An investigation into thiol-ene surface chemistry of poly(ethylene glycol) acrylates, methacrylates and CCTP polymers *via* Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)

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Supplementary info

Experimental

Materials

All reagents and solvents were used as received unless stated otherwise. Rhodamine acrylate was prepared by modifying a known procedure[1] and characterisation matched common literature[2]. CoBF was prepared previously in the Haddleton group[3]. The molecular weight of protein α-keratin is 3.5 kDa.

Instruments and Analysis

All polymerisations were carried out using standard Schlenk line conditions, under inert atmosphere of nitrogen unless otherwise mentioned. Monomer conversions were calculated by ^{1}H NMR by monitoring the disappearance of the peaks corresponding to the protons adjacent to the ester group ($\delta = 4.3$ ppm) compared to the corresponding proton signals of the polymer ($\delta = 4.1$ ppm). DP was also monitored using ^{1}H-NMR by integrating the vinyl end group peaks ($\delta = 6.1$ ppm and 5.52 ppm) and comparing to the polymer peak.

Molar mass distributions were measured using size exclusion chromatography (SEC), on a system equipped with two PL gel 5 µm mixed D-columns (300 x 7.5 mm) and one PL gel 5 mm guard column (50 x 7.5 mm) (Polymer Laboratories) with differential refractive index detection using dimethylformamide with 1 % lithium bromide as the eluent. Poly(MMA) standards were used to calibrate the SEC. The aqueous system employed PL aquagel-OH 40, 30, 30 columns (Polymer Laboratories), pH 8.2 buffer as eluent, differential refractive index detection and poly(ethylene oxide) and poly(methacrylic acid) calibrants.

NMR spectra were obtained on a Bruker DPX400 spectrometer. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances. The molecular weight of the polymers M_n (NMR) are calculated by comparing the integrals of the chain-end signals and appropriate peaks related to the polymer backbone.

FTIR spectra were obtained on a VECTOR-22 Bruker spectrometer using a golden gate diamond total attenuated reflection cell.

Confocal fluorescent microscopy images were captured using a Zeis Laser Scanning microscopy (LSM) 510 and associated LSM software.

QCM-D was conducted using the Q-Sense E4 System: QE 401 Electronics Unit, QCP 401 Chamber Platform, QFM 401 Flow Module with Ismatec IPCN Pump. Silicon dioxide coated quartz sensors [Frequency: 4.95 MHz +/-50 kHz; Cut: AT; Diameter: 14 mm; Thickness: 0.3 mm; Finish: Optically polished, surface roughness of electrode <3 nm (RMS); Electrode layer: 40nm- 1µm] were cleaned using piranha solution, rinsed with deionised water, ethanol and dried under nitrogen gas before use.

Contact angle measurements were made using the Krüss drop shape analyser (DSA) 100 with automated dosing in sessile drop method at ambient temperature. The average and standard deviation of ten measurements were measured using DSA3 software.

Characterisation of sensors after silinization

FT-IR of the substrate before and after reaction with MPTS:
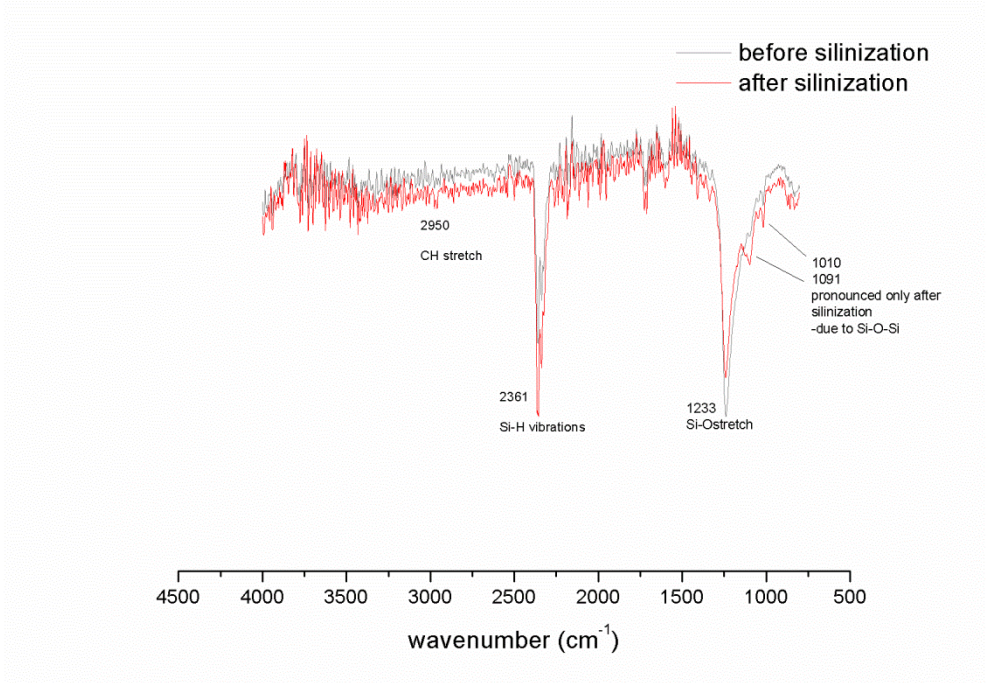
Successful chemical modification of the surface with MPTS can be determined by the appearance of peaks (red trace) after silinization at 1010 and 1091 cm^{-1} which correspond to Si-O-Si bonds. The small CH stretch from MPTS can be observed at 2950 cm^{-1}.

The contact angles of the substrate before (6 ° ± 0.5) and after (71 ° ± 0.7) reaction were measured and corresponding images are shown below.

Synthesis

Polymer	[CTA]/[M]	Composition	DP†	$M_n^{†}$/ g.mol^{-1}	M_n^{*}/ g.mol^{-1}	M_w^{*}/ g.mol^{-1}	PDI	Conversion/ %
P1	4.53x10^{-5}	PEG$_{300}$	4	1220	1230	1640	1.33	79
P2	5.00 x10^{-5}	PEG$_{1100}$	12	13200	11700	15900	1.36	83
P3	4.74x10^{-5}	DEG:AMA(5%)	5	1600	2000	3000	1.46	87

CCTP of di(ethylene glycol) methyl ether methacrylate: CCTP (pDEGMEMA)
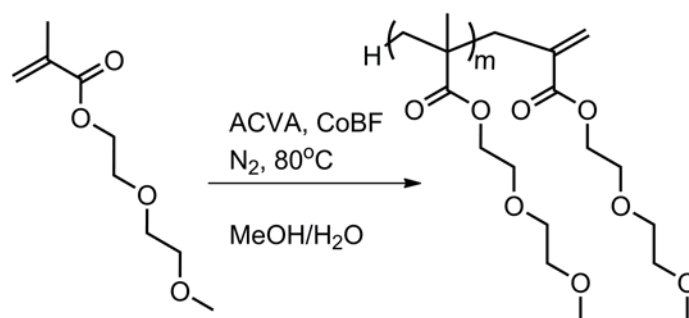
Methanol (30 mL) and demineralised water (46 mL) were placed into a round bottomed flask containing initiator 4,4'-azobis(4-cyano-valeric acid) (ACVA) (0.28 g, 8.21 x 10^{-4} mol) and a magnetic stirrer bar, sealed with a suba-seal, para-film and purged with nitrogen for 2 hours prior to the experiment starting. Di(ethylene glycol) methyl ether methacrylate (DEGMEMA) monomer (29.41 mL, 0.16 mol) was placed into a round bottom flask, sealed with a suba-seal, para-film and purged with nitrogen for 2 hours. Bis(boron difluorodimethylglyoximate) cobalt (II) (CoBF, chain transfer agent) (3.1 mg, 7.97 x 10^{-6} mol)was placed into a round bottom flask with a magnetic stirrer bar, sealed with a suba-seal, para-film and purged with nitrogen for 2 hours.

The MeOH/H$_2$O/initiator mixture was heated to 80 °C in an oil bath with a fuzzy-logic temperature controller. DEGMEMA was cannulated into the round bottom flask containing CoBF and 3.2 mL of this solution was transferred into the solvent/initiator round bottom flask using a degassed syringe. A feed pump was used to supply the remaining monomer/CoBF mixture into the solvent/CVA mixture at a rate of 0.43 mL/ min (feed completed after 60 minutes) and samples for analysis were taken periodically using a degassed syringe. After five hours the reaction was removed from the oil bath and air was bubbled through the reaction solution. For purification the remaining monomer and solvent in the reaction were removed using a vacuum pump with the collection flask cooled in liquid nitrogen, yielding a straw coloured viscous liquid. The sample flask was heated to 30 °C to stop the solution from freezing. Yield= 20.0 g (66 %)

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 6.1 (s, vinyl peak 1H), 5.52 (s, vinyl peak 1H), 4.10 (m, COOC$\underline{H}_2$CH$_2$,2H), 3.65 (t, OCH$_2$C$\underline{H}_2$,2H), 3.58 (s, repeat unit CH$_2$ 4nH), 3.42 (s, methyl, OCH$_3$ 3nH), 2.188 (d, C$\underline{H}_2$C=CH$_2$, 2H) 1.83 (m, CH$_3$(C$\underline{H}_2$CCH$_3$COOR), 2nH) 1.056 (s, CH$_3$ methyl 3nH),0.90 (s, terminal methyl, 3H). IR v (cm^{-1}): 2800 (CH$_3$/CH$_2$ stretch), 1750 sharp (C=O stretch), 1450 (>C-H$_2$ scissor deformation), 1100 (C-O ester stretch), 800 (C=C Hydrogen out-of-plane bends). LCST (1 mg ml^{-1}): 44.0 °C, M$_n$ (GPC$_{DMF}$)= 1840 g. mol^{-1}, M$_w$ (GPC$_{DMF}$) = 2800 g. mol^{-1}, PDi= 1.52, DP (NMR) = 13, M$_n$ (NMR) = 2450 g. mol^{-1}, Conversion (NMR)= 81 %,

CCTP of poly(ethylene glycol) methyl ether methacrylate (pPEGMEMA)

The same reaction procedure was carried out as explained above with the only change being the monomer shown in the table below:

Compound	Mass (g)	Moles (M)	MW (g . mol^{-1})
PEGMEMA$_{300}$	30	0.1	300
PEGMEMA$_{1100}$	20	0.018	1100

PEGMEMA$_{300}$

For purification, the remaining monomer and solvent in the reaction were removed using dialysis tubing with a molecular weight cut off of 1000 g. mol^{-1} yielding a clear viscous liquid. Yield= 22 g (93 %).
LCST (1 mg ml^{-1}): 92.0 °C, (M$_n$ (GPC)=1230 g. mol^{-1}, MW (GPC)= 1640 g. mol^{-1}, PDi=1.33, DP (NMR)= 4, M$_n$ (NMR)= 1220 g. mol^{-1}, Conversion (NMR)= 79 %

PEGMEMA$_{1100}$

This polymerisation was not carried out by a feed method due to the monomer being a solid and in solution highly viscous. For purification, the remaining monomer and solvent in the reaction were removed using dialysis tubing with a molecular weight cut off of 1000 g. mol^{-1} yielding a white waxy solid after freeze drying. Yield= 11.66 g (58 %).
M$_n$ (GPC) = 11700 g. mol^{-1}, M$_w$ (GPC)= 15900 g. mol^{-1}, PDi= 1.36, DP (NMR) = 6, M$_n$ (NMR)= 13200 g. mol^{-1}, Conversion (NMR)= 83%

1   Syrett, J. A.; Mantovani, G.; Barton, W. R. S.; Price, D.; Haddleton, D. M., *Polym. Chem.*, (2010) **1**, 102.
2   Qi, Y.; Li, N.; Xu, Q.; Xia, X.; Ge, J.; Lu, J., *React. Funct. Polym.*, (2011) **71**, 390.
3   Slavin, S.; Khoshdel, E.; Haddleton, D. M., *Polym. Chem.*, (2012) **3**, 1461.