Synthesis and self-assembly of cytidine- and guanosine-based copolymers

Supporting Information

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Calculation methods

Monomer conversion was calculated following eq. 1 from the crude reaction mixture. $\int_{H(polymer)}$ equals the integration of the polymer backbone peak, $\int_{H(monomer)}$ the peak integration of the vinyl proton of the monomer.

$$conversion = \frac{\int_{H(polymer)}}{\int_{H(monomer)} + \int_{H(polymer)}} \times 100\ \% \quad (1)$$

The calculation of the theoretical molecular weight ($M_{n,\,theory,\,NMR}$) is based on the conversion using eq. 2:

$$M_{n,\,theory,\,NMR} = \left(\frac{c_{monomer}}{c_{CTA}} \times conversion \times M_{monomer}\right) + M_{CTA} \quad (2)$$

where $c_{monomer}$ and c_{CTA} are the initial concentrations of monomer and CTA. $M_{monomer}$ and M_{CTA} indicate the molecular masses of monomer and CTA. “Livingness” was determined with following eq. 3:

$$L = \frac{c_{CTA}}{c_{CTA} + 2fc_I(1 - e^{-k_d t})(1 - \frac{f_c}{2})} \times 100 \quad (3)$$

where c_{CTA} and c_I are the initial concentrations of CTA and initiator. The expression "2" refers to the formation of two primary radicals with a certain efficiency f from one initiator molecule. The expression "2" refers to the formation of two primary radicals from one initiator molecule with a certain efficiency f, which is typically 0.5 for diazo-initiators. The resulting chain number at radical termination is given as "1-f_c/2", where f_c is the coupling factor. k_d describes the decomposition coefficient of the initiator, while t is the reaction time.

$M_{n,UV\text{-}Vis}$ was determined using a Specord 210 spectrophotometer. by using Beer-Lambert eq. 4:

$$A = \frac{\varepsilon d c_{mass}}{M_{n,\,UV-Vis}} \quad (4)$$

where A is the absorption, ε the extinction coefficient, d the optical path length and c_{mass} the concentration. $\frac{\varepsilon d}{M_{n,\,UV-Vis}}$ represents the slope, which results in the calculation of $M_{n,\,UV\text{-}Vis}$ with the following eq. 5:

$$M_{n,\,UV-Vis} = \frac{\varepsilon \times d}{slope} \quad (5)$$

The average hydrodynamic radius and therefore the diameter of the formed aggregates were derived from the Stokes-Einstein eq. 6:

$$r = k_B T / 6\pi\eta D \quad (6)$$

where k_B is the Boltzmann’s constant, T the absolute temperature, η the dynamic viscosity and D the diffusion coefficient.

Table 1. Analytical data of pHPMA **10**.

Monomer	Conversion	Polymer	$M_{n,\ theory,\ NMR}$	$M_{n,\ NMR}$	$M_{n,\ UV\text{-}Vis}$	$M_{n,\ SEC}$[a]	PDI
10	75 %	**9**	7.8 kDa	38.7 kDa (DP: 267)	38.2 kDa (DP: 263)	9.1 kDa	1.66

[a]*DMF, PMMA standard.*

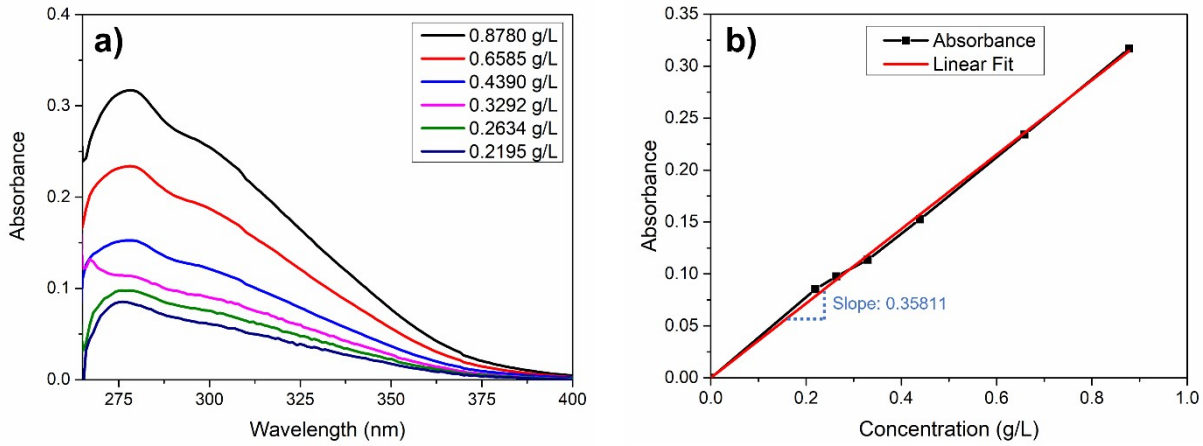

Figure 1. a) UV-Vis spectrum of pHPMA **10** at different concentrations and b) linear fit of absorbance maximum to concentration.

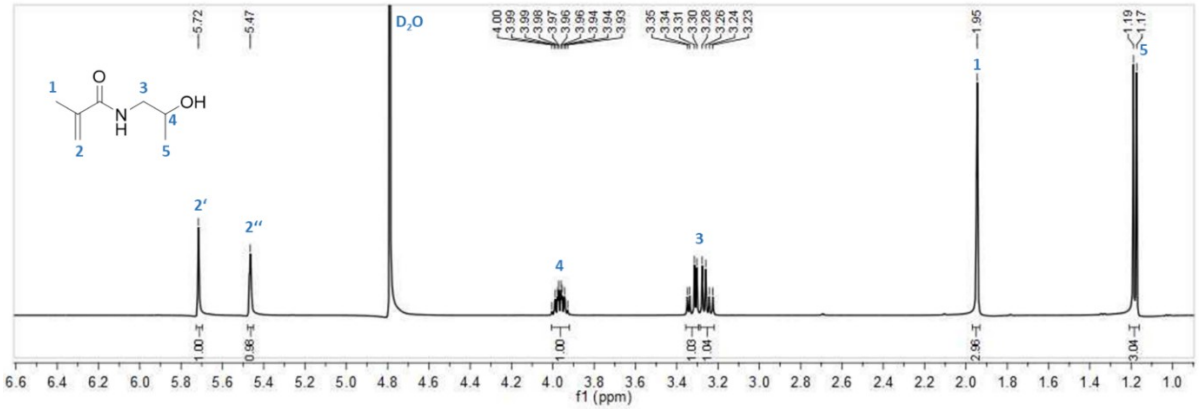

Figure 2. ^{1}H NMR spectrum of HPMA **10** in D_2O.

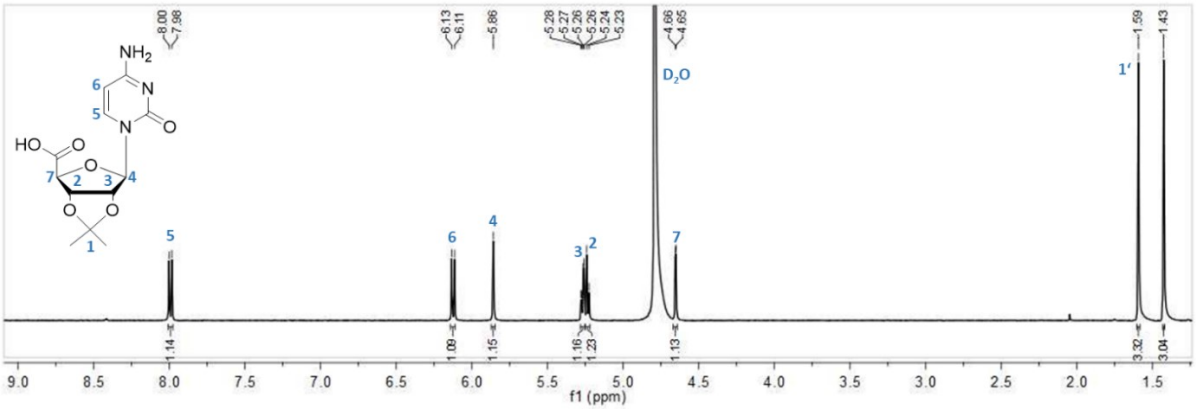

Figure 3. ^{1}H NMR spectrum of iC-COOH **3** in D_2O.

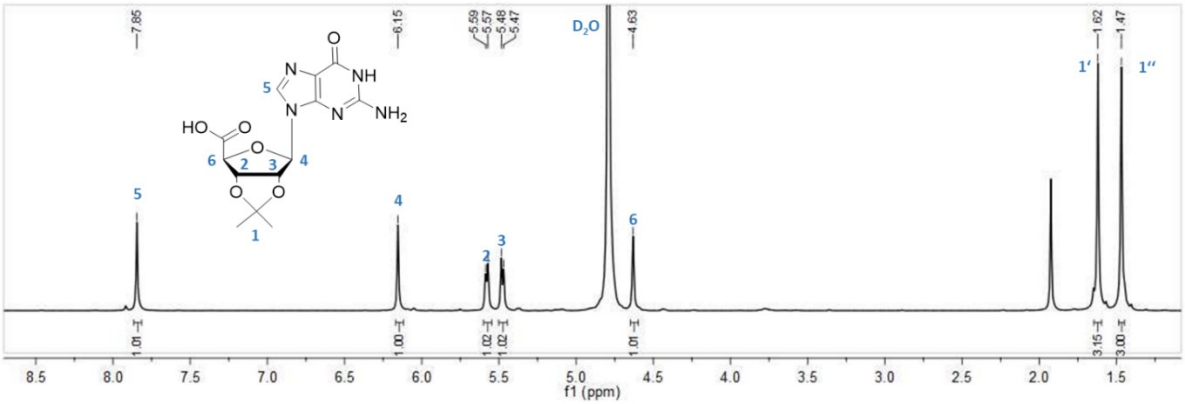

Figure 4. ^{1}H NMR spectrum of iG-COOH **4** in D_2O.

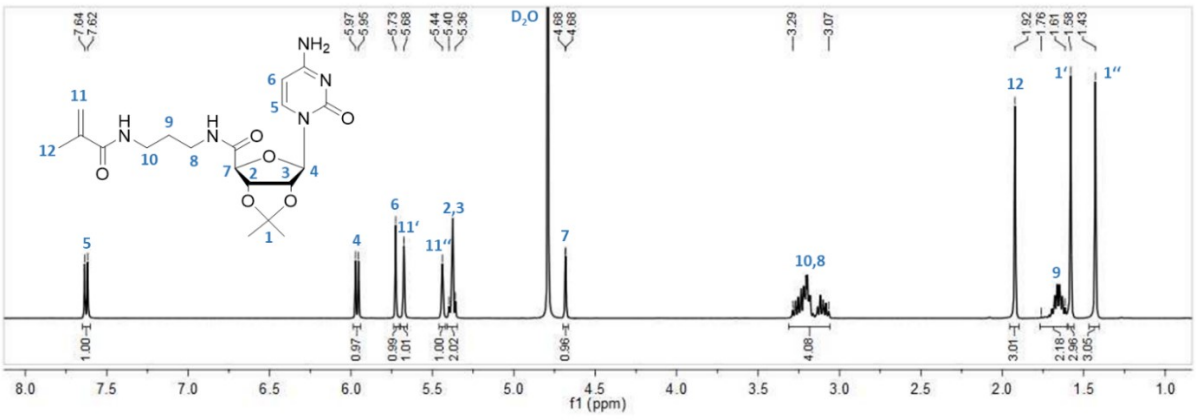

Figure 5. ^{1}H NMR spectrum of monomer iCPMA **1** in D_2O.

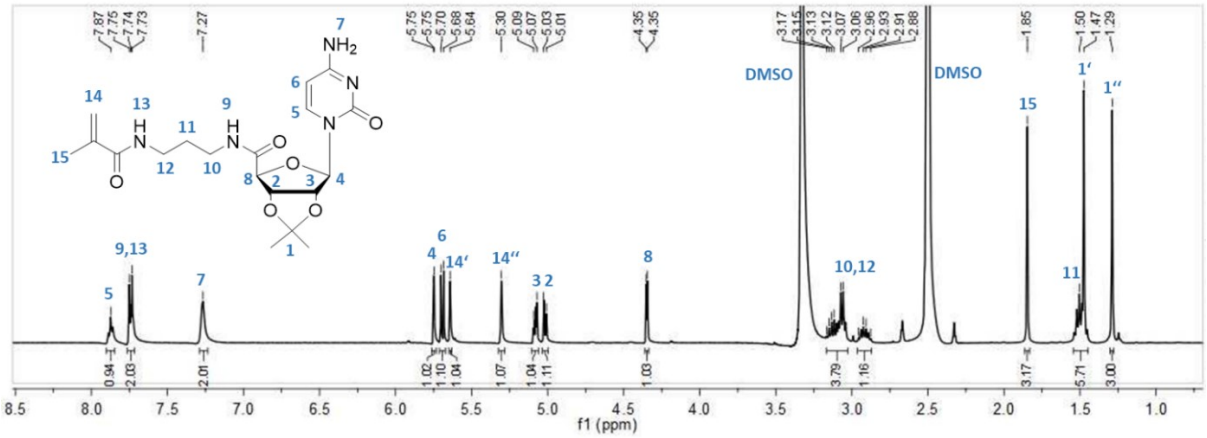

Figure 6. ^{1}H NMR spectrum of monomer iCPMA **1** in DMSO-d_6.

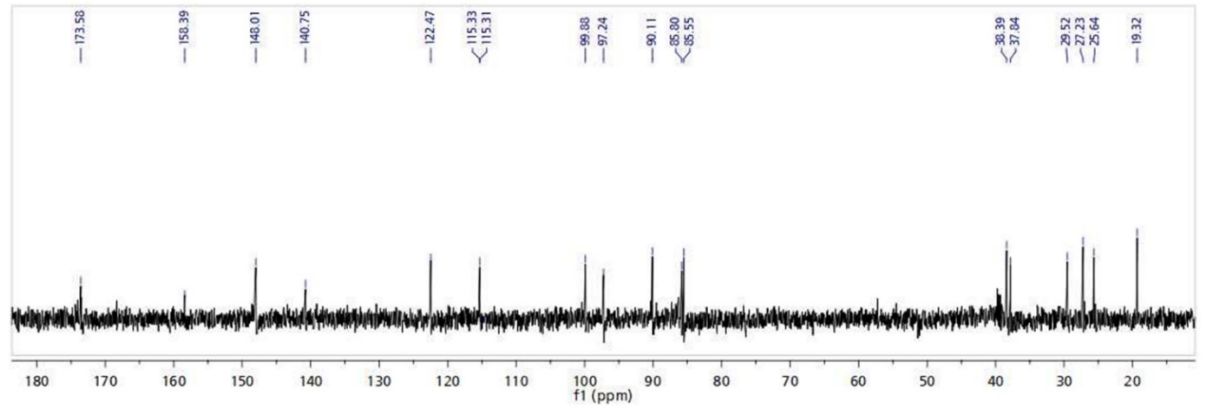

Figure 7. ^{13}C NMR spectrum of monomer iCPMA **1** in D_2O + DMSO-d_6.

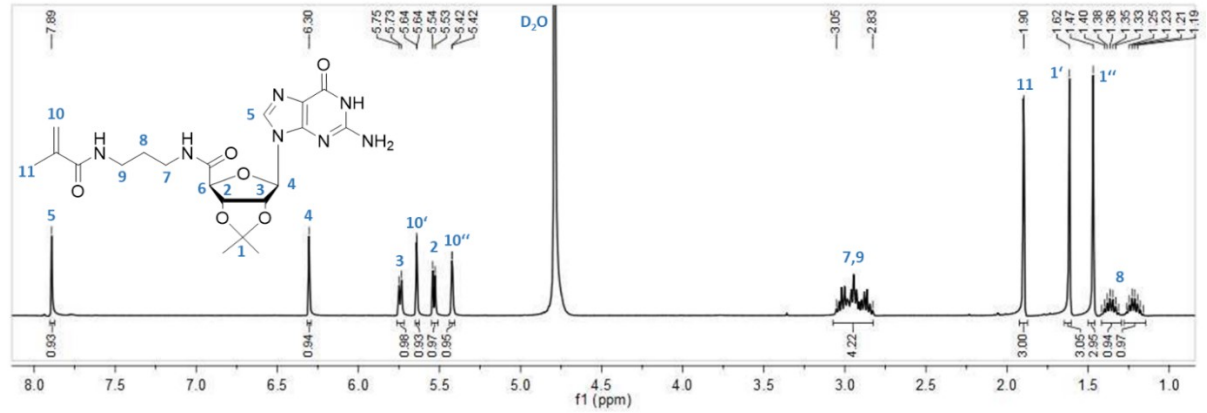

Figure 8. ^{1}H NMR spectrum of monomer iGPMA **2** in D_2O.

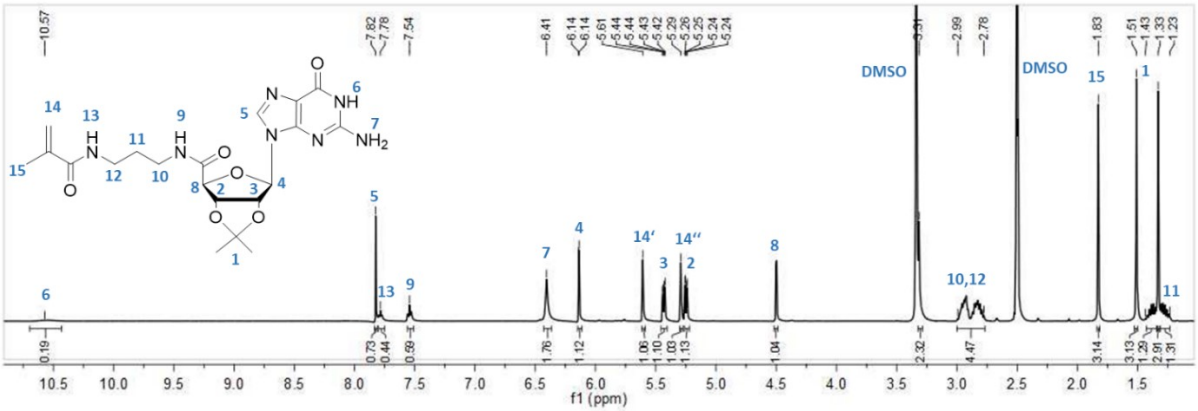

Figure 9. ^{1}H NMR spectrum of monomer iGPMA **2** in DMSO-d_6.

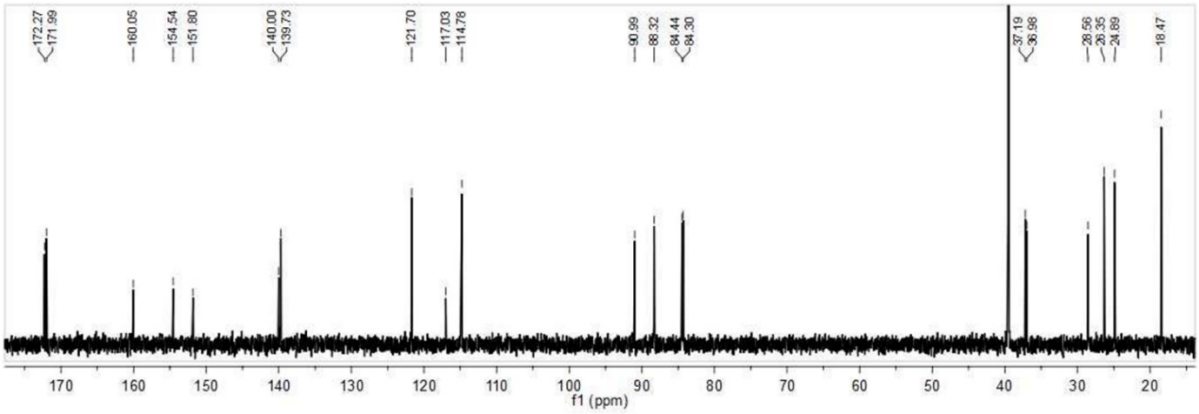

Figure 10. ^{13}C NMR spectrum of monomer iGPMA **2** in D_2O + DMSO-d_6.

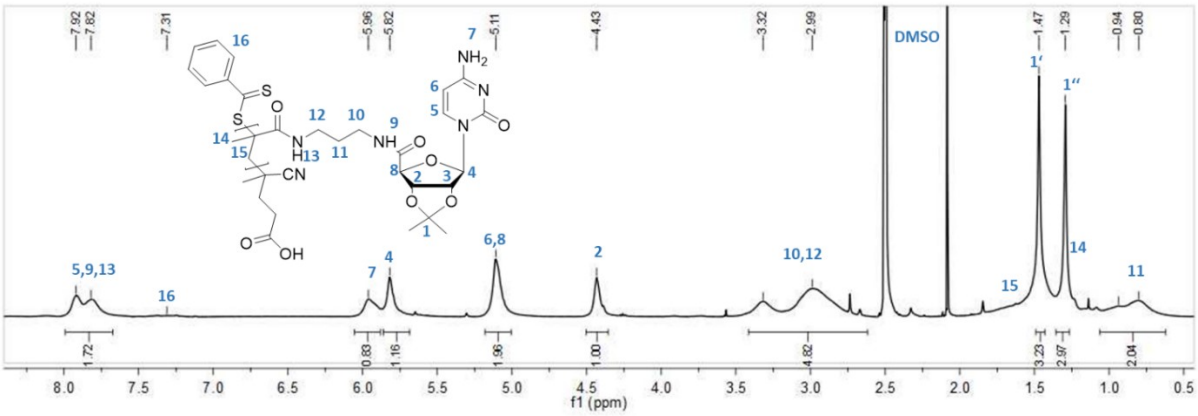

Figure 11. ^{1}H NMR spectrum of homopolymer piCPMA **5** in DMSO-d_6.

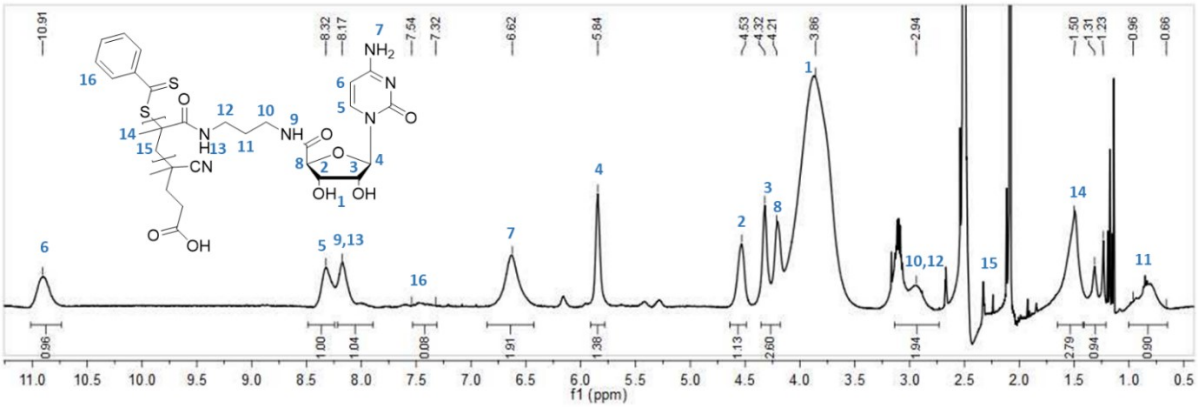

Figure 12. ^{1}H NMR spectrum of deprotected homopolymer pCPMA **7** in DMSO-d_6.

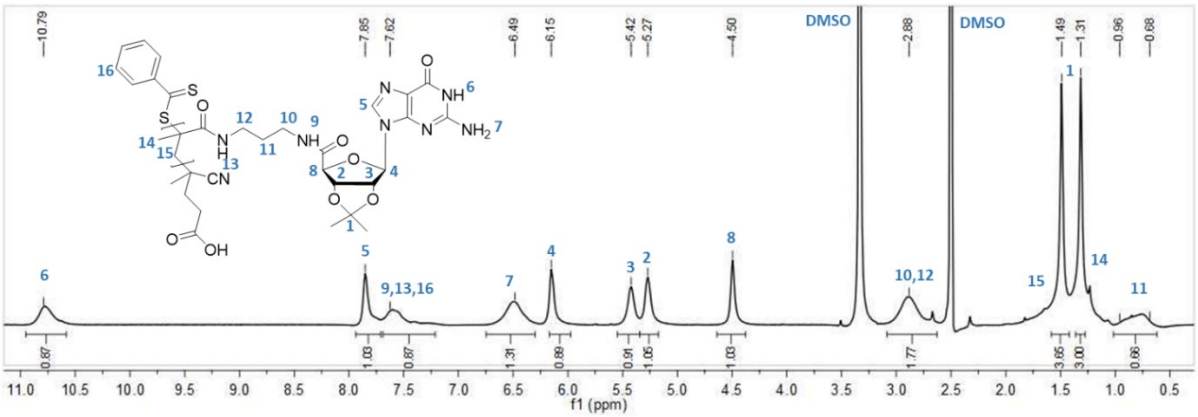

Figure 13. ^{1}H NMR spectrum of homopolymer piGPMA **6** in DMSO-d_6.

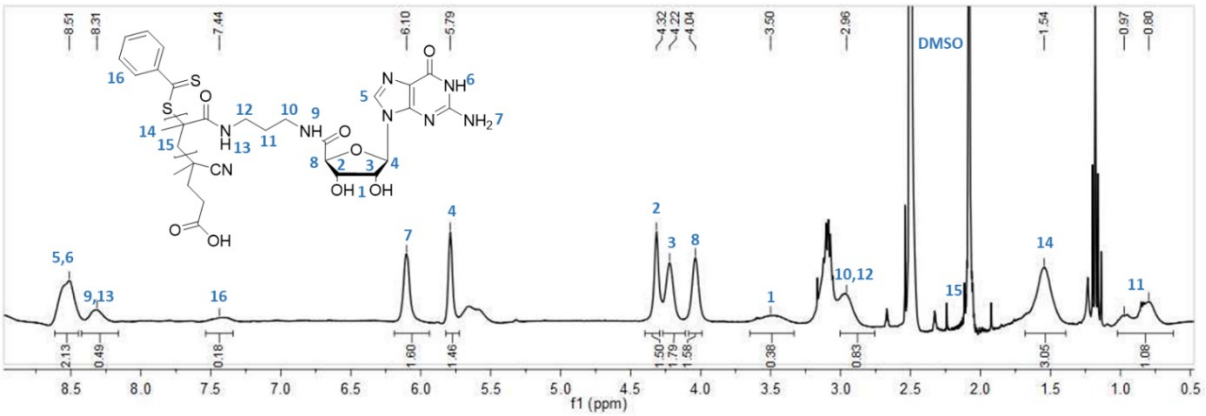

Figure 14. ^{1}H NMR spectrum of deprotected homopolymer pGPMA **8** in DMSO-d_6.

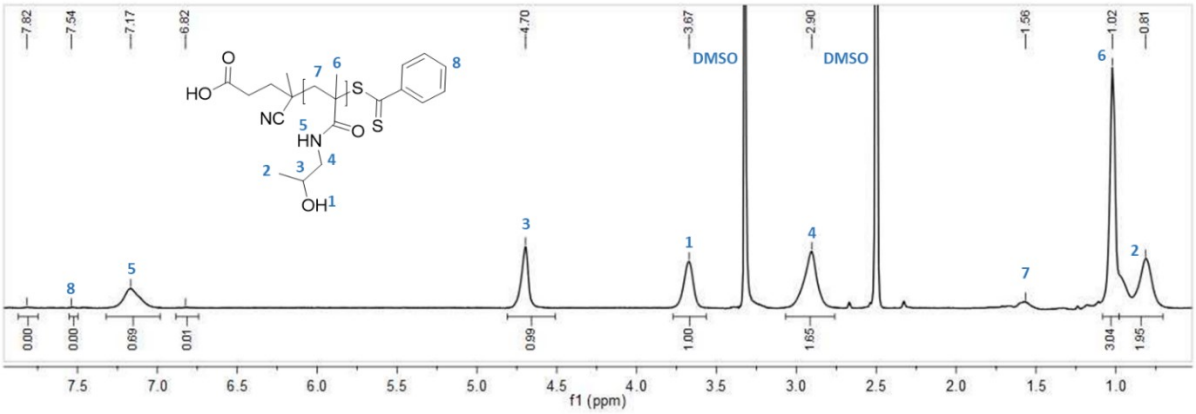

Figure 15. ^{1}H NMR spectrum of pHPMA **9** in DMSO-d_6.

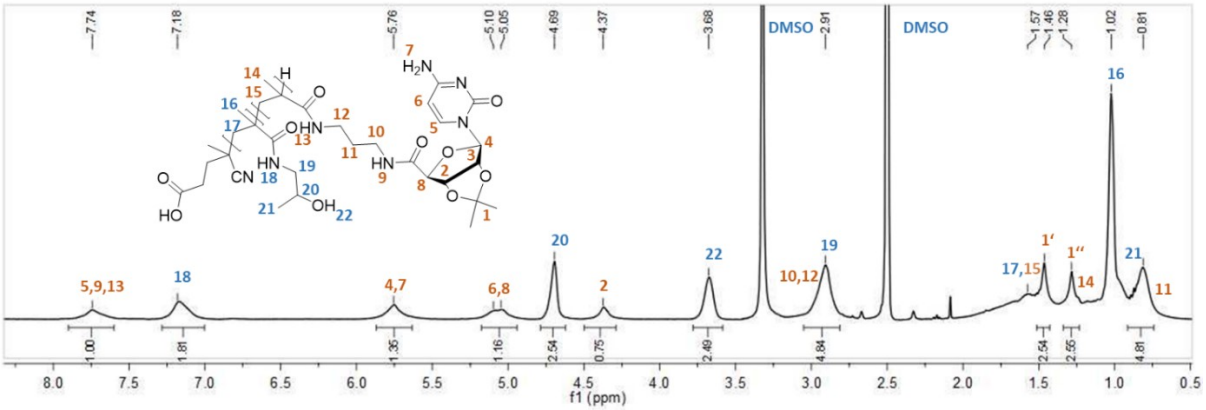

Figure 16. ^{1}H NMR spectrum of blockcopolymer pHPMA-b-piCPMA **11** in DMSO-d_6.

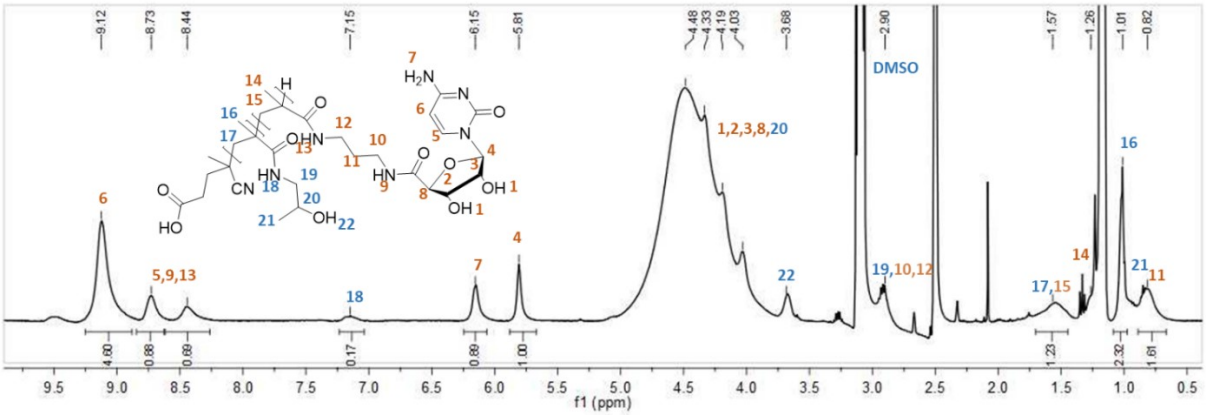

Figure 17. ^{1}H NMR spectrum of deprotected blockcopolymer pHPMA-*b*-CPMA **13** in DMSO-d_6.

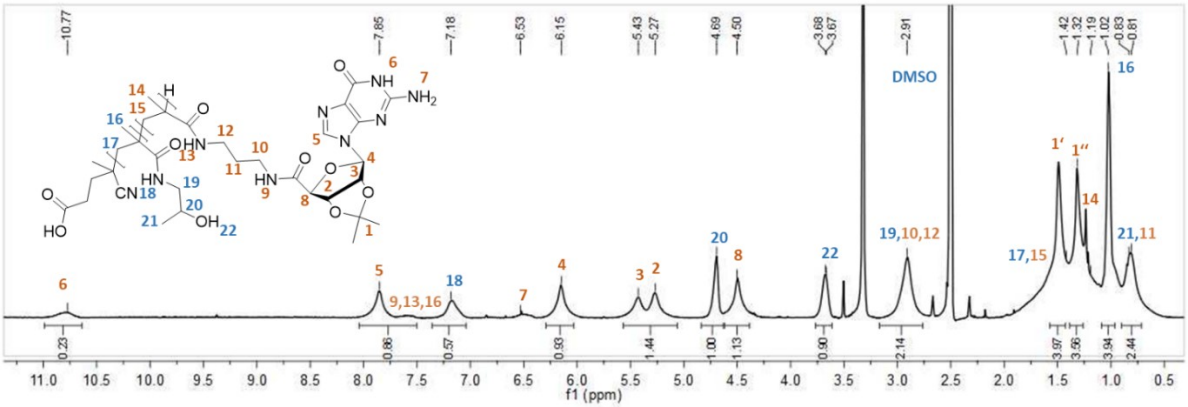

Figure 18. ^{1}H NMR of blockcopolymer pHPMA-*b*-piGPMA **12** in DMSO-d_6.

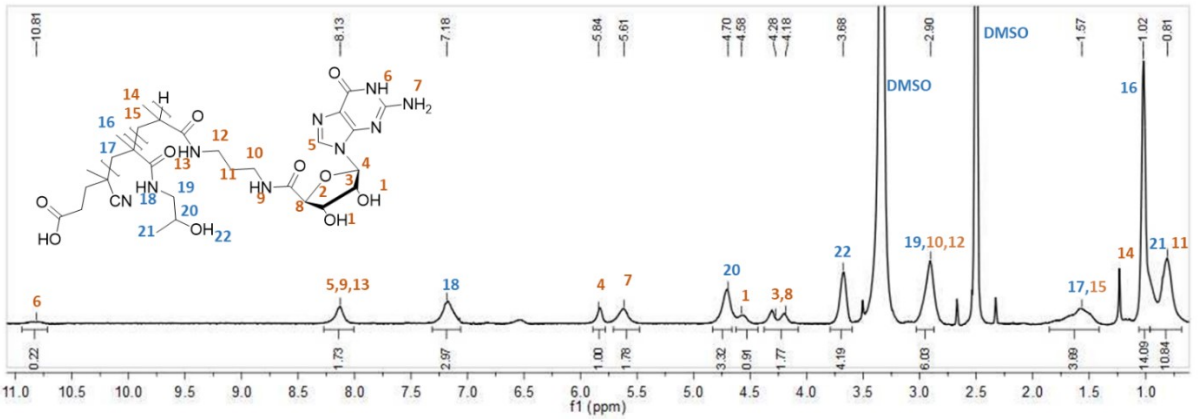

Figure 19. ^{1}H NMR spectrum of depreotected blockcopolymer pHPMA-*b*-pGPMA **14** in DMSO-d_6.

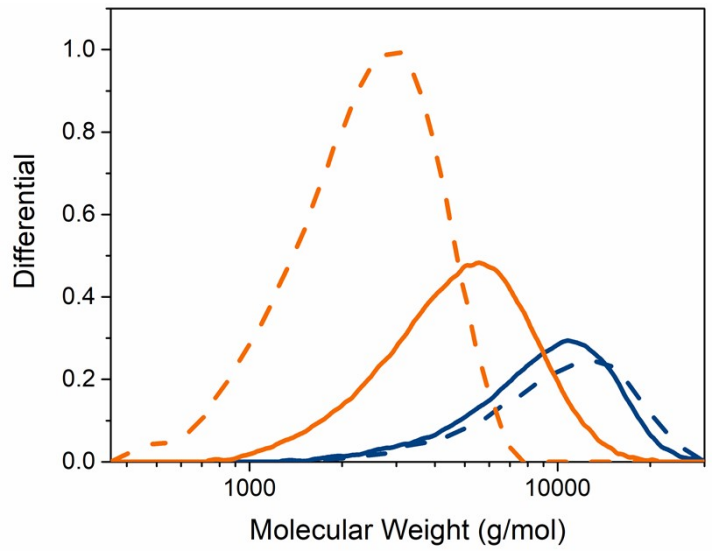

Figure 20. SEC analysis of piCPMA **5** (orange) and piGPMA **6** (blue) synthesized in DMF/H_2O (straight) or 1,4-dioxane/H_2O (dashed), respectively.

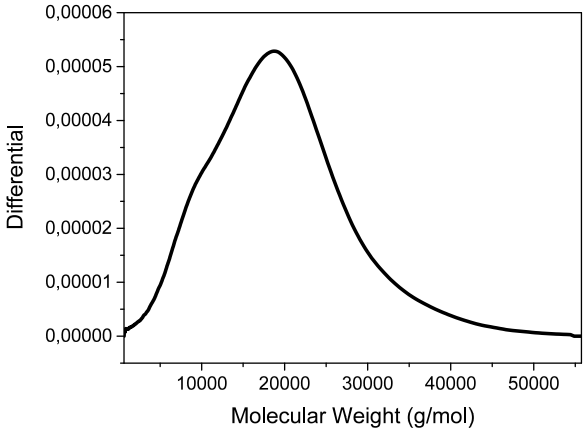

Figure 21. SEC analysis of pHPMA **9**.

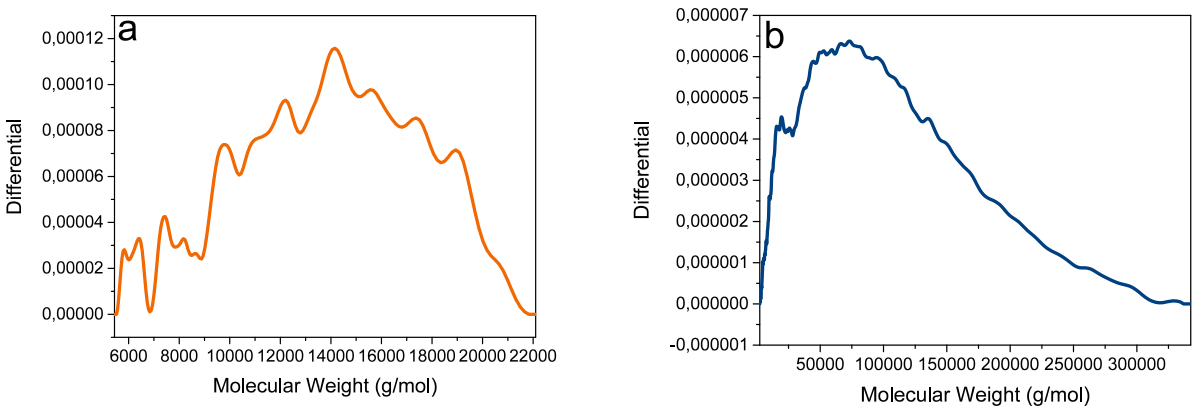

Figure 22. SEC analysis of a) pHPMA-*b*-piCPMA **11** and b) pHPMA-*b*-piGPMA **12**.

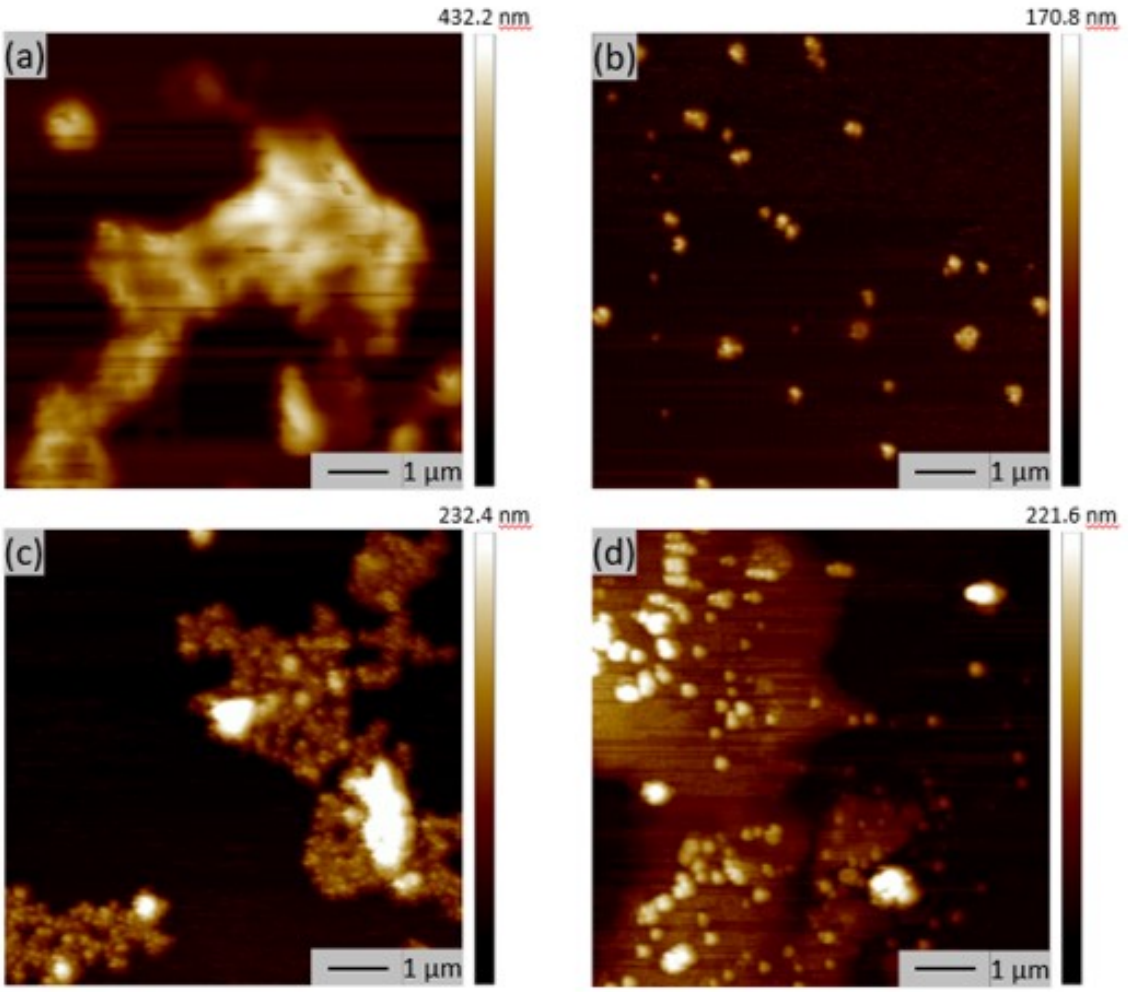

Figure 23. AFM images of (a) pHPMA-b-pCPMA **13**, (b) pHPMA-b-pGPMA **14**, (c) mixture of **13** and **14** before heating and (d) mixture of **13** and **14** after heating.