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Polymer-solvent interactions as a tool to engineer material properties

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Experimental and Theoretical Methods

Materials

All chemicals were obtained from Sigma Aldrich and used as received unless otherwise specified. To remove inhibitors, oligo(ethylene glycol methyl ether methacrylate) (500 g mol^{-1}, OEGMA 500) and methacrylic acid (MAA) were passed through a basic alumina column immediately before use. Membranes for dialysis (molecular weight cut-off of 3500 Da) were purchased from Thermo Fisher Scientific.

Characterization

^{1}H NMR (400 MHz) spectra was recorded using a Bruker Ascend 400 spectrometer using DMSO-d_6 as solvent. UV−vis measurements were conducted on an GBC Scientific Equipment Cintra 2020 spectrophotometer using 3 mL quartz cuvettes and DMSO as solvent. Gel permeation chromatography (GPC) spectra were recorded using an Agilent 1260 Infinity II system with a flow rate of 2.000 mL/min and a dimethylacetamide as the solvent phase, utilising polystyrene standards. Dynamic mechanical analysis (DMA) was performed using a Netzsch DMA242E Artemis dynamic mechanical analyzer. Samples were cut from a bulk, 0.45 mm thick, films. The test was run using a tensile holder under dynamic thermal conditions from 0 to 80 ºC (heating rate: 1 °C /min) at a frequency of 2 Hz, and under isothermal conditions from 0.33 to 100 Hz at room temperature.

Synthesis of poly(methacrylic acid-*co*-OEGMA)

OEGMA (500 g/mol, 6.28 mL), MAA (2.24 mL), 2-cyano-2-propyl benzodithioate (CDTPA) (56.5 mg) as chain transfer agent, and AIBN (6.72 mg) as initiator, were dissolved in anhydrous DMSO (6.0 mL). The flask was sealed with a rubber septum and the solution was deoxygenated by sparging with nitrogen gas for 20 min. After 24 h at 65 °C, the reaction was cooled to 0 °C in an ice batch and exposed to air. The viscous polymer solution was diluted with 1 mL DMF and precipitated into 10 x diethyl ether (by volume) three times, purified by dialysis in water for 72 h and freeze dried to remove water before post-functionalization.

Representative synthesis of poly(methacrylic acid -co-anthracene methacrylate-co-oligoethylene glycol methacrylate)

Poly(MAA-*co*-OEGMA) (500 mg (2.20 mmol of methacrylic acid units)), anthracene methanol (167 mg, 2.20 mmol), 4-(dimethylamino)pyridine (DMAP) (98 mg, 0.8 mmol) and DCC (413 mg, 2.00

mmol) were separately dissolved in anhydrous DMF (5.0 mL) and stirred at room temperature for 24 h in dark conditions. After syringe filtration, the liquid was collected and precipitated into 10 x diethyl ether (by volume). The functionalized copolymer was filtered, collected and dried under vacuum.

Solvent Vapour Swelling

Each polymer was dissolved in DMF and cast into a film which was fully dried *in vacuo* at 50 ºC. These films were then cut, weighed and placed into individual vials within which contained a second, open, vial with 2.5 mL of solvent (water, THF or DMF). The vial was sealed and left in dark, atmospheric conditions for 72 hours, after which the sample was weighed again to measure solvent uptake (**Table S1**).

Table S1: Polymer swelling as a percentage of dry weight for each of the solvents

	Polymer swelling as a % increase of dry weight		
Anthracene content (%)	**Water (H_2O, 18 g mol^{-1})**	**Tetrahydrofuran (THF, 72 g mol^{-1})**	**Dimethylformamide (DMF, 73 g mol^{-1})**
2	12	52	63
4	8.1	40	51
20	4.4	20	54

Molecular Dynamics Simulations

All simulations were performed using GROMACS 2018.3[1] with the GROMOS 54a7[2] force field under periodic boundary conditions. United atom parameters and co-ordinates for the monomers (ATB ID 583981 (anthracene), 582485 (MAA), 370656 (OEGMA)) were obtained using the Automated Topology Builder (ATB) and are publicly available on the ATB website.[3] The monomers were built into a 25-mer using the GROMACS 2018.3 package *pdb2gmx* as $PMAA_{20}$-$POEGMA_{5}$, $PMAA_{18}$-$POEGMA_5$-$PAnth_2$, $PMAA_{16}$-$POEGMA_5$-$PAnth_4$, $PMAA_{12}$-POEGMA5-$PAnth_8$ (the monomer sequence is outlined in table S2 below). Note that for $PMAA_{18}$-$POEGMA_5$-$PAnth_2$, the mean results of both sequences were combined after analysis. For each system, 20 identical polymers were randomly arranged in a 1000 nm^3 (10*10*10 nm) cubic box.

Table S2: *Sequence of monomer units in each 25-mer calculated*

Composition	Sequence
PMAA$_{20}$-POEGMA$_5$ (M$_{20}$-O$_5$)	M$_2$ **P** M$_4$ **P** M$_4$ **P** M$_4$ **P** M$_4$ **P** M$_2$
PMAA$_{18}$-POEGMA$_5$-PAnth$_2$ (M$_{18}$-O$_5$-A$_2$)	M$_2$ **P** M$_4$ **P** M ***A*** M$_3$ **P** M ***A*** M$_3$ **P** M$_4$ **P** M$_2$
PMAA$_{18}$-POEGMA$_5$-PAnth$_2$	M$_2$ **P** M ***A*** M$_3$ **P** M$_4$ **P** M$_4$ **P** M ***A*** M **P** M$_2$
PMAA$_{16}$-POEGMA$_5$-PAnth$_4$	M$_2$ **P** M ***A*** M$_3$ **P** M ***A*** M$_3$ **P** M ***A*** M$_3$ **P** M ***A*** M **P** M$_2$
PMAA$_{12}$-POEGMA5-PAnth$_8$	M$_2$ **P** M ***A*** M ***A*** **P** M ***A*** M ***A*** **P** M ***A*** M ***A*** **P** M ***A*** M ***A*** **P** M$_2$

Each system was explicitly solvated using either water, THF or DMF. The simple point charge (SPC) model was used for water. The overall system charge was neutralized using sodium and chloride ions. The temperature of each system was maintained at 300 K using a v-rescale thermostat with a coupling constant of 0.1 ps. The pressure was maintained at 1 Bar using an isotropic Berendsen barostat with an isothermal compressibility of 4.5x10^{-5} bar and a coupling constant of 0.5 ps. Long-range electrostatics were calculated using the particle-mesh Ewald method, implementing a 1 nm cutoff. The LINCS algorithm was used to constrain covalent bond lengths.

Prior to production simulations, all systems were minimized using a steepest descent for 10,000 steps and equilibrated for 2 ns at constant pressure and temperature. Production simulations were run for 500 ns with a 2 fs timestep. For each system, replicate systems were prepared in triplicate systems in which the initial position of molecules was randomised to remove conformational bias. To initiate each system, random velocities were assigned. Data was collected at 0.1 ns intervals and analysed using inbuilt GROMACS 2018.3 analysis tools and the python package MDTraj.[4] Images of trajectory frames were produced using VMD version 1.9.3.[5]

Quantum Mechanical Calculations

All calculations in this study were carried out using Gaussian 16.[6] Geometries were optimized in the gas phase, at the M06-2X/6-31+G(p) level of theory, followed by frequency calculations at the same level to confirm the nature of the calculated stationary points. All calculations are reported as Gibbs free energies (G) at the M06-2X/6-31+G(p) level of theory. Standard textbook formulae, based on the statistical thermodynamics of an ideal gas under the harmonic oscillator and rigid-rotor approximation, were used to determine the thermal and entropic corrections at 298.15 K and hence the gas-phase Gibbs free energies (G). Free energies of solvation (ΔG_{solv}) were calculated using the SMD/M06-2X/6-31+G(p) method in water, dimethylformamide and tetrahydrofuran. Using the thermocycle approach, free energies in solution were determined as the sum of the gas phase free energies with the corresponding free energies of solvation and the phase change correction term.

Polymer Characterisation

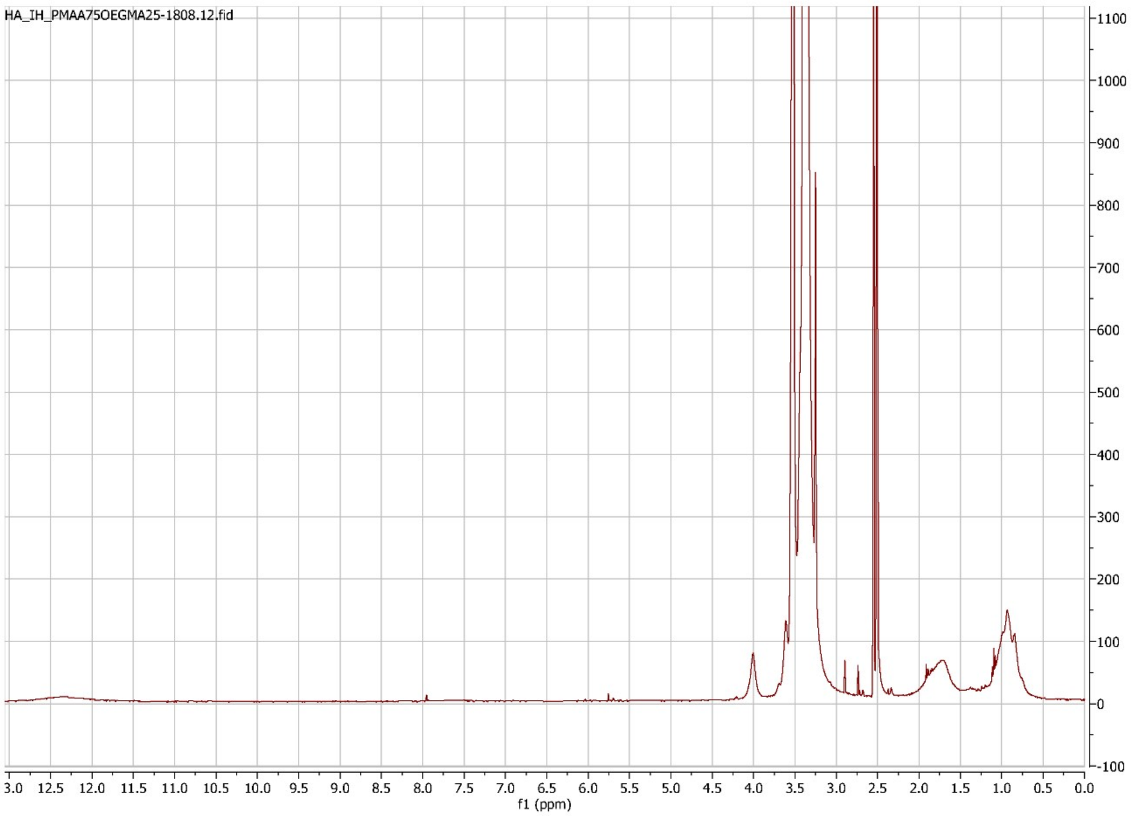

Figure 1. NMR Spectrum of poly(methacrylic acid-*co*-OEGMA)) in DMSO-d_6

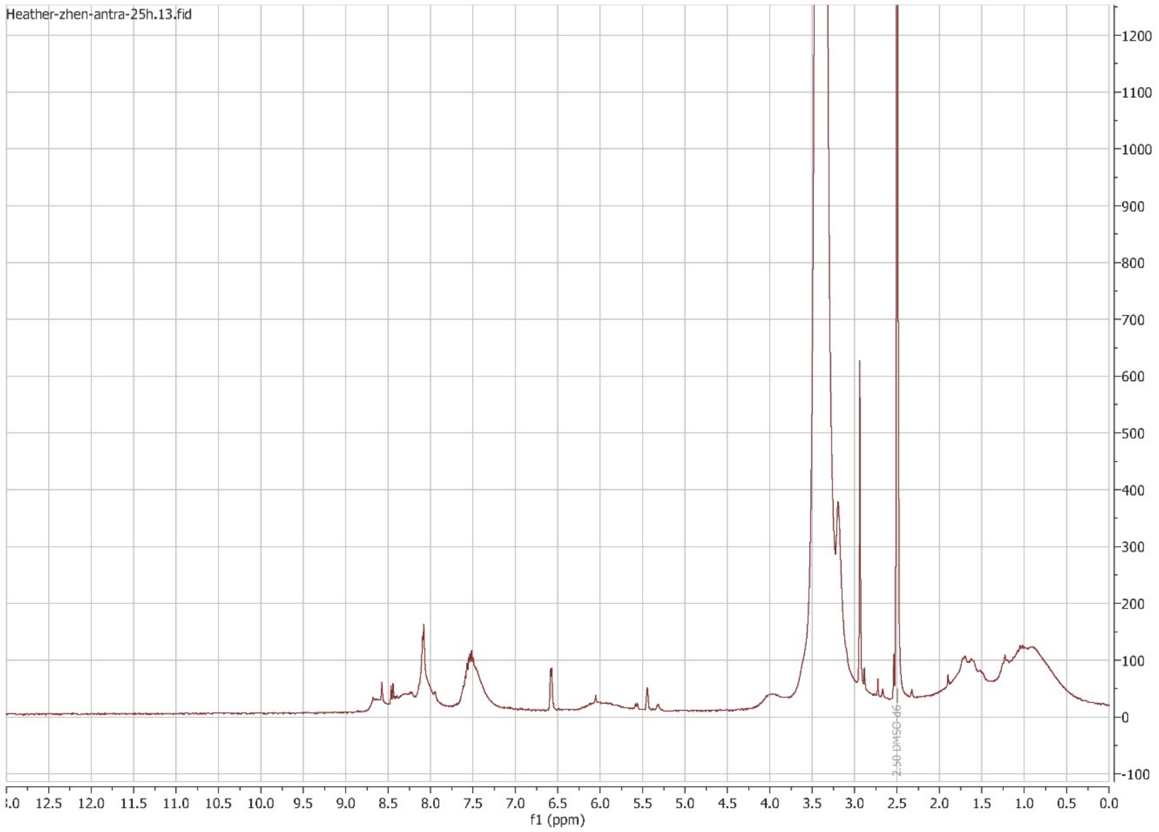

Figure 2. NMR Spectrum of post-functionalised poly(methacrlyic acid -co-anthracene methacrylate-co-oligoethylene glycol methacrylate) (as ($PMAA_{87}$-*co*-$POEGMA_{39}$-*co*-$PAnth_{31}$)) in DMSO-d_6

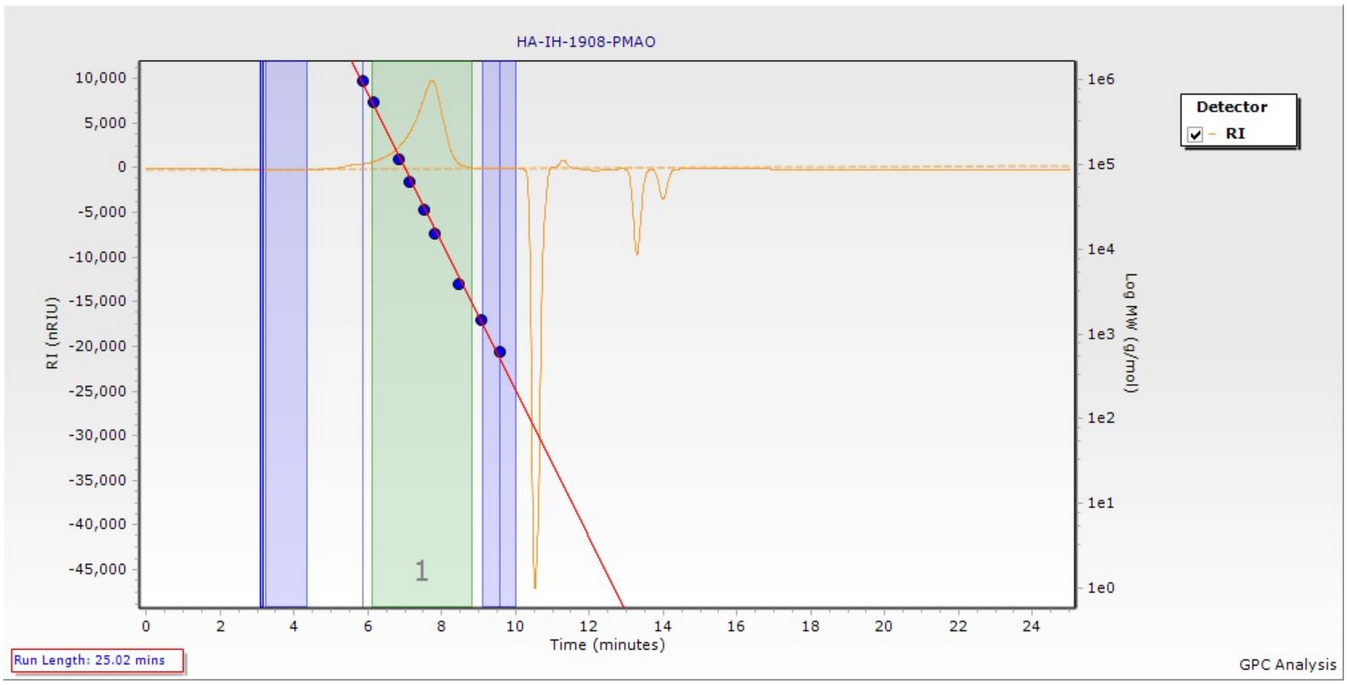

Figure 3. GPC Spectrum of poly(methacrylic acid-*co*-OEGMA) in DMAC

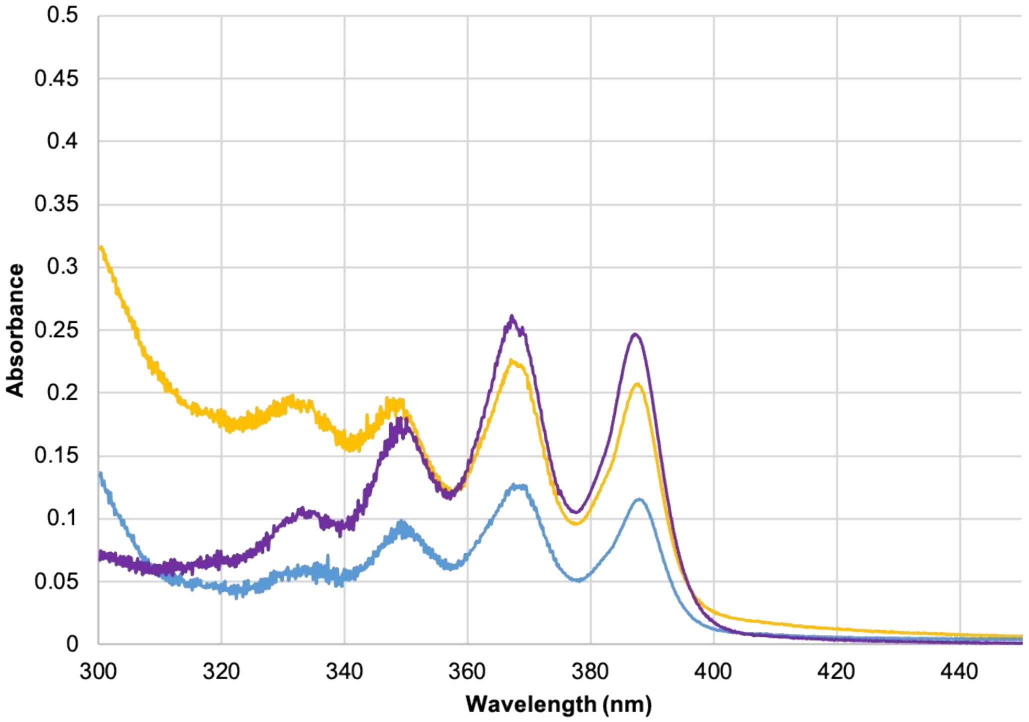

Figure 4. UV absorbance spectra of anthracene region of 1.5 mg of poly(methacrlyic acid -co-anthracene methacrylate-co-oligoethylene glycol methacrylate) samples in 3 mL DMSO. $PMAA_{115}$-*co*-$POEGMA_{39}$-*co*-$PAnth_3$ (blue) and $PMAA_{112}$-*co*-$POEGMA_{39}$-*co*-$PAnth_6$ (yellow) and ($PMAA_{87}$-*co*-$POEGMA_{39}$-*co*-$PAnth_{31}$) (purple, 10x dilution)

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