Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

MULTI-STIMULI-RESPONSIVE COPOLYMERS BASED ON 1-PYRENOL POLYPHOTOACIDS

Leonid I. Kaberov[a,b], Maria Sittig[b,c,d], Avinash Chettri[c,d], Abdelrahman Ibrahim[c], Benjamin Dietzek-Ivanšić[b,c,d]*, Felix H. Schacher[a,b]*

a Institute of Organic Chemistry and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstrasse 10, 07743 Jena (Germany)

b Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena (Germany)

c Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich Schiller University Jena, Helmholtzweg 4, 07743 Jena (Germany)

d Department of Functional Interfaces, Leibniz Institute of Photonic Technology Jena e. V., Albert-Einstein-Strasse 9, 07745 Jena (Germany)

E-mail: felix.schacher@uni-jena.de, benjamin.dietzek@leibniz-ipht.de

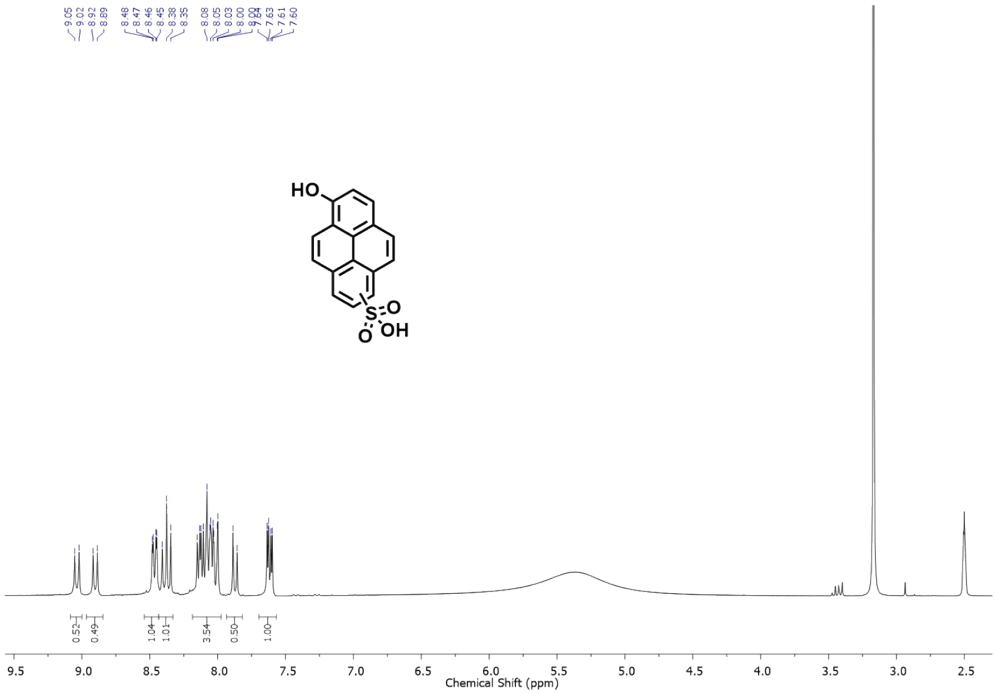

Figure S1. ^{1}H NMR spectrum of 6/8-hydroxypyrene-1-sulfonic acid in DMSO-d6.

Comment [FS]: Aleays add the NMR solvent in the caption

Comment [LK]: Done

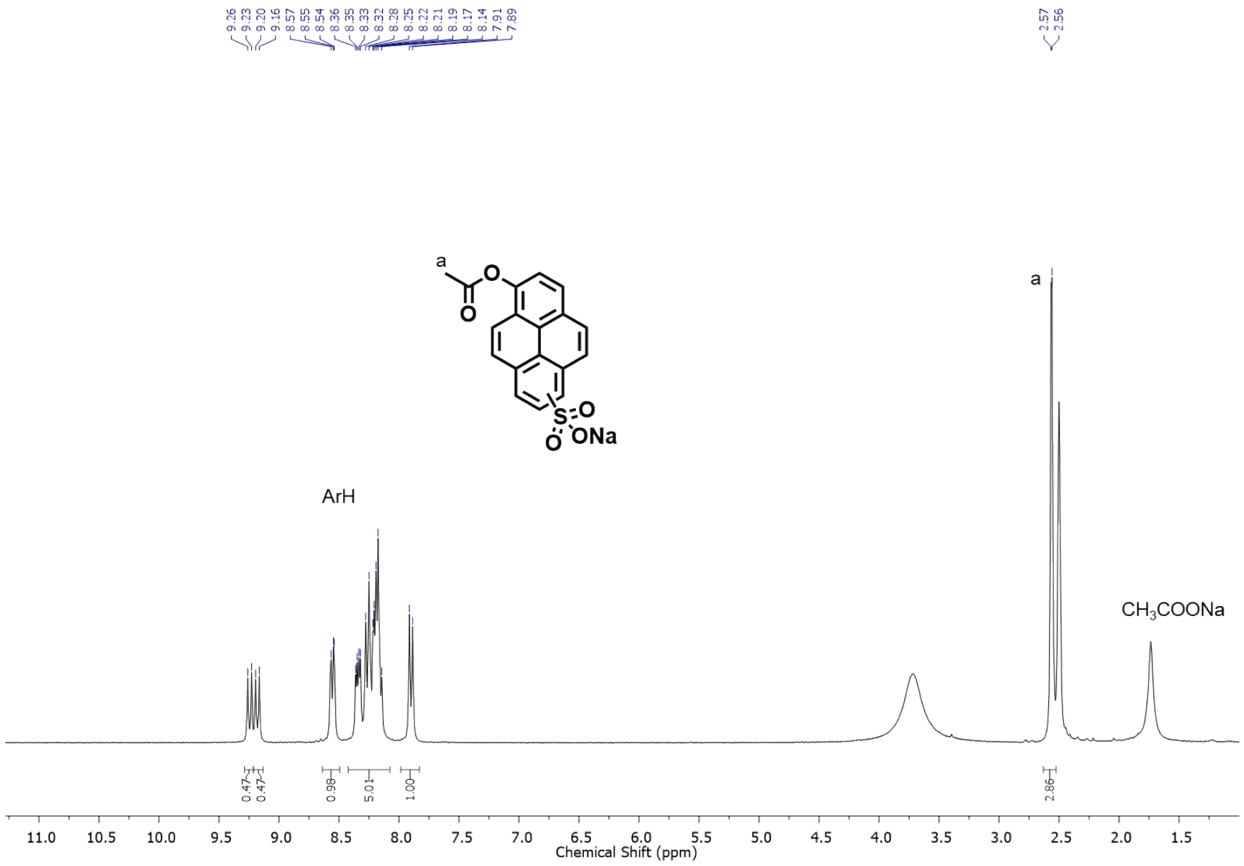

Figure S2. ^{1}H NMR spectrum of sodium 6/8-acetoxypyrene-1-sulphonate in DMSO-d6.

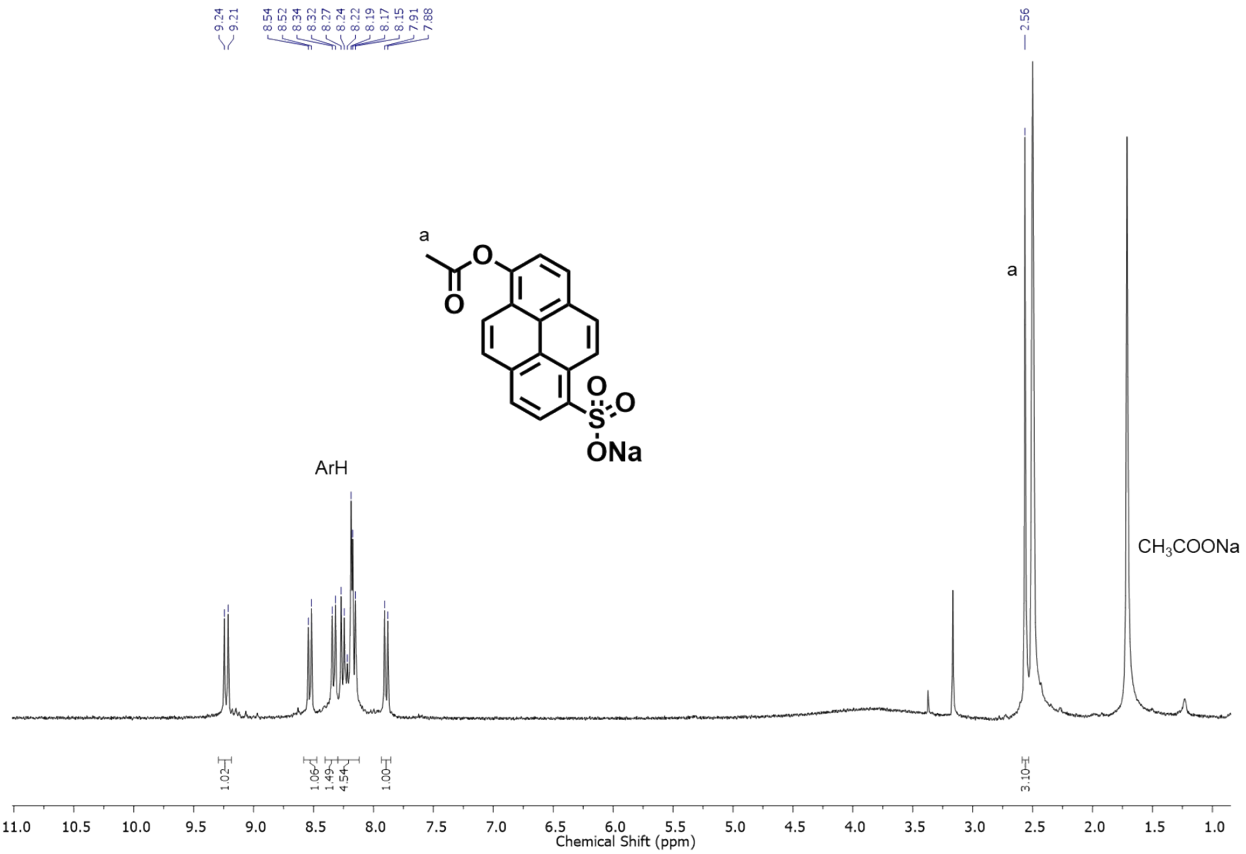

Figure S3. ^{1}H NMR spectrum of sodium 6-acetoxypyrene-1-sulphonate in DMSO-d6.

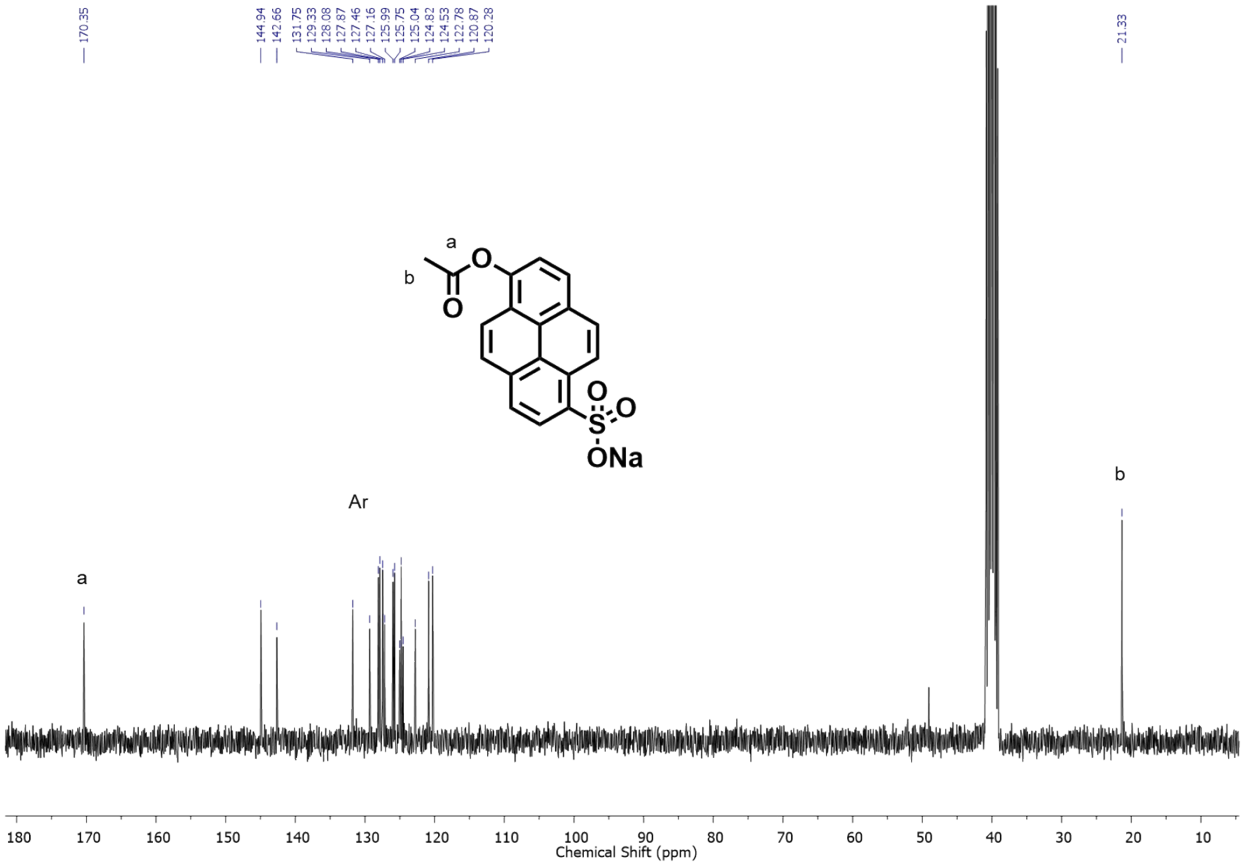

Figure S4. ^{13}C NMR spectrum of sodium 6-acetoxypyrene-1-sulphonate in DMSO-d6.

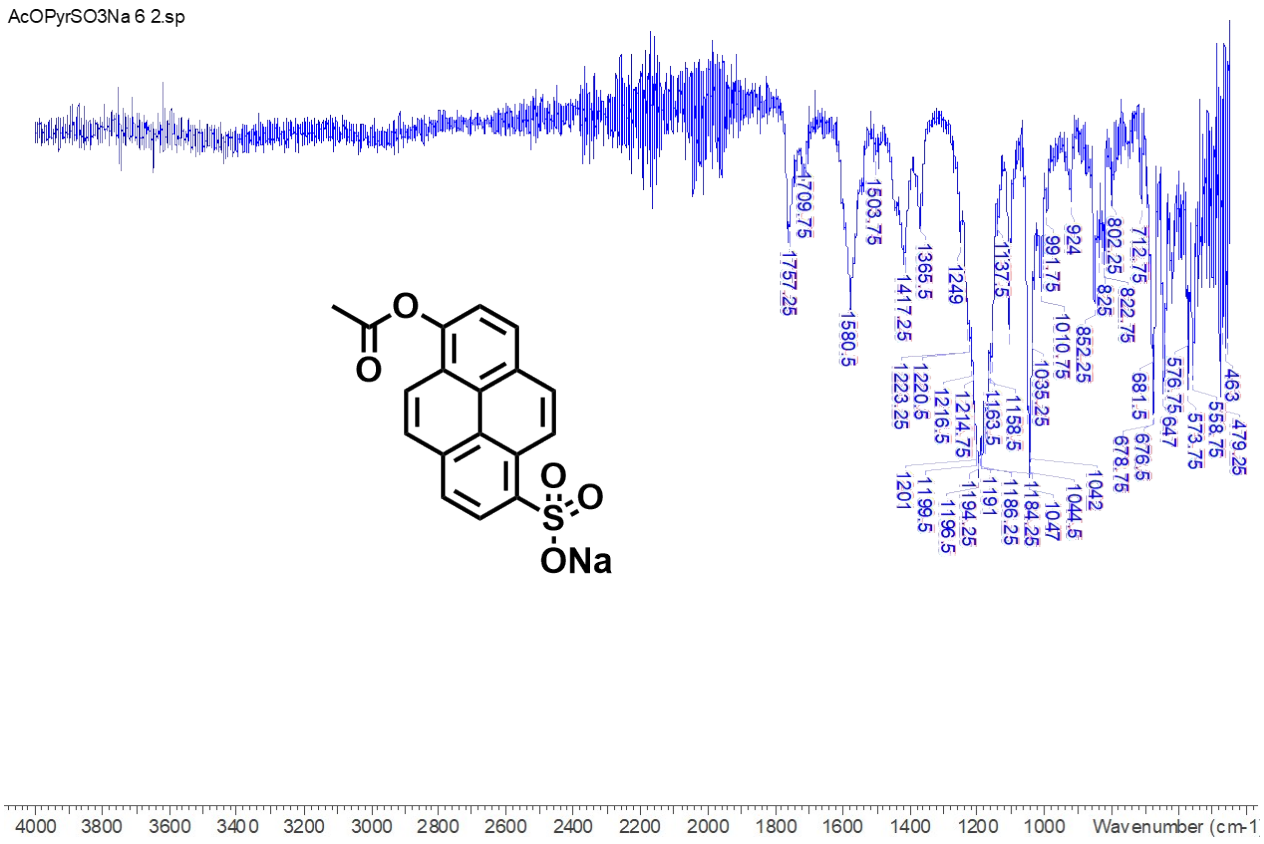

Figure S5. FT-IR spectrum of sodium 6-acetoxypyrene-1-sulphonate.

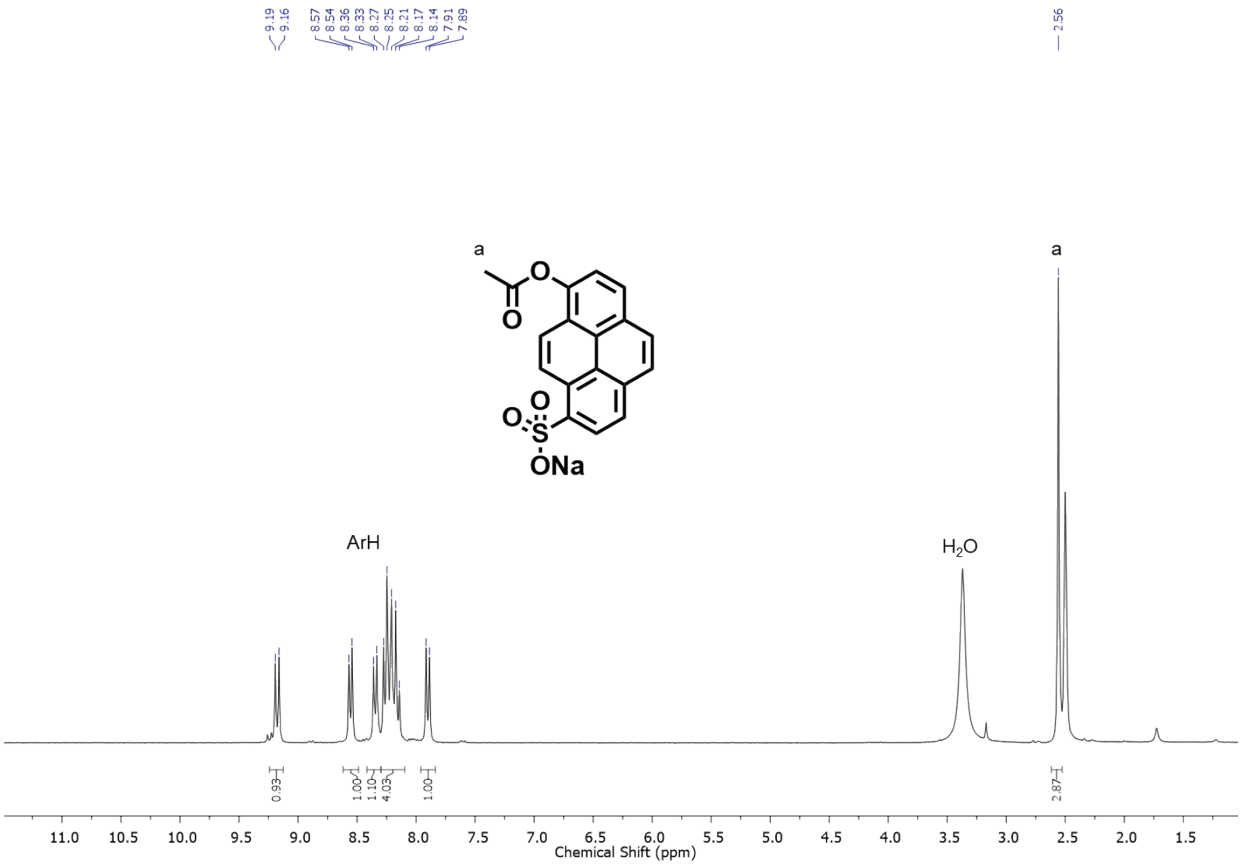

Figure S6. ^{1}H NMR spectrum of sodium 8-acetoxypyrene-1-sulphonate in DMSO-d6.

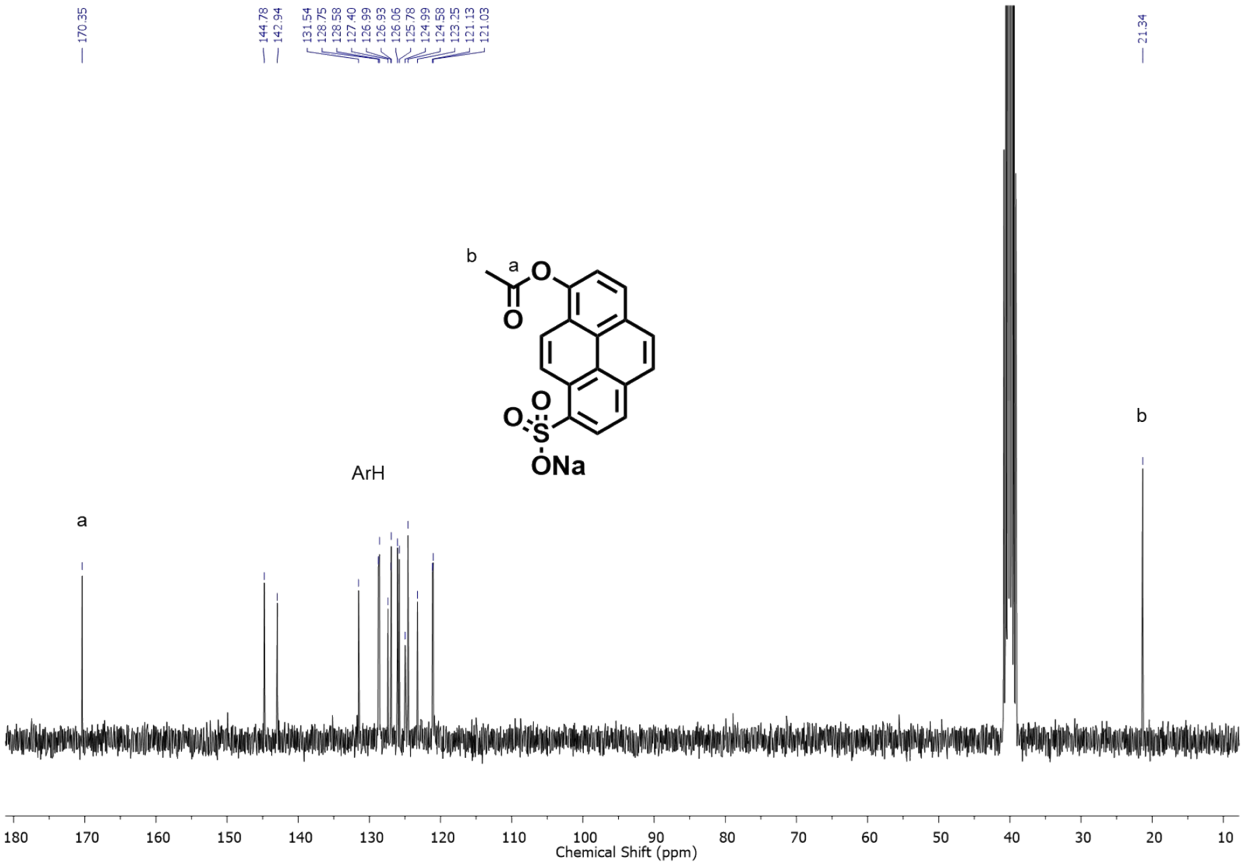

Figure S7. ^{13}C NMR spectrum of sodium 8-acetoxypyrene-1-sulphonate in DMSO-d6.

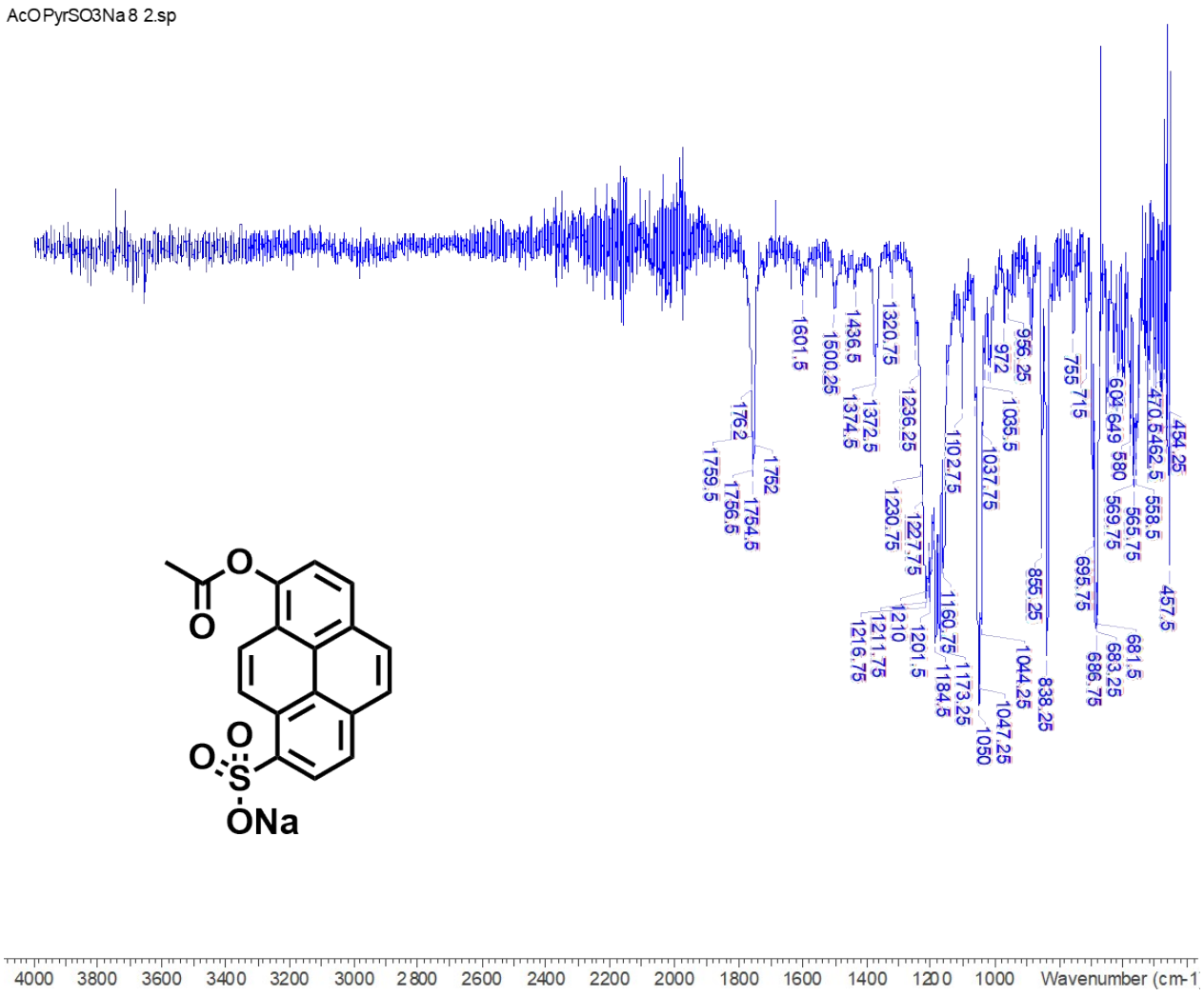

Figure S8. FT-IR spectrum of sodium 8-acetoxypyrene-1-sulphonate.

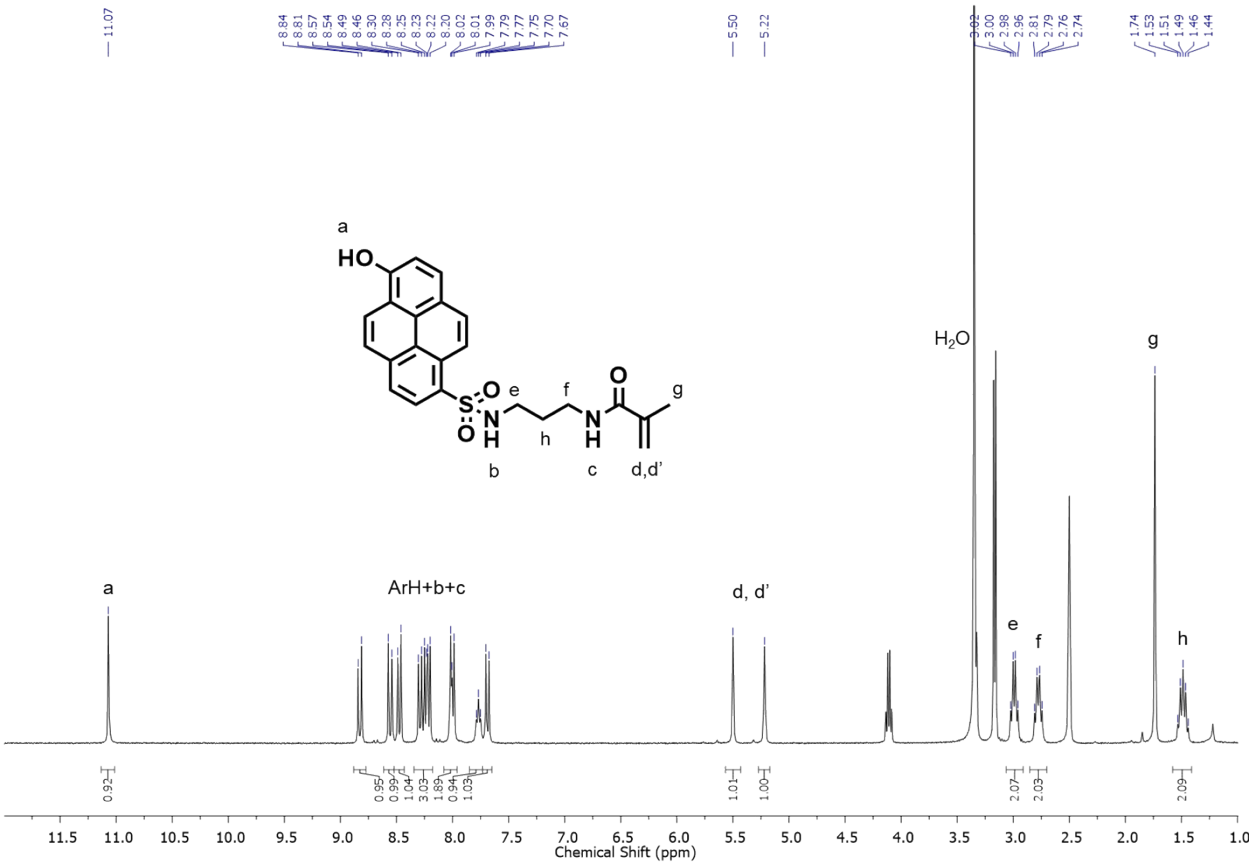

Figure S9. ^{1}H NMR spectrum of *N*-(3-((6-Hydroxypyrene)-1-sulfonamido)propyl)methacrylamide (HPSAPMA) in DMSO-d6.

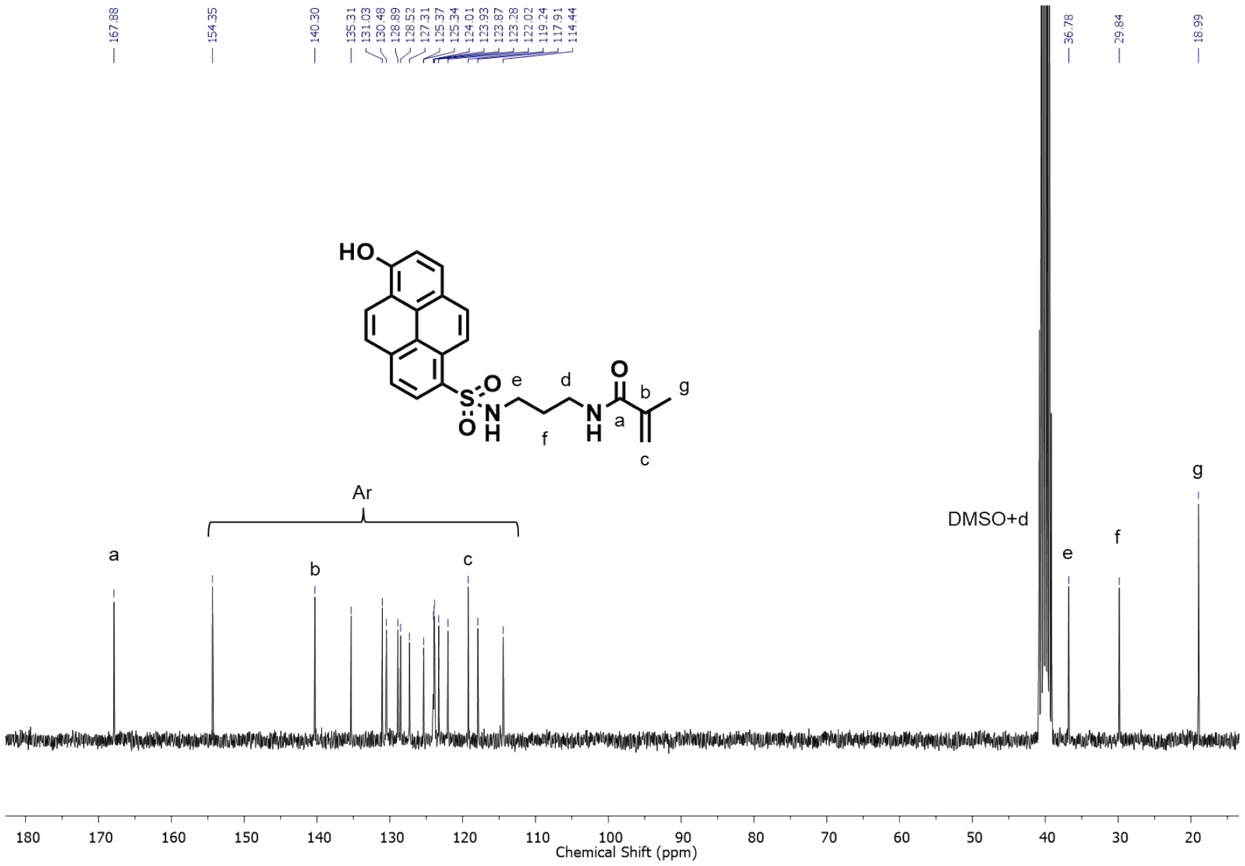

Figure S10. ^{13}C NMR spectrum of *N*-(3-((6-Hydroxypyrene)-1-sulfonamido)propyl)methacrylamide (HPSAPMA) in DMSO-d6.

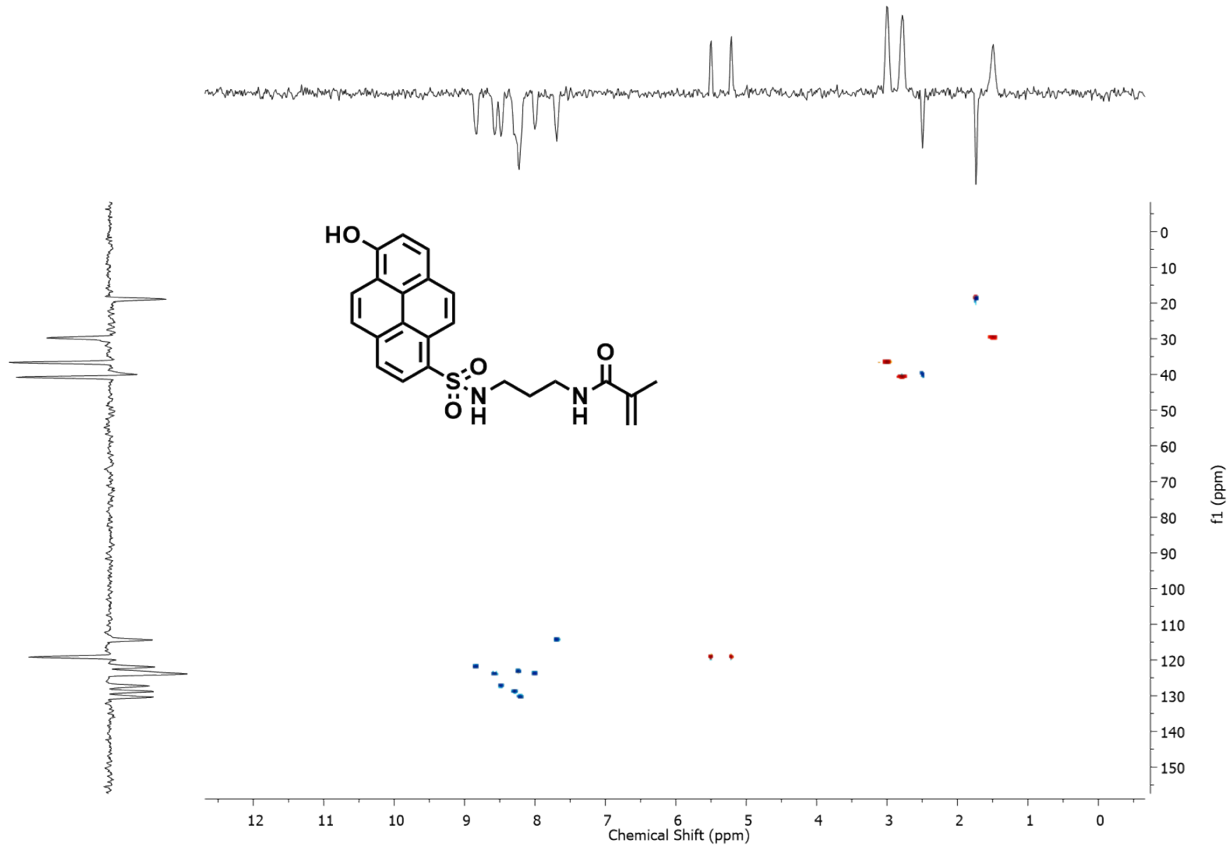

Figure S11. ^{1}H-^{13}C DEPT-HSQC spectrum of *N*-(3-((6-Hydroxypyrene)-1-sulfonamido)propyl)methacrylamide (HPSAPMA) in DMSO-d6.

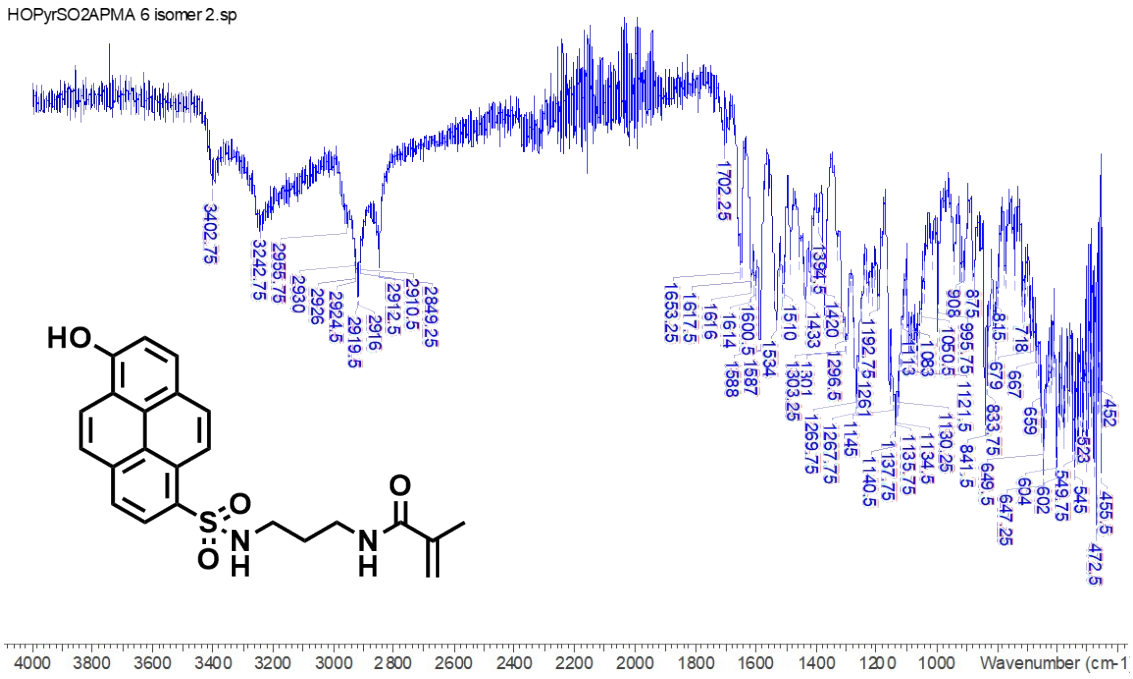

Figure S12. FT-IR spectrum of *N*-(3-((6-Hydroxypyrene)-1-sulfonamido)propyl)methacrylamide (HPSAPMA).

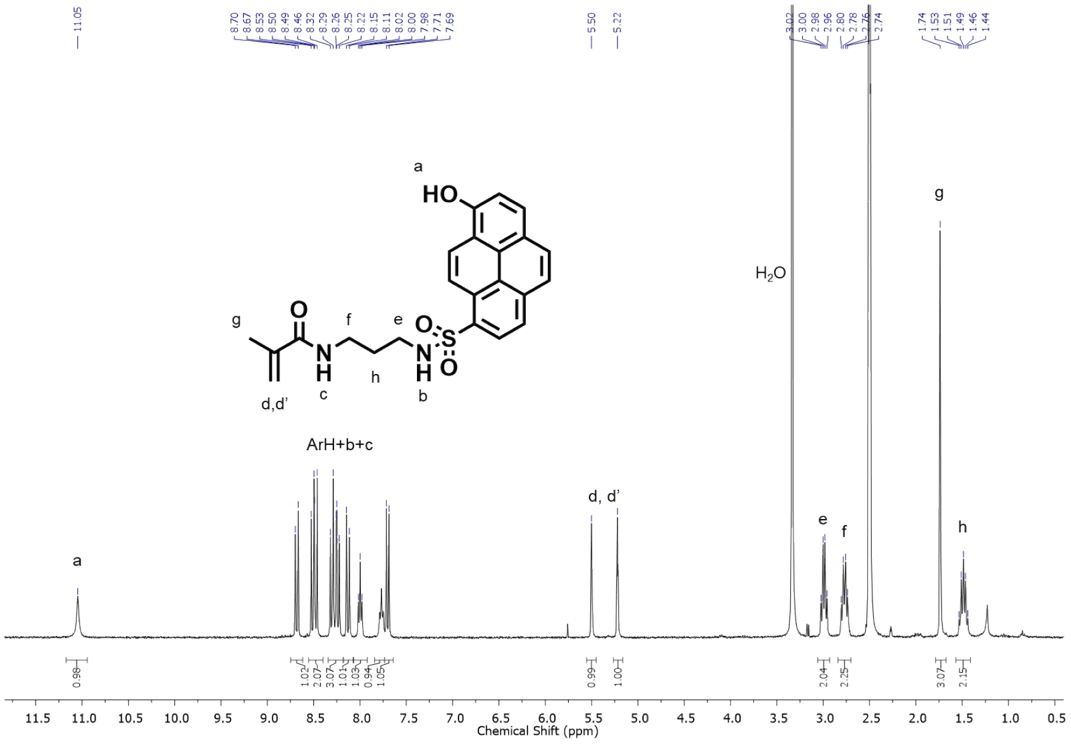

Figure S13. ^{1}H NMR spectrum of *N*-(3-((8-Hydroxypyrene)-1-sulfonamido)propyl)methacrylamide (HPSAPMA) in DMSO-d6.

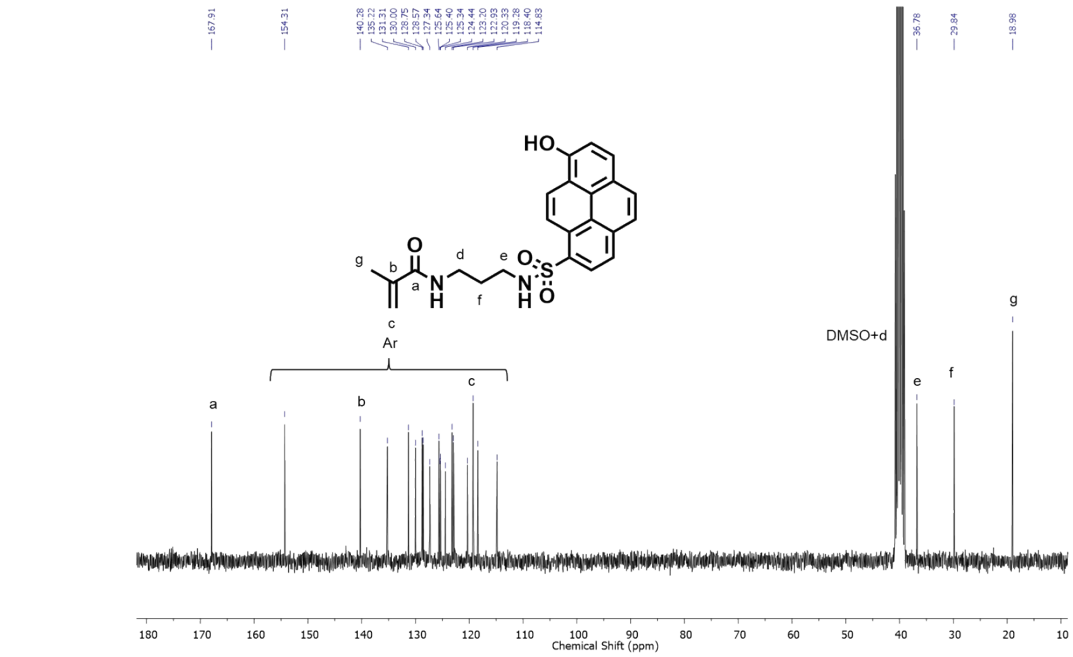

Figure S14. ^{13}C NMR spectrum of *N*-(3-((8-Hydroxypyrene)-1-sulfonamido)propyl)methacrylamide (HPSAPMA) in DMSO-d6.

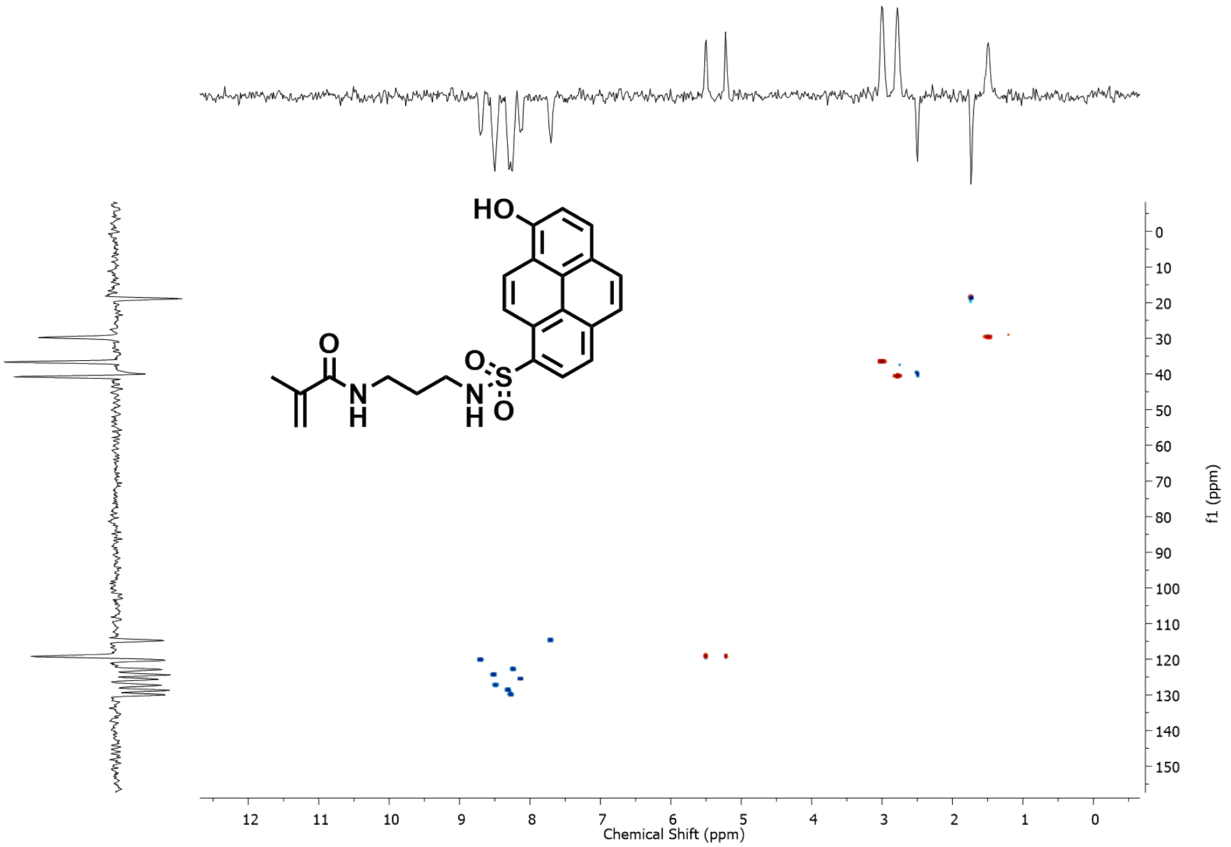

Figure S15. ^{1}H-^{13}C DEPT-HSQC spectrum of *N*-(3-((8-Hydroxypyrene)-1-sulfonamido)propyl)methacrylamide (HPSAPMA) in DMSO-d6.

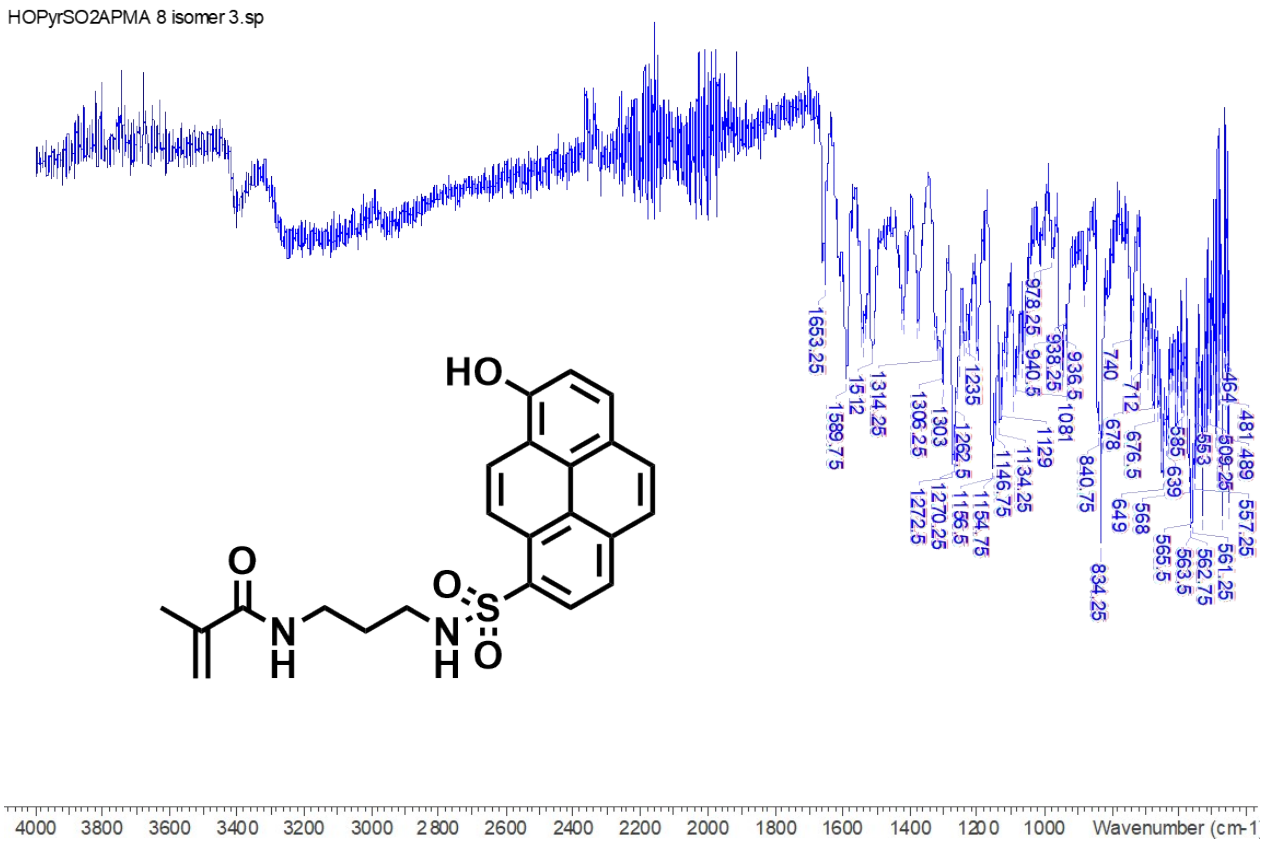

Figure S16. FT-IR spectrum of *N*-(3-((8-Hydroxypyrene)-1-sulfonamido)propyl)methacrylamide (HPSAPMA).

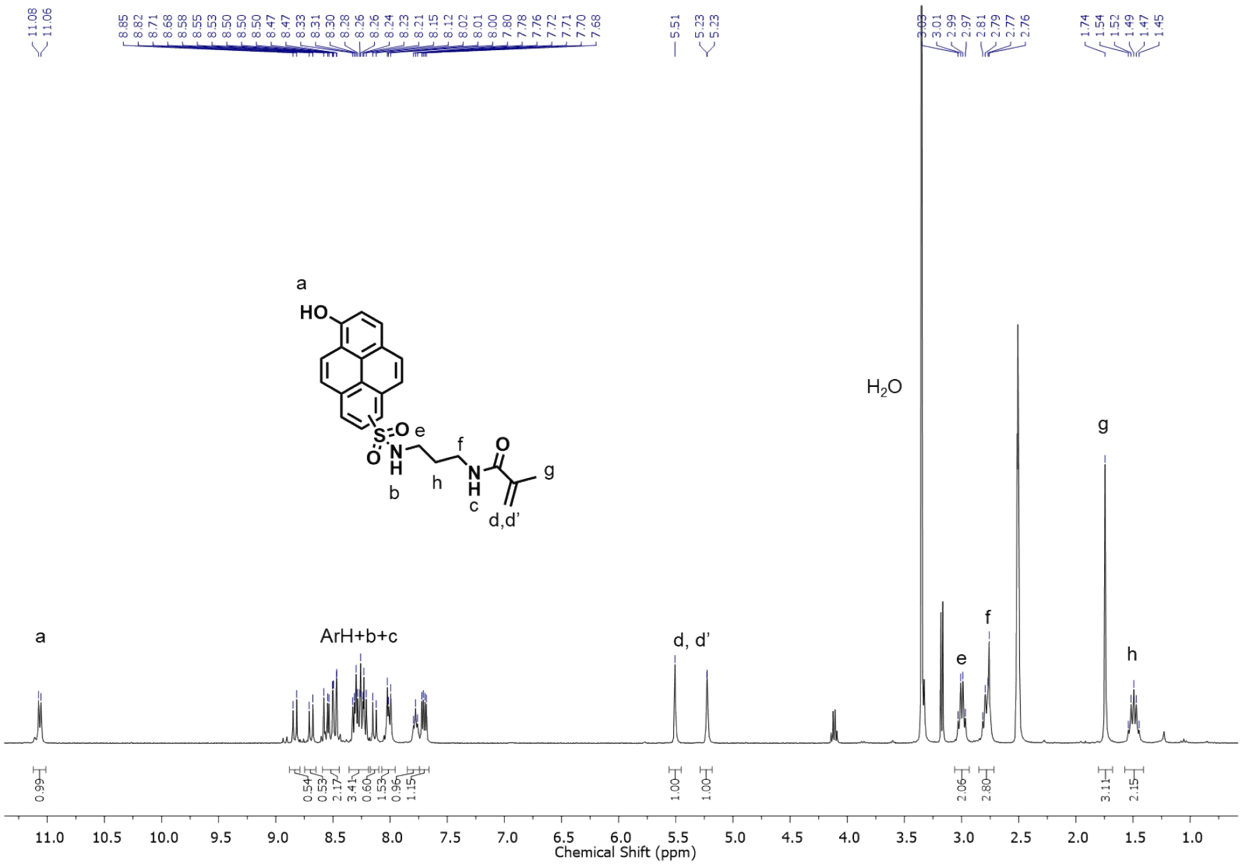

Figure S17. ^{1}H NMR spectrum of *N*-(3-((6/8-Hydroxypyrene)-1-sulfonamido)propyl)methacrylamide (HPSAPMA, 1:1 mixture of 6 and 8 isomers) in DMSO-d6.

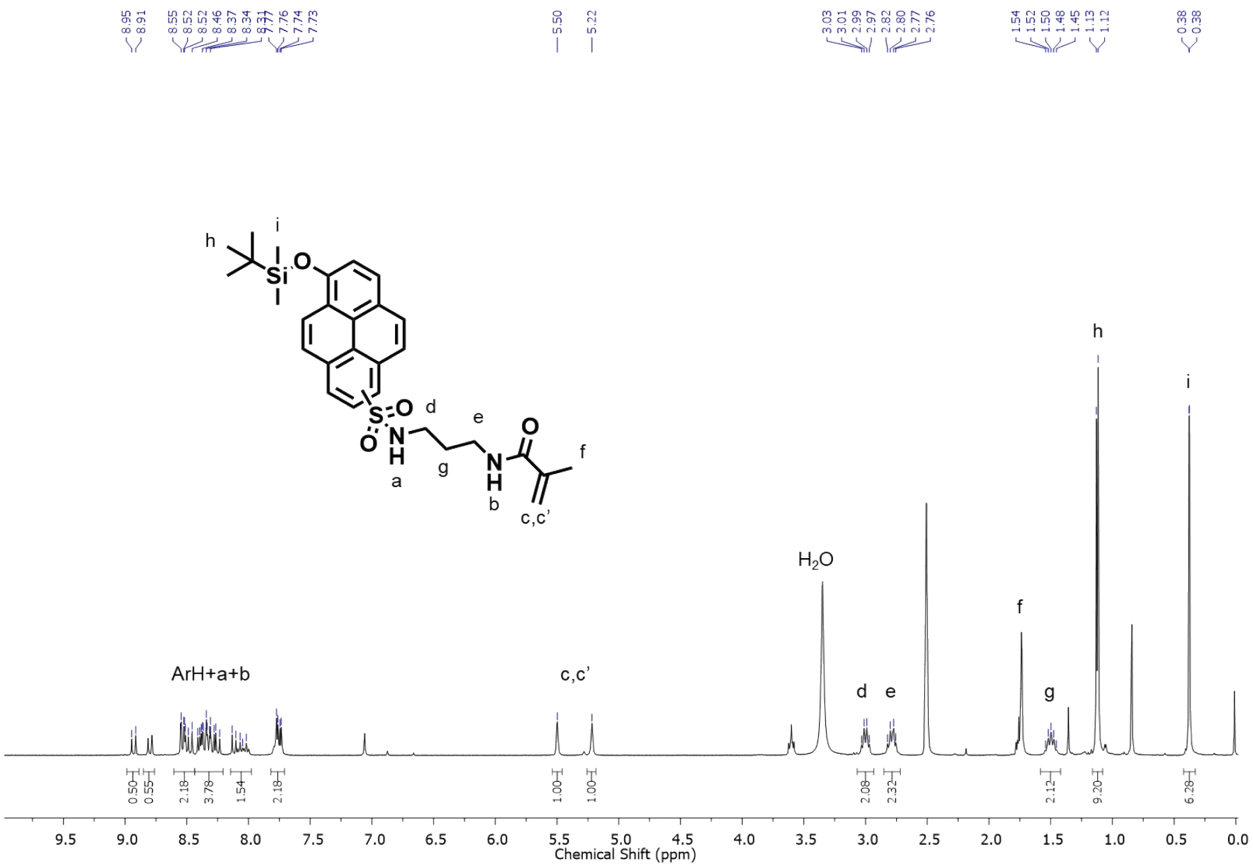

Figure S18. ^{1}H NMR spectrum of *N*-(3-((6/8-((Tert-butyldimethylsilyl)oxy)pyrene)-1-sulfonamido)propyl)methacrylamide (tHPSAPMA, 1:1 mixture of 6 and 8 isomers) in DMSO-d6.

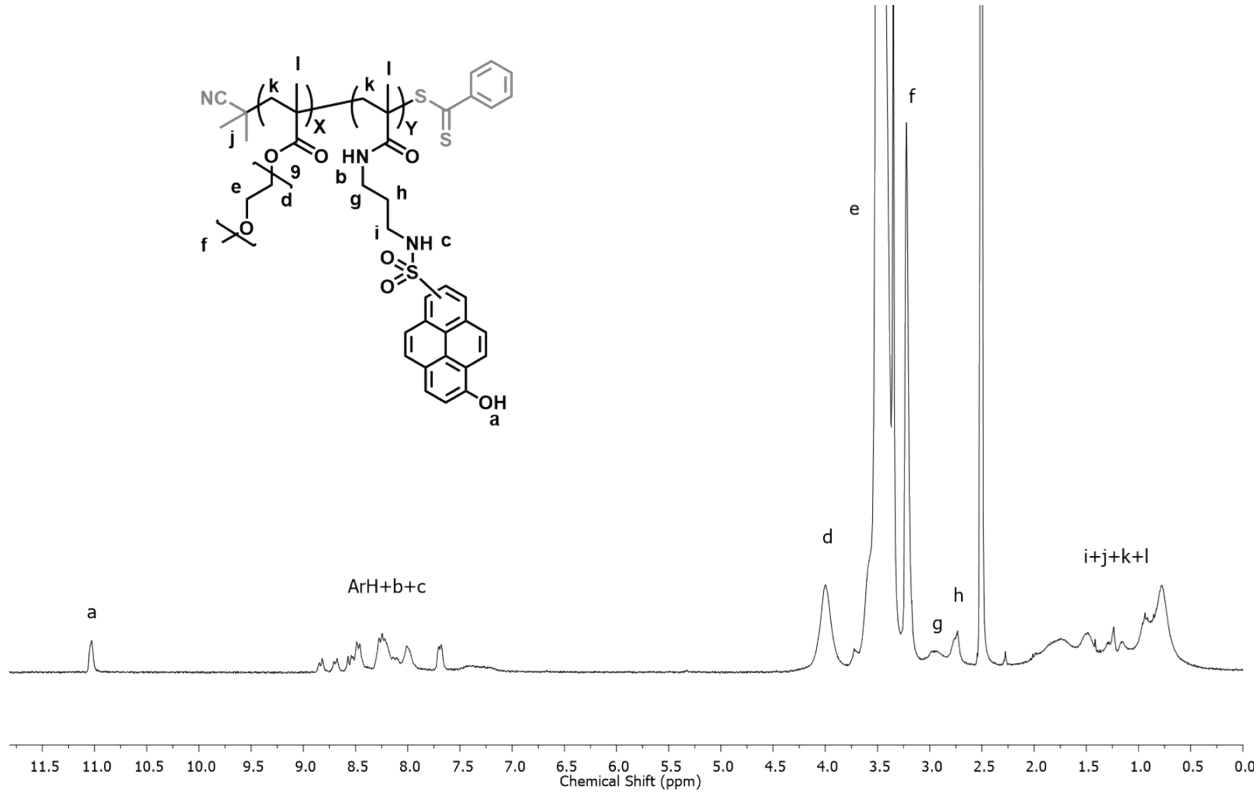

Figure S19. ^{1}H NMR spectrum of P[$(OEG_9MA)_{0.78}$-*co*-$HPSAPMA_{0.22}$] in DMSO-d6.

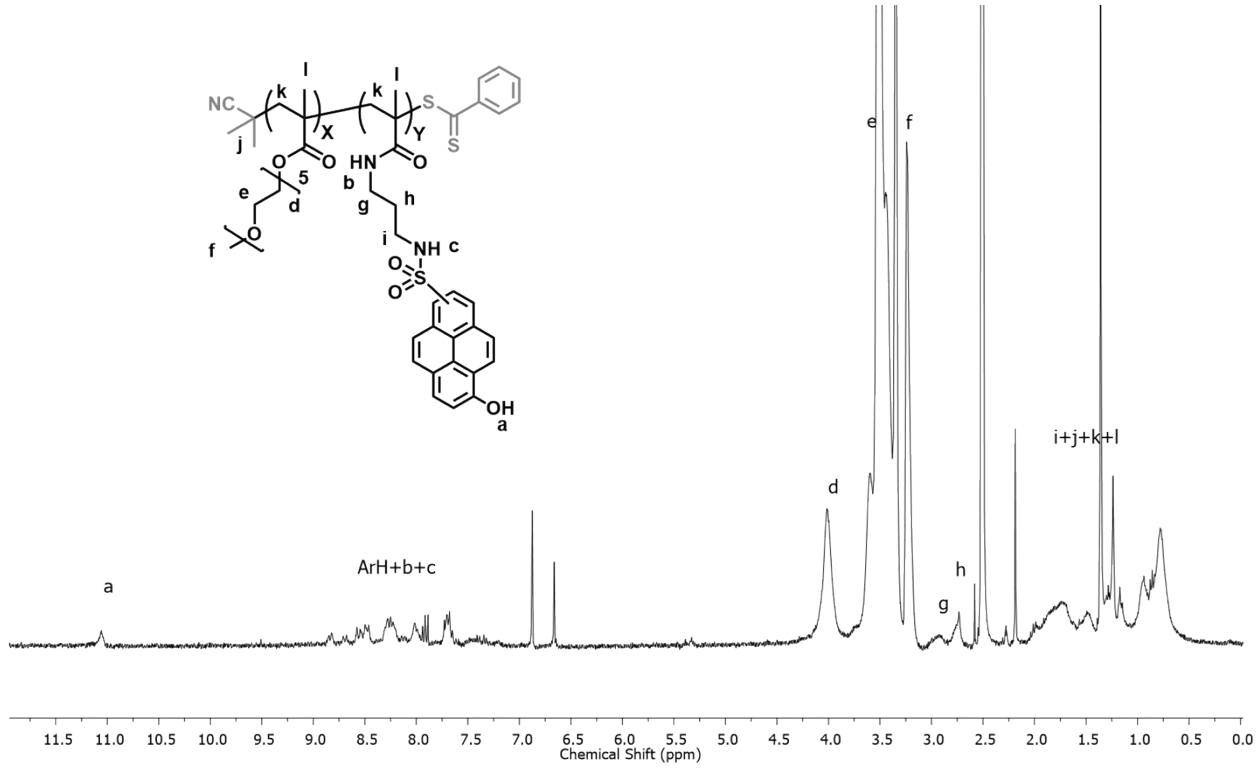

Figure S20. ^{1}H NMR spectrum of P[$(OEG_5MA)_{0.81}$-*co*-$HPSAPMA_{0.19}$] in DMSO-d6.

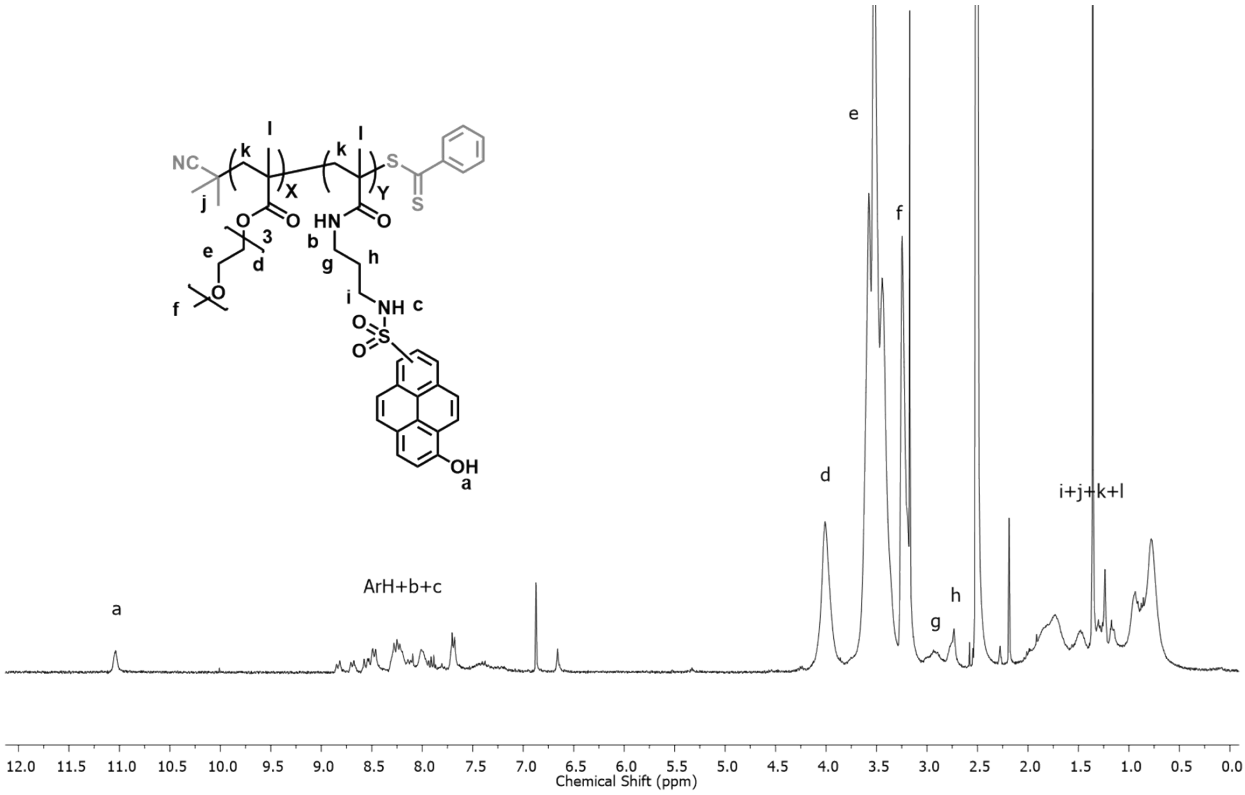

Figure S21. ^{1}H NMR spectrum of P[$(OEG_3MA)_{0.86}$-*co*-$HPSAPMA_{0.14}$] in DMSO-d6.

Spectroscopic Studies

For pH titration experiments, a stock solution was prepared by dissolving 1 mg of the polymer in 1 mL of DMSO. 20 µL from the stock was added to a 2100 µL of buffer in a quartz cell (giving a concentration for the pyrenol unit of ~4.1 µM) and mixed thoroughly for 30 seconds following which absorption, emission and excitation spectra were recorded. For pH range from 1.2-3.4 glycine-HCl buffers were used whereas for the preparation of pH ranging from 4.0-8.0 phosphate buffers were used. Glycine-NaOH buffers were used to prepare solutions with pH ranging from 8.5 to 10.0. Commercially available buffer solutions from Carl Roth were used for measurements in pH 11, 12 and 13. For measurements at pH 1, a 0.1 (M) HCl solution was used instead.

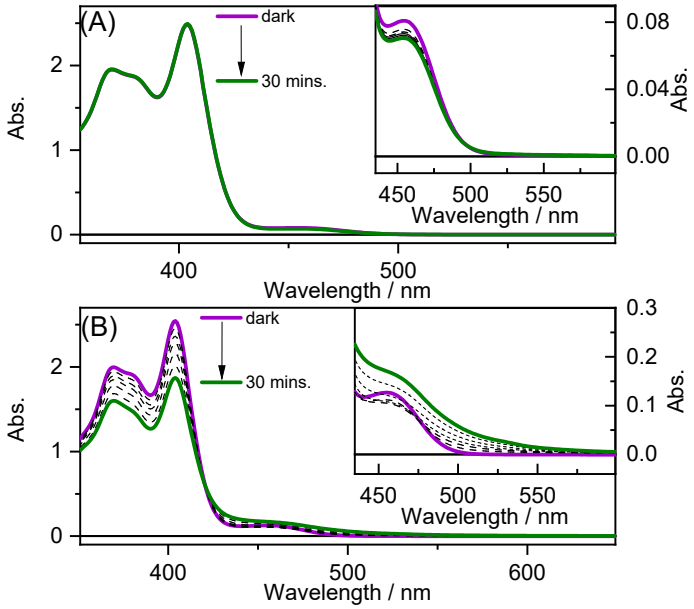

Figure S22. (A) UV/vis absorption spectra of trisodium 8-hydroxypyrene-1,3,6-trisulfonate (HPTS, C=140 μM) in inert water at different illumination times with a LED at 405 nm. Inset shows slight changes in the absorption spectra which is likely a consequence of photo-bleaching. (B) UV/vis absorption spectra of HPTS (C=140 μM) in aerated water at different illumination times using a LED at 405 nm. Inset shows a formation of a broad band extending to 600 nm which is not observed in (A).

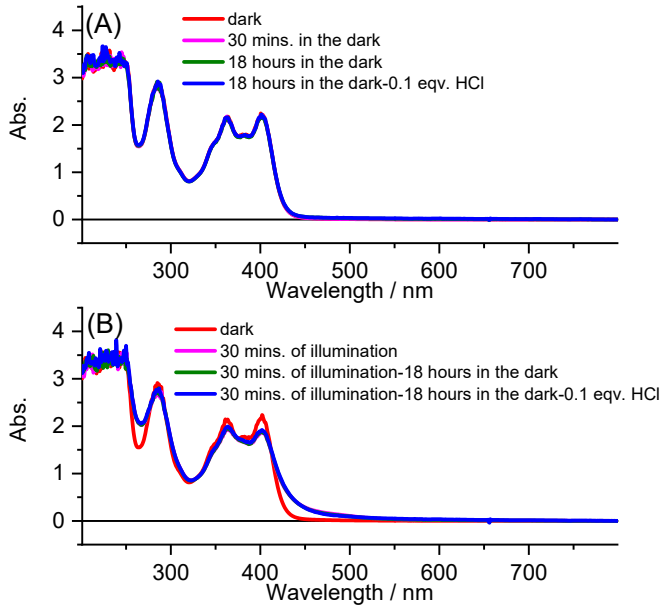

Figure S23. (A) UV/vis absorption spectra of P[$(OEG_9MA)_{0.75}$-co-$HPSAPMA_{0.25}$] (C=150 μM) recorded at different times in the absence of light. The unchanging absorption spectra over time indicates that the changes observed in (B) is due to light triggered reactions. (B) UV/vis absorption spectra of P[$(OEG_9MA)_{0.75}$-co-$HPSAPMA_{0.25}$] (C=150 μM) recorded at 30 minutes after illumination (magenta) with a LED of 405 nm (power = 20 mW). Following illumination, the sample was kept in the dark for 18 hours. The unchanging absorption spectrum (green), indicates that the photo-product is stable. Moreover, upon addition of 0.1 equivalent HCl (blue), the spectrum does not revert back to the absorption spectrum observed prior to illumination, indicating that the species is may not be a pyrenolate anion.

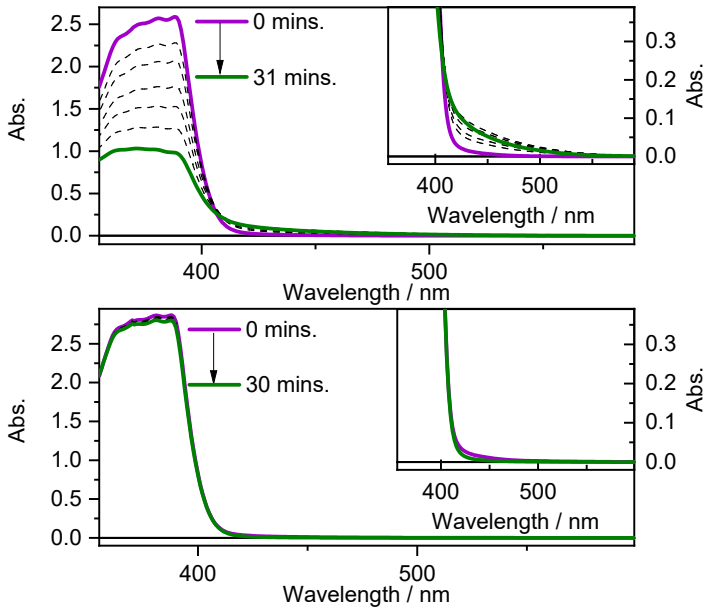

Figure S24. (A) UV/vis absorption spectra of the monomer *N*-(3-((6/8-Hydroxypyrene)-1-sulfonamido)propyl) methacrylamide (HPSAPMA, C=140 µM) in aerated tetrahydrofuran (THF) at different illumination times using a LED at 405 nm. Inset shows a formation of a broad band extending to 600 nm which is not observed in (B). (B) UV/vis absorption spectra of the monomer HPSAPMA (C=140 µM) in inert THF at different illumination times with a LED at 405 nm. Inset shows no change in the absorption spectra during the time course of illumination.

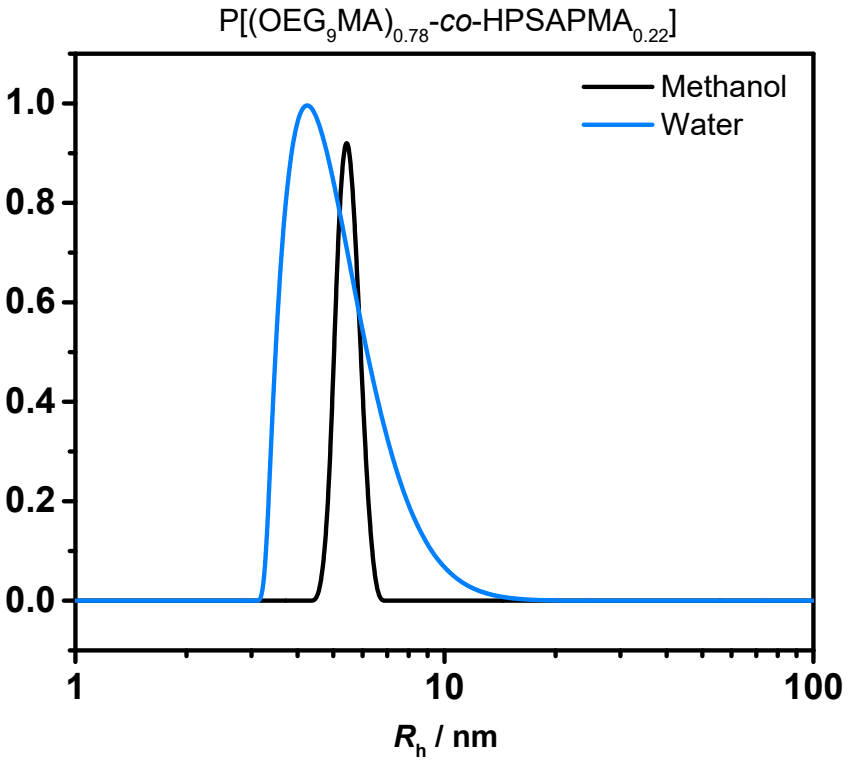

Figure S25: Distribution functions of the hydrodynamic radius R_h for P[$(OEG_9MA)_{0.78}$-*co*-$HPSAPMA_{0.22}$] solutions in water (5 mg/mL) and methanol (1 mg/mL).

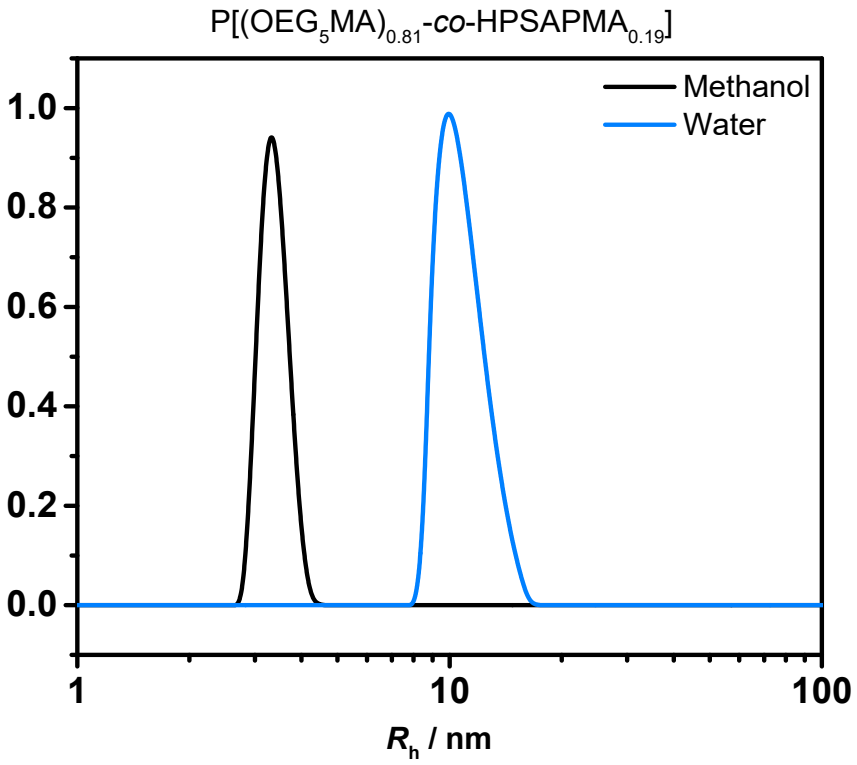

Figure S26: Distribution functions of the hydrodynamic radius R_h for P[$(OEG_5MA)_{0.81}$-*co*-$HPSAPMA_{0.19}$] solutions in water (1 mg/mL) and methanol (1 mg/mL).

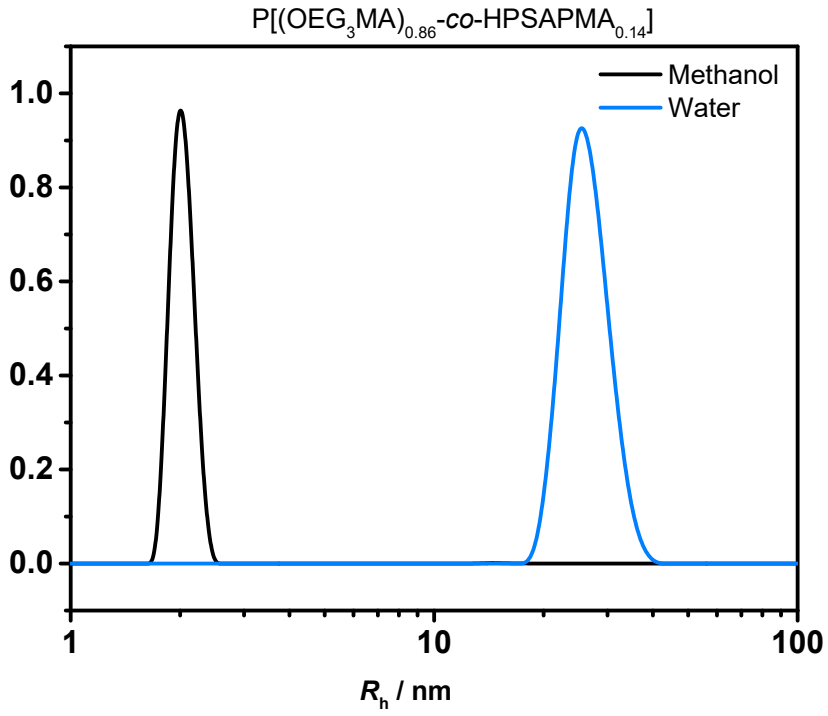

Figure S27: Distribution functions of the hydrodynamic radius R_h for P[$(OEG_3MA)_{0.86}$-*co*-$HPSAPMA_{0.14}$] solutions in water (1 mg/mL) and methanol (1 mg/mL).

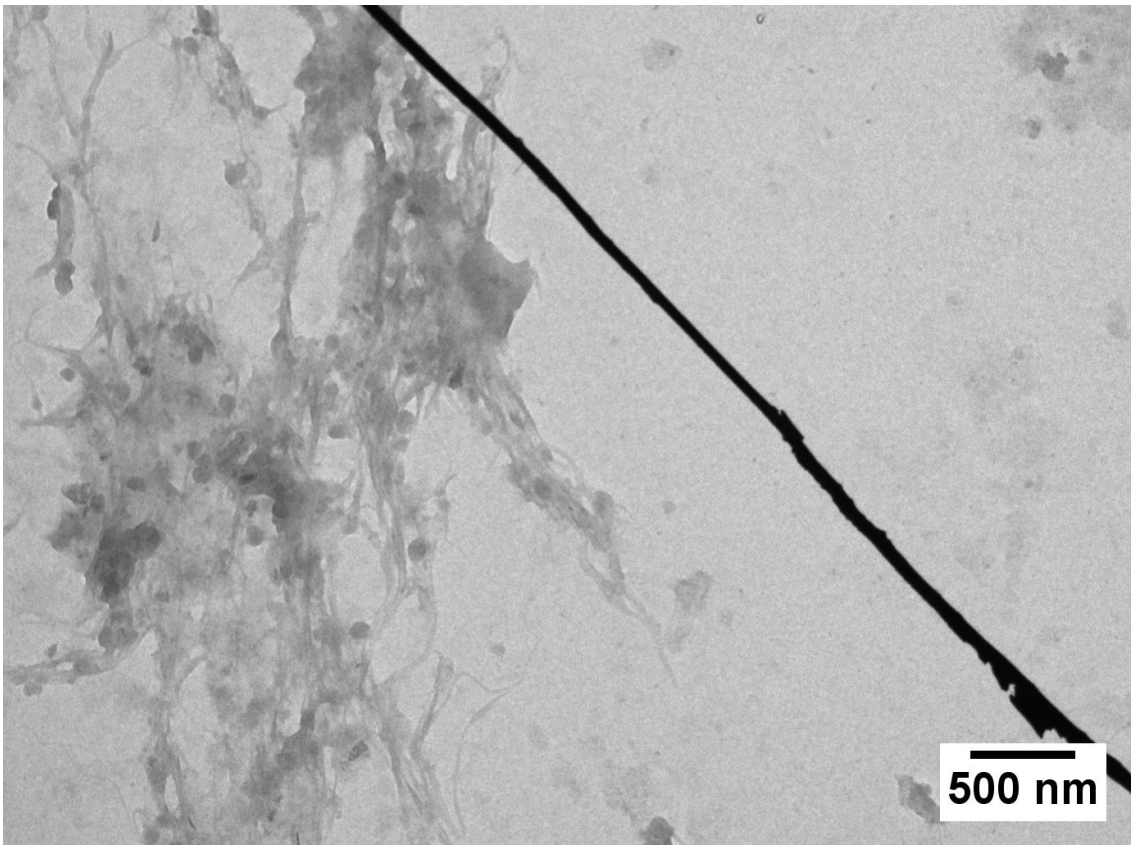

Figure S28: TEM micrograph of aggregates formed by P[$(OEG_3MA)_{0.9}$-*co*-$HPSAPMA_{0.1}$] in aqueous solution.

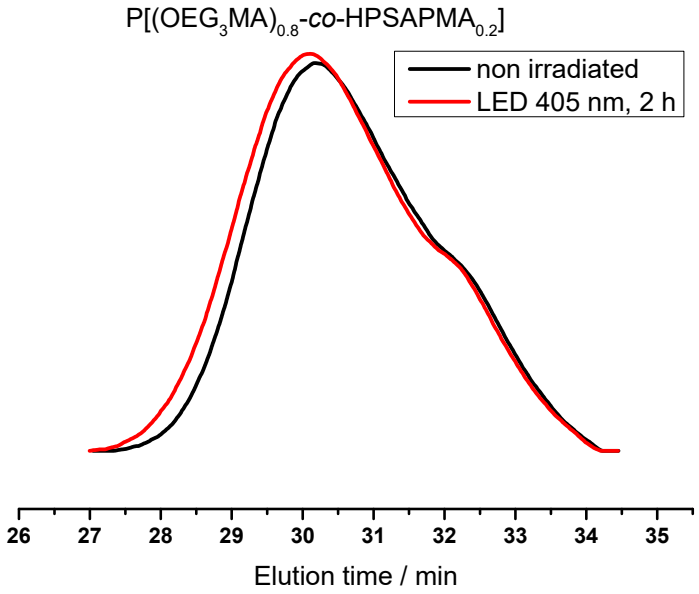

Figure S29. SEC (DMSO/LiCl) eluagrams of P[$(OEG_3MA)_{0.8}$-*co*-$HPSAPMA_{0.2}$] before and after illumination at (λ_{CWL} = 405 nm, t = 2 h, power = 40 mW). The graph serves to prove the absence of chain coupling under visible light exposure.

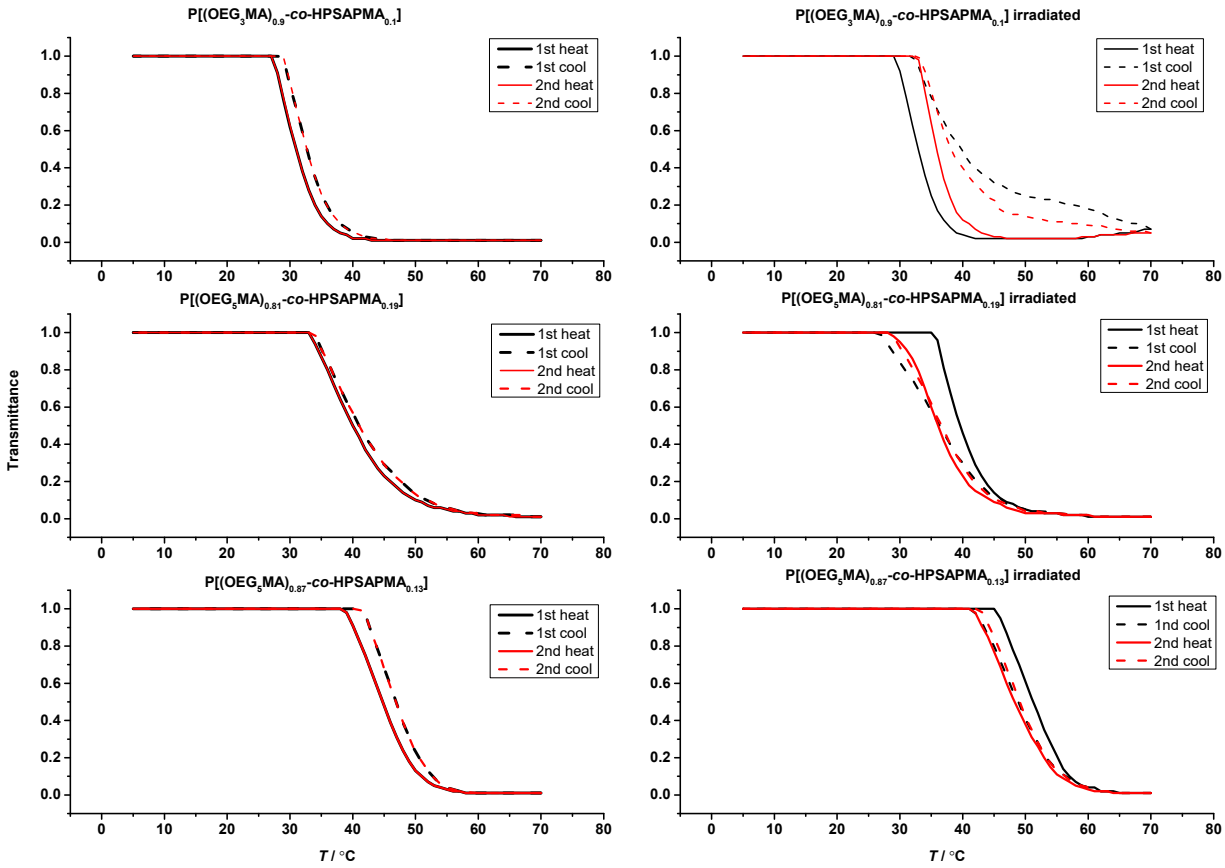

Figure S30. Transmittance vs. temperature plots for the polyphotoacids in aqueous solutions before and after irradiation. Two heating-cooling cycles.

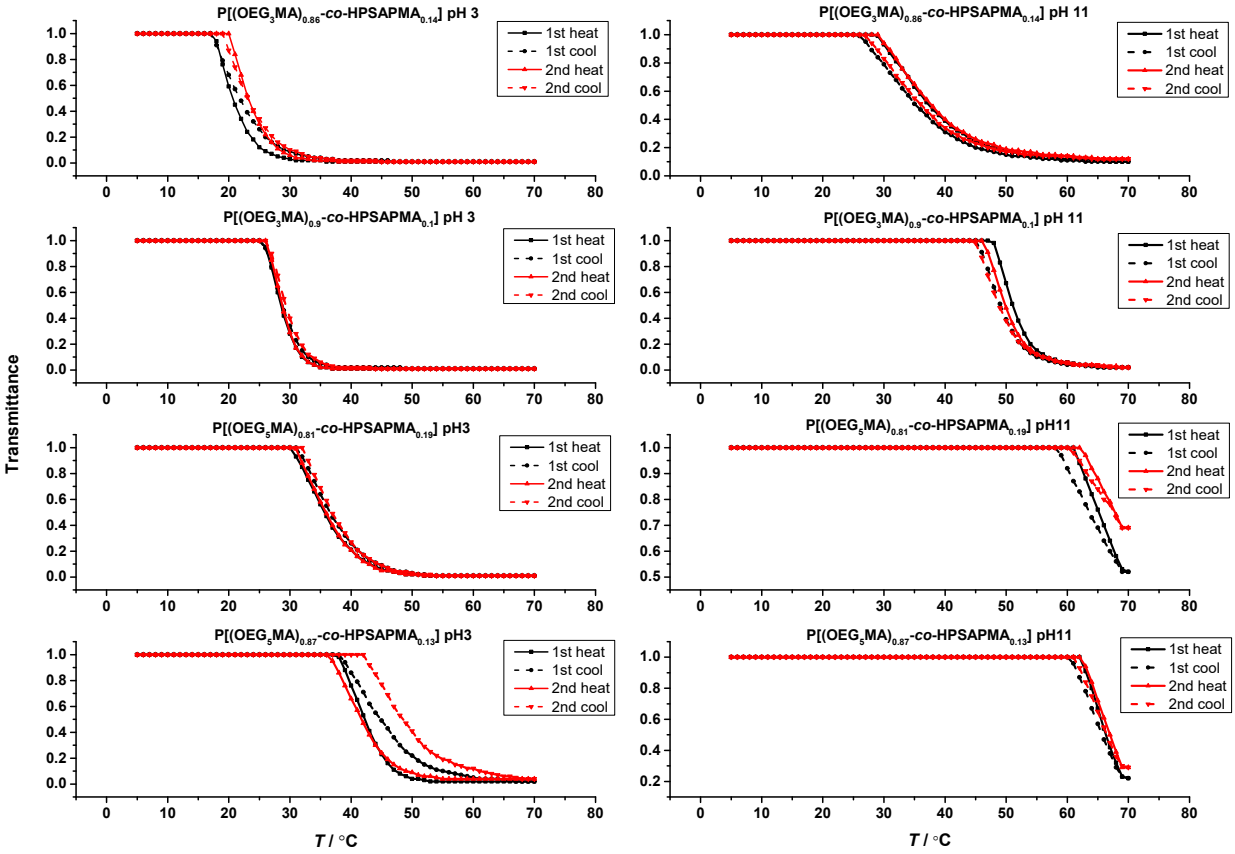

Figure S31. Transmittance vs. temperature plots for the polyphotoacids in aqueous solutions at pH3 and pH11. Two heating-cooling cycles.