 1.61 (s), 1.84 (br), 1.94 (br), 3.42 (s), 3.59 (br), 3.66-3.69 (br), 4.13 (br) ppm.

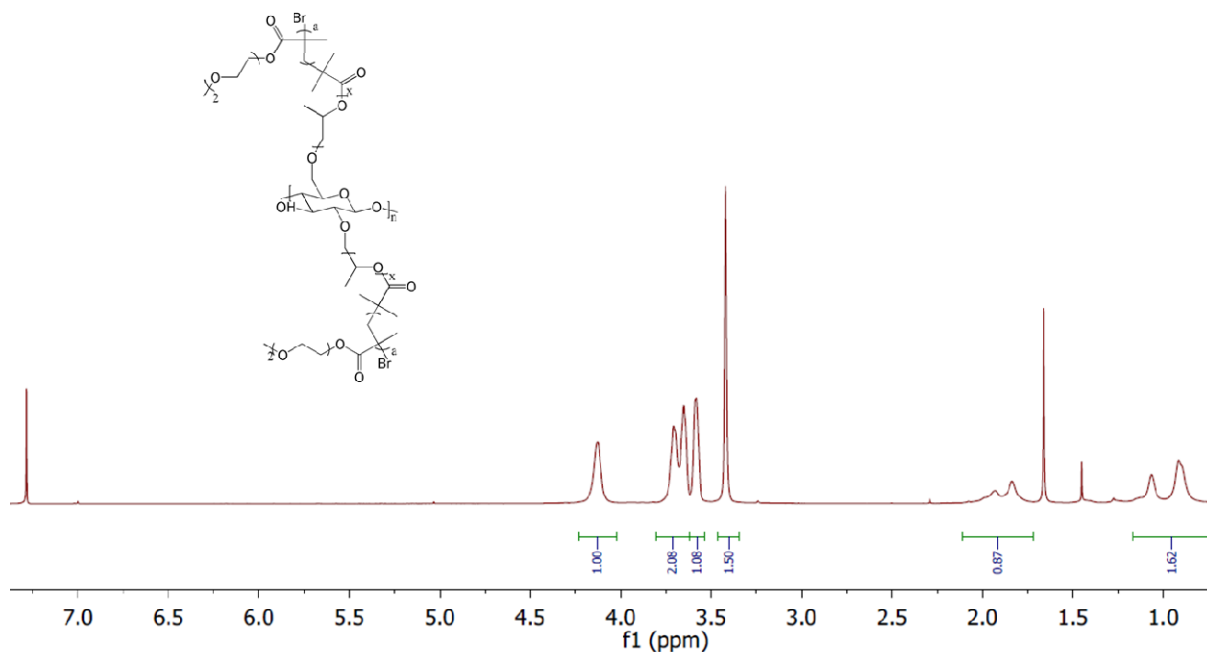


Fig. ESI.11. $^1\text{H-NMR}$ of HPC-g-PDEGMA in CDCl_3 . $^1\text{H-NMR}$ (CDCl_3): δ 0.91 (br), 1.06 (br), 1.45 (s), 1.66 (s), 1.83 (br), 1.92 (br), 3.42 (s), 3.59 (s), 3.65-3.71 (br), 4.13 (br) ppm.

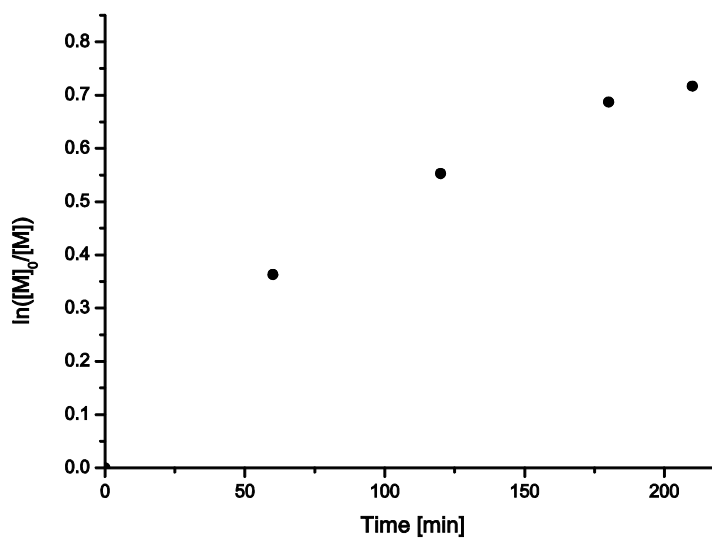


Fig. ESI.12. Kinetic plot for ARGET ATRP of P(OEGMA₁₉-co-DEGMA₈₁) (Table 1, entry 3 in the article).

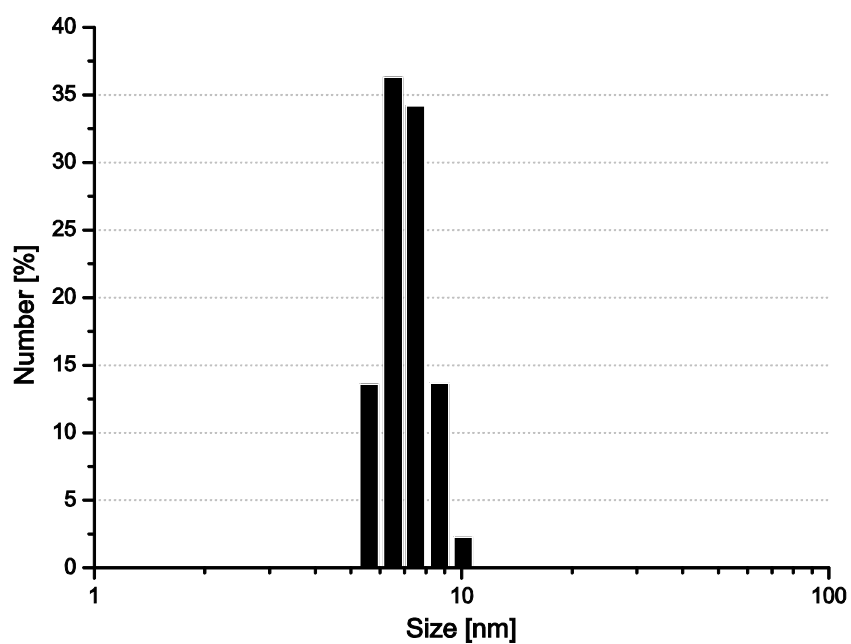


Fig. ESI.13. Size distribution of PDEGMA (Table 1, entry 1 in the main article) from DLS measurement at 26 °C.

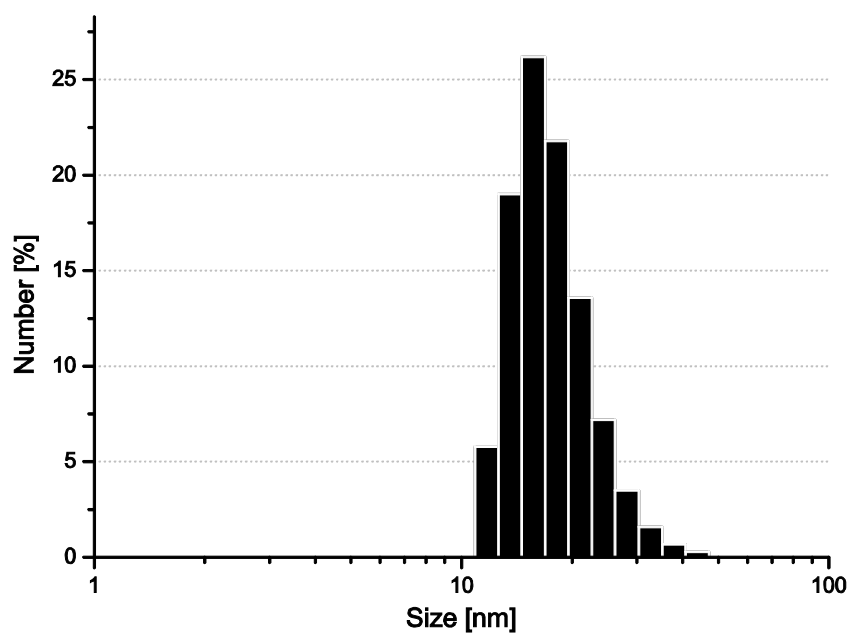


Fig. ESI.14. Size distribution of HPC-g-PDEGMA (Table 2, entry 2 in the main article) from DLS measurement at 22 °C.