

Chimeric Polymers Formed from a Monomer Capable of Free-Radical, Oxidative and Electrochemical Polymerisation

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Electronic Supporting Information

Experimental

Materials and Methods: All chemicals and solvents used within this work were purchased from Sigma-Aldrich and were of analytical grade. A JEOL ECX400 MHz was used for NMR measurements and FTIR spectra were obtained using a Nicolet Avatar-370 spectrometer. A Philips UV lamp (8 mWcm²) was used to irradiate samples. Sessile water contact angle measurements were made using a Cam 100 optical Angle Meter (KSV Instruments Ltd., Finland) together with the software provided. AFM images were obtained using a PicoScan instrument (Molecular Imaging Corporation). Ellipsometry measurements were made using a SE 400 Ellipsometer (Mi-Net Technologies Ltd.). The determinations of specific surface area were performed using a NOVA “e” surface area and pore size analyser (Quantachrome) based on the nitrogen BET. The adsorption and desorption of nitrogen was used to measure the specific surface area of materials and also the pore size and distribution. Before gas adsorption, the polymer powdered sample (70 mg) was degassed in vacuum at 100 °C for 2 hours. Powdered polymer samples were compressed at 10 Ton using a standard KBr press to form pellets of 1mm thickness. Conductivity through the pellet was determined using a 2 probe method with a Precision Gold Academy model PGMO12 multimeter. X-Ray Photoelectron Spectroscopy (XPS) measurements were carried out on a VG ESCA lab-Mark-2 X-ray Photoelectron Spectrometer (East Grinstead, UK). The X-ray gun was operated at 14 kV and 20 mA. Survey and high resolution spectra were collected at 50eV and 100 eV respectively with Mg K α 1253.6 eV radiation. The vacuum in the analysis chamber was about 10⁻⁹ mBar. High resolutions scan with a good signal ratio have been obtained in the C1s, N1s, O1s, and S2p regions of the spectrum. The decomposition of the XPS peaks into different components and the quantitative interpretation have been performed after subtraction of the background using the Shirley method.¹

Free radical polymerisation of NPEDMA: NPEDMA and mixtures of NPEDMA with ethylene glycol dimethacrylate (EGDMA) were polymerised in DMF by thermal free radical polymerisation, using the initiator 1,1'-azo-bis-(cyclohexane-1-carbonitrile), according to Tab S1. Monomer(s) (200 mg) and initiator (2 mg, 1 %) were dissolved in DMF (400 mg) in a glass vial and the mixtures purged with a stream of argon for 5 min before sealing under an argon atmosphere and transferring to an oil bath held at 80 °C for 16 h. The resultant material was precipitated into water (PNPEDMA) or washed with methanol (PNPEDMA-X where X is the percentage weight of EGDMA). Dried polymers were ground in a mortar and washed with further methanol (5 × 5 mL) and dried in an oven.

Oxidation of aniline moieties: N-phenylethylene diamine methacrylamide was dissolved in 1 M HCl (25 mL) to give a final monomer concentration of 1 M and the solution cooled to 0 °C. An equal volume of a 1 M solution of ammonium persulphate was slowly added with stirring. After 1

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hour the resultant solid product was filtered, washed repeatedly with 1 M HCl and vacuum dried, yield 90%. For comparison, two samples of polyaniline were also synthesised by this method, one where the reaction took place at 0 °C and the other at room temperature. A similar method was utilised to oxidise the polymers. Polymer (100 mg of PNPEDMA, PNPEDMA-5, PNPEDMA-10, PNPEDMA-25 or PNPEDMA-50) was slurried with 1 M HCl (25 mL) and cooled to 0 °C, with stirring, before the addition of an equal volume of 1 M ammonium persulphate in water, slowly over 5 minutes. After 1 h, the polymer particles were removed by filtration and washed with water and oven dried. The material was pressed into disks of approx 1 cm diameter at 10 Ton as described above. Conductivity was measured by the two-probe method using a digital multimeter.

Electropolymerisation of NPEDMA: An Autolab PSTAT 10 instrument (Eco-Chemie BV, Utrecht, Netherlands) was utilised for all electrochemical experiments. A conventional three-electrode cell with a gold (evaporated 45 nm Au over 5 nm Cr film) on glass working electrode, a platinum counter electrode and a silver/silver chloride (Ag/AgCl) reference electrode was utilised. The gold electrode was cycled (15 cycles) between - 0.4 V and +1.0 V (vs. Ag/AgCl) at a scan rate of 50 mVs⁻¹ in a solution of NPEDMA (2.44 mM) in HClO₄ (50 mM). Alternatively an ITO-coated glass slide (working area 1 x 2.5 cm) was utilised as the working electrode to allow optical spectra of the film to be taken. Electropolymerised films were rinsed in a stream of 50% methanol and deionised water and dried in a stream of nitrogen.

Iniferter-grafting and photocrosslinking of electropolymerised film of NPEDMA: The electropolymerised film of NPEDMA, formed on a gold electrode, was immersed in a 5mM solution of *N,N*-diethyldithiocarbamic acid benzyl ester (iniferter) in hexane contained within a glass Petri dish (25 mm diameter). Oxygen was removed by purging with argon for 10 minutes. The Petri dish was covered with a flat glass plate and the edges sealed with Parafilm® to maintain an inert atmosphere over the solution. The film was then irradiated for 15 minutes through the solution using a Philips UV lamp mounted at 8 cm from the sample to activate the iniferter and generate benzyl radicals to react with the double bonds present on the polymer. The film was then rinsed in a stream of 50% methanol and deionised water and dried in a stream of nitrogen.

Photografting of poly(methacrylic acid) to an electropolymerised film of NPEDMA: An electropolymerised film of NPEDMA treated with iniferter (as above) was immersed in a solution of methacrylic acid (0.1M in water). The solution was degassed with argon for 10 minutes before irradiation with UV for 15 minutes. The passage of argon was continued at a low flow rate during the polymerisation period. The electrode was recovered and the polymer surface was rinsed in a stream of 50% methanol and deionised water and dried in a stream of nitrogen.

Gel permeation chromatography (GPC) of free radical polymerised NPEDMA: GPC was performed in THF was performed using an Agilent 1100 Series instrument, (Agilent, UK) with 5µm phenogel column, 300 × 7.80 mm (Phenomenex). Calibration was performed against polystyrene standards (Phenomenex).

Polymerisation of N-phenylethylene diamine by oxidation with persulphate: *N*-phenylethylene diamine (25 mmol) was dissolved in 1 M HCl (25ml) and solution was cooled to 0 °C. An equal volume of a 1 M solution of ammonium persulphate was slowly added with stirring. After 1 hour the resultant solid product was filtered, washed repeatedly with 1M HCl and vacuum dried, yield 80%. The material was pressed into a disk of approximate 1 cm diameter at 10 Ton, as described above. Conductivity was measured by the two-probe method using a digital multimeter. Conductivity was 0.02 Scm⁻¹.

Preparation of the acetyl derivative of N-phenyl ethylene diamine (NPEDAc):

N-phenylethylene diamine (1.0 g, 0.96 mL, 7.3 mmol) was dissolved in methanol (20 mL) which was cooled in ice before the addition of acetic anhydride (0.725 g, 0.67 mL, 7.1 mmol). The stirred mixture was kept at 0 °C for 3h before warming to RT. The solvent was removed using a rotary evaporator and the residue was dispersed in diethyl ether (25 mL). The ether phase was washed with 0.1M NaOH, (4 × 25 mL) followed by water (1 × 25 mL), dried over anhydrous magnesium sulphate and evaporated. The resulting oil was stored in a refrigerator.

Polymerisation of NPEDAc by oxidation with persulphate: NPEDAc (100 mg) was taken in 1M HCl (25 mL) and cooled to 0 °C, with stirring before the addition of an equal volume of 1M ammonium persulphate in water, slowly over 5 minutes. After 1 h, the polymer particles (gel type) were removed by filtration and washed with water and dried. The material was pressed into disks of approximately 1cm diameter at 10Ton, as described above, and conductivity was measured by the two probe method.

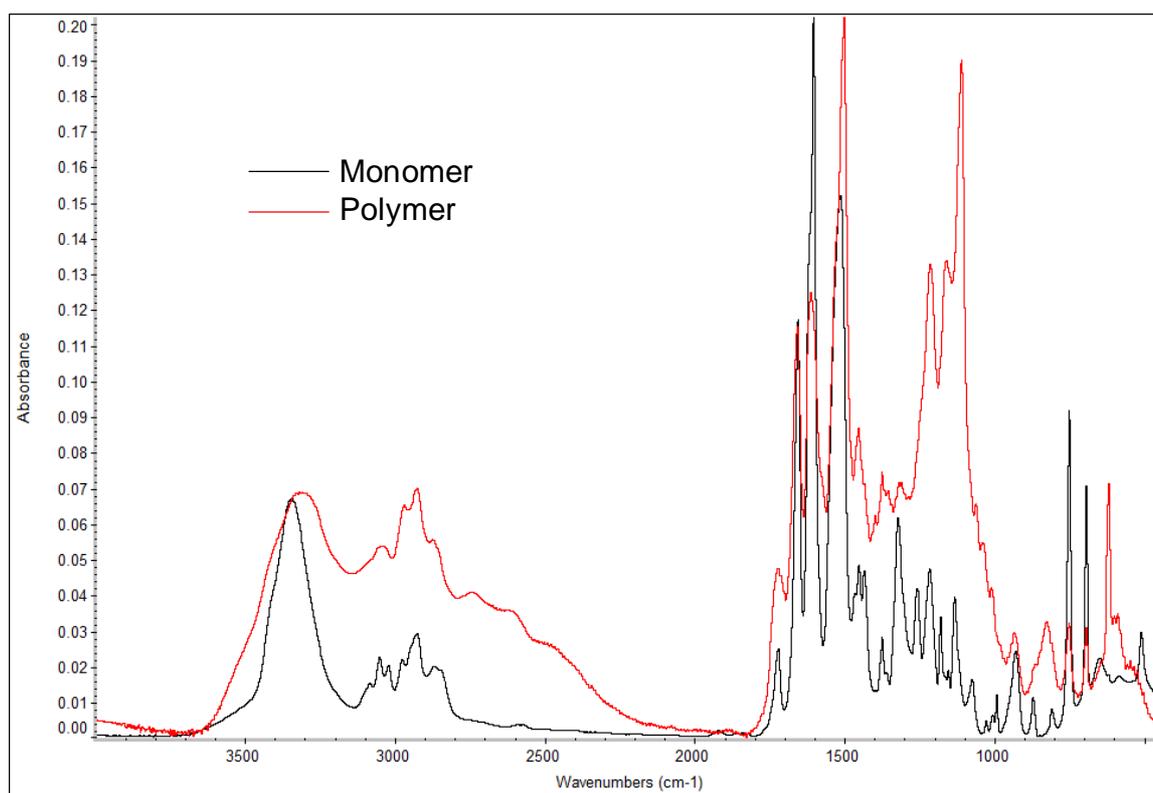
References

- 1 D. A. Shirley, *Phys. Rev. B*, 1972, **5**, 4709.

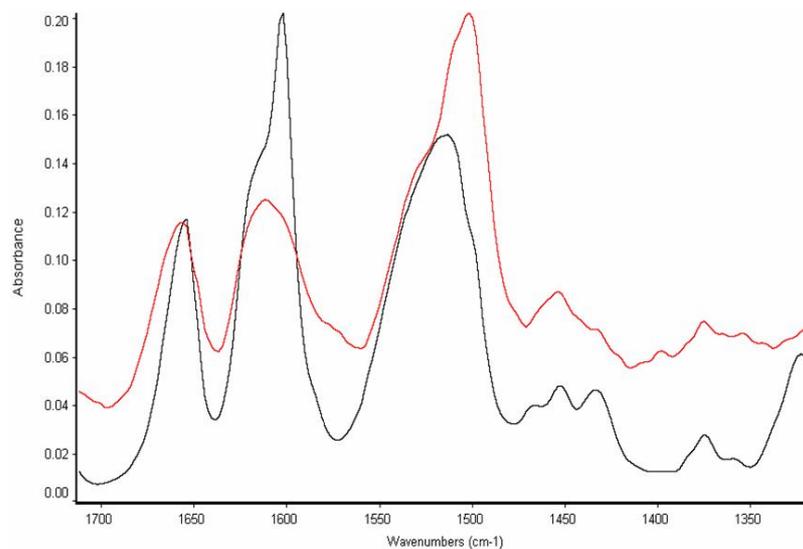
Table S1. Composition of polymers and copolymers of NPEDMA made by free radical polymerisation

Polymer	NPEDMA	EGDMA
	[mg]	[mg]
PNPEDMA	200	0
PNPEDMA-5	190	10
PNPEDMA-10	180	20
PNPEDMA-25	150	50
PNPEDMA-50	100	100

A)



B)



C)

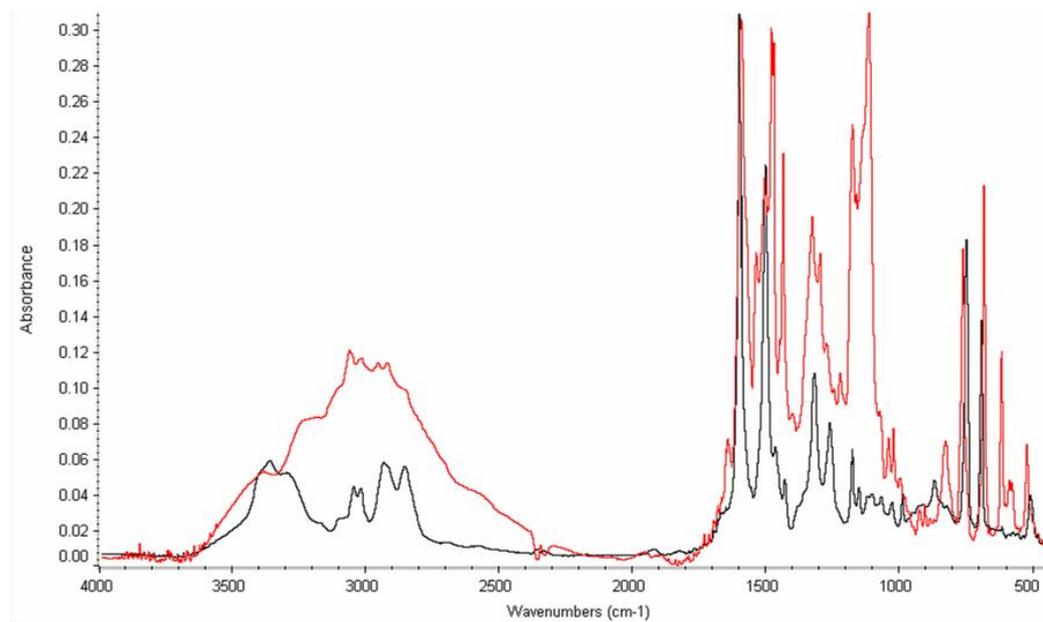


Figure S1. A) FTIR spectra of NPEDMA (in black) and its polymer (red) formed by reaction with ammonium persulphate; B) Expansion of the spectra shown in part (A), showing the carbonyl region in more detail; C) FTIR spectra of the monomer precursor, *N*-phenylethylene diamine (in black) and its polymer (red) formed by reaction with ammonium persulphate.

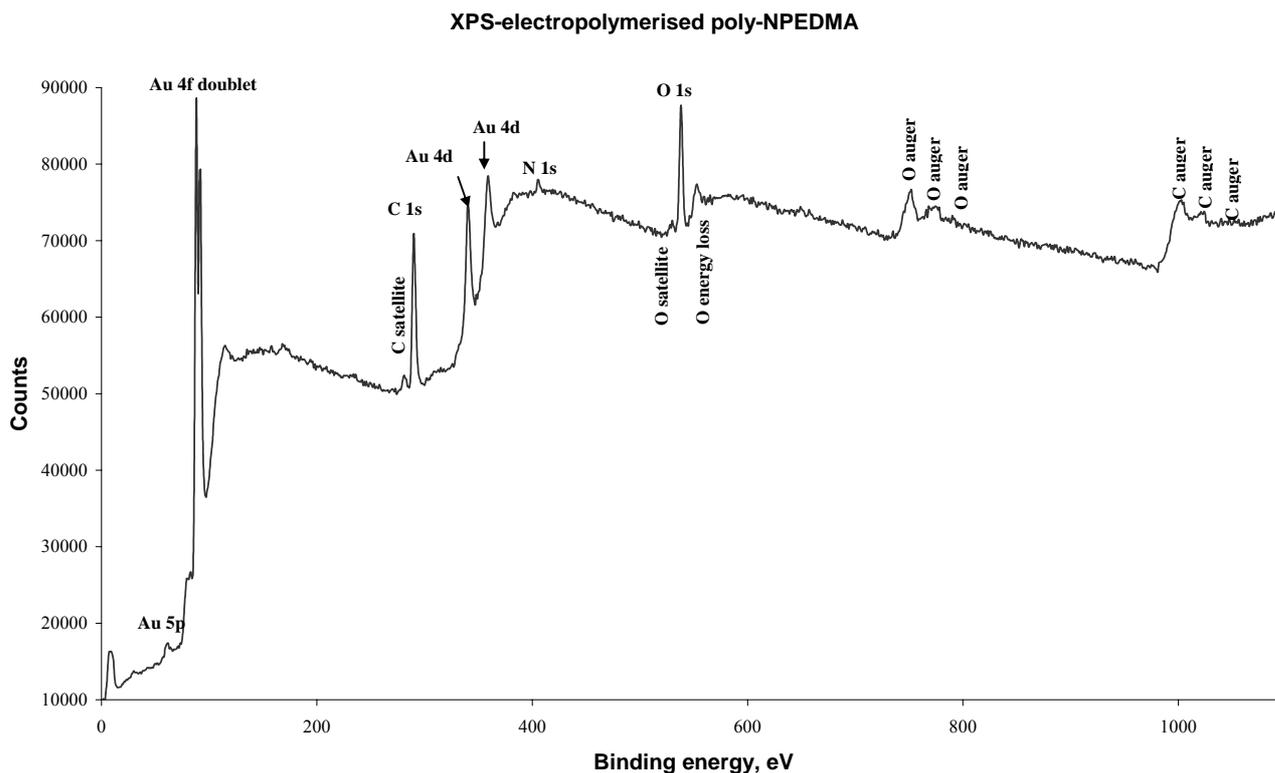


Figure S2. X-ray photoelectron spectroscopy analysis of poly-NPEDMA film.

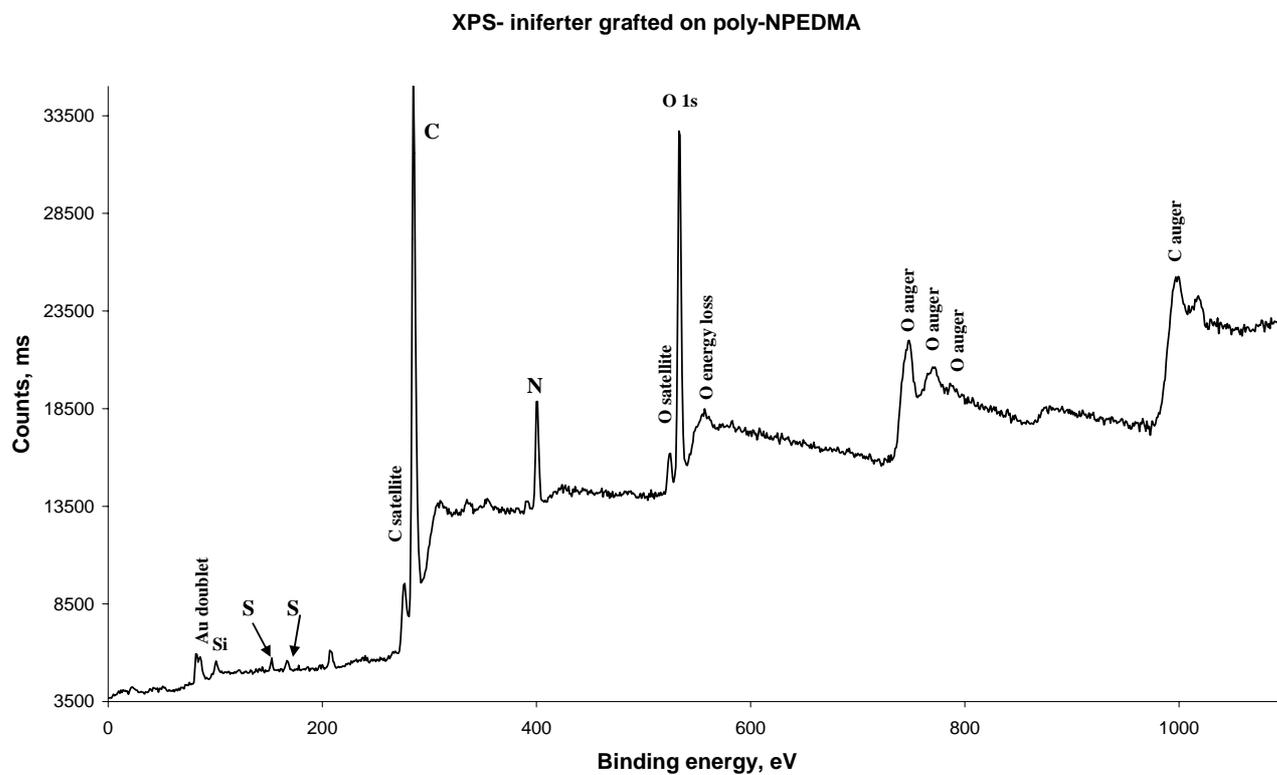


Figure S3. X-ray photoelectron spectroscopy analysis of poly-NPEDMA film with grafted iniferter.

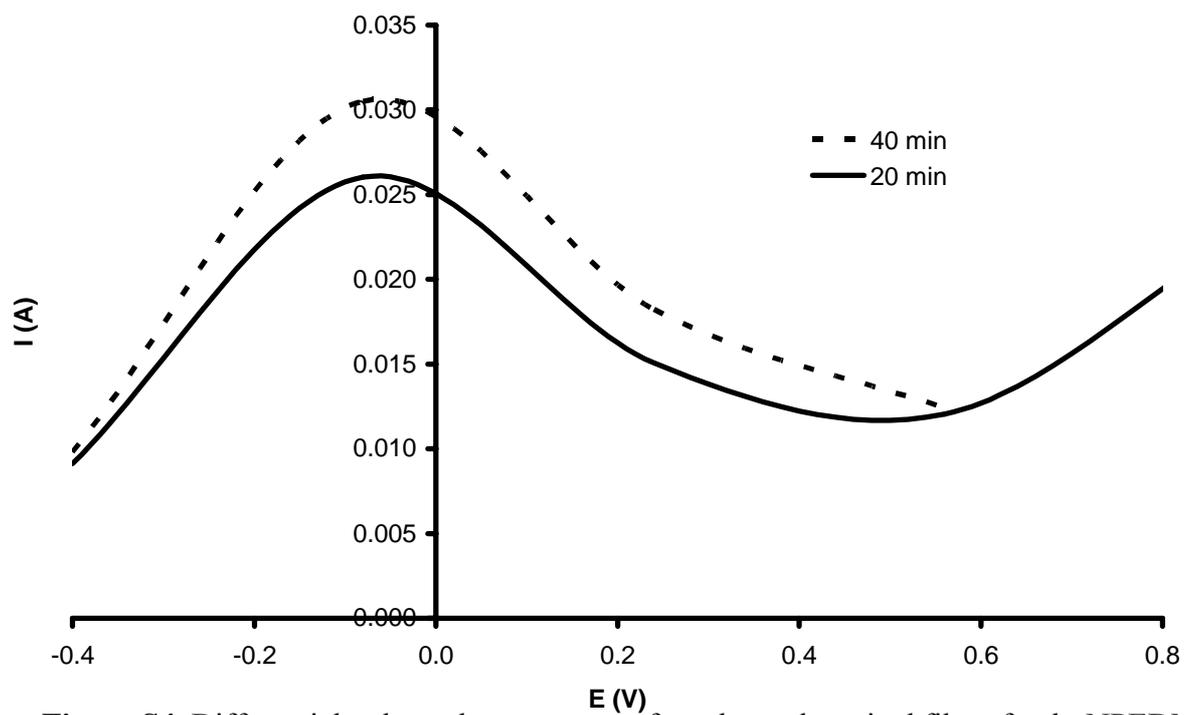


Figure S4. Differential pulse voltammogram of an electrodeposited film of poly-NPEDMA, after 20 and 40 minutes UV irradiation.

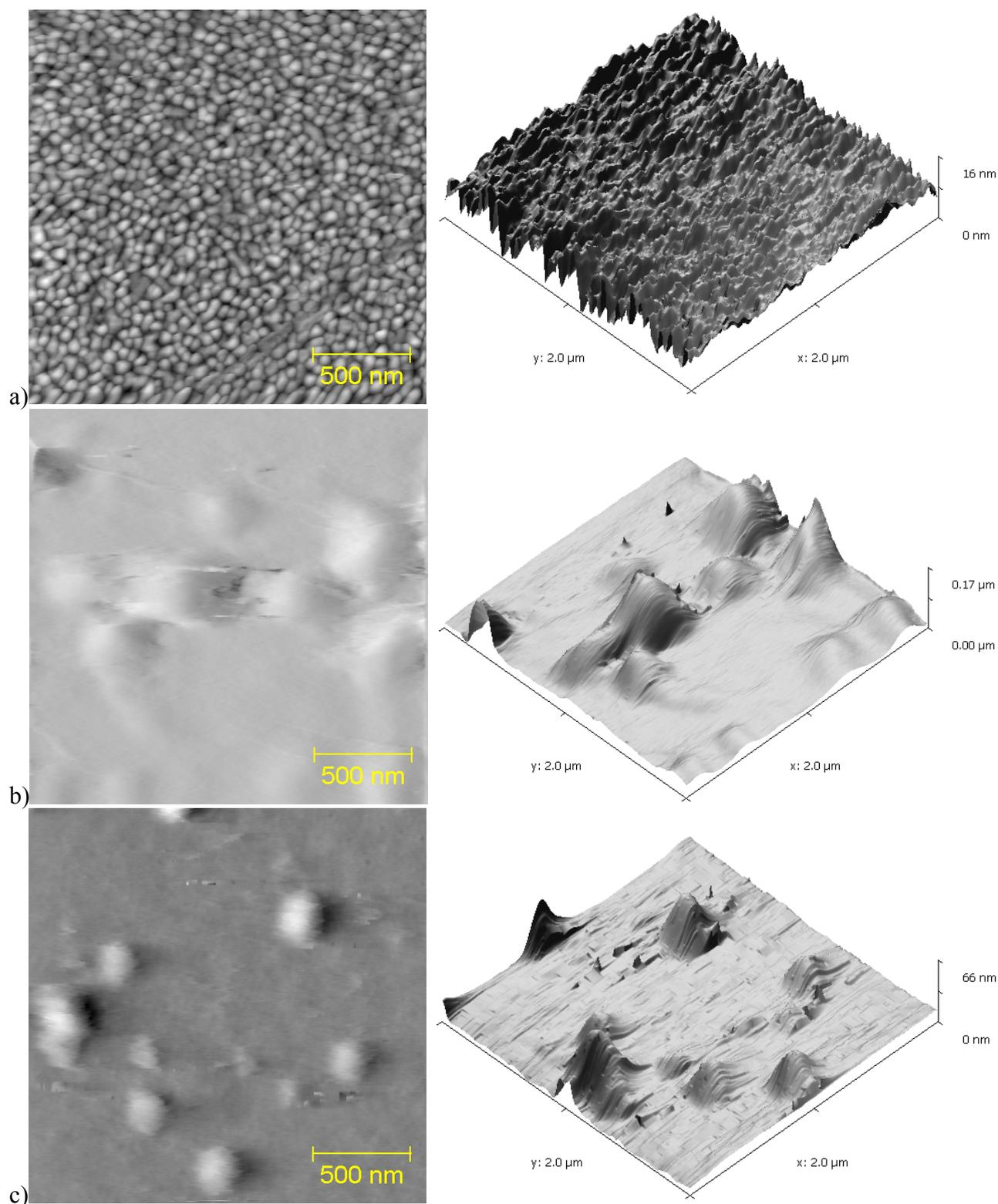


Figure S5. AFMs of (a) bare gold electrode, (b) electropolymerised NPEDMA film on gold, (c) poly(methacrylic acid) film grafted over electropolymerised NPEDMA following iniferter activation. RMS surface roughness: (a) 1.14 ± 0.05 nm, (b) 20.97 ± 5.41 nm, (c) 3.97 ± 2.16 nm. Water contact angle: (a) $77.63 \pm 0.17^\circ$, (b) $69.28 \pm 0.22^\circ$, (after iniferter attachment: $71.34 \pm 0.65^\circ$) (c) $62.20 \pm 0.26^\circ$. Measurements of roughness and contact angle were performed in triplicate on three replicate samples.

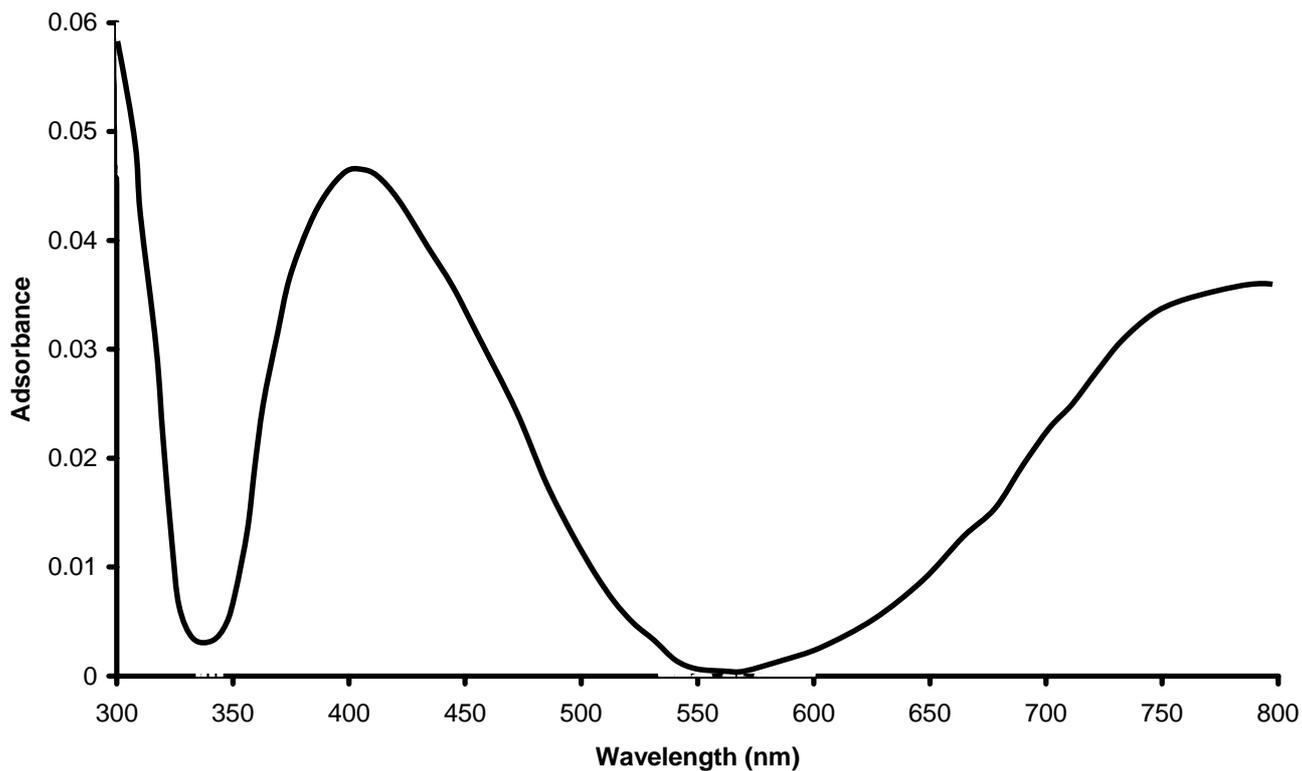


Figure S6. UV-vis spectrum of an electrodeposited polymer of NPEDMA on ITO-coated glass.

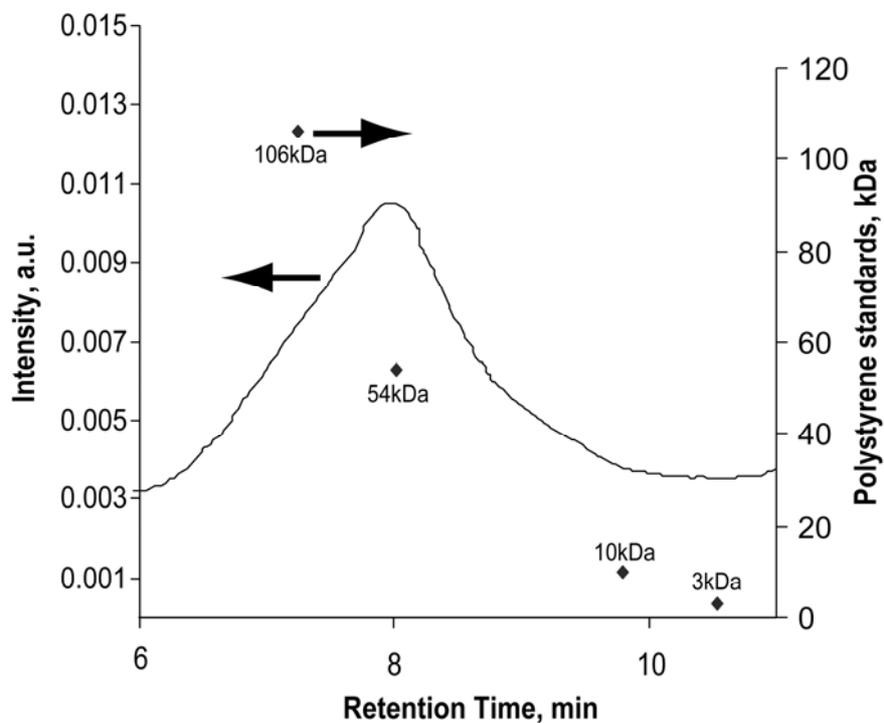


Figure S7. GPC profile of the peak from the product of free radical polymerisation of NPEDMA in toluene and the corresponding calibration plot obtained with polystyrene standards.

Also supplied as separate files:

400MHz ^1H NMR spectrum of NPEDMA in CDCl_3 , filename: NPEDMA_1H.pdf

100Mz ^{13}C NMR spectrum of NPEDMA in CDCl_3 , filename: NPEDMA_13C.pdf