

Supporting Information

One-step grafting of polymers to graphene oxide

Helen R Thomas, Daniel J Phillips, Neil R Wilson, Matthew I Gibson and Jonathan P Rourke**

Synthesis of pNIPAM	p2
Synthesis of GO-pNIPAM	p4
FTIR	p5
EDX	p6
SSNMR	p7
Raman	p9
XPS	p10
TGA	p14
Contact angle	p15

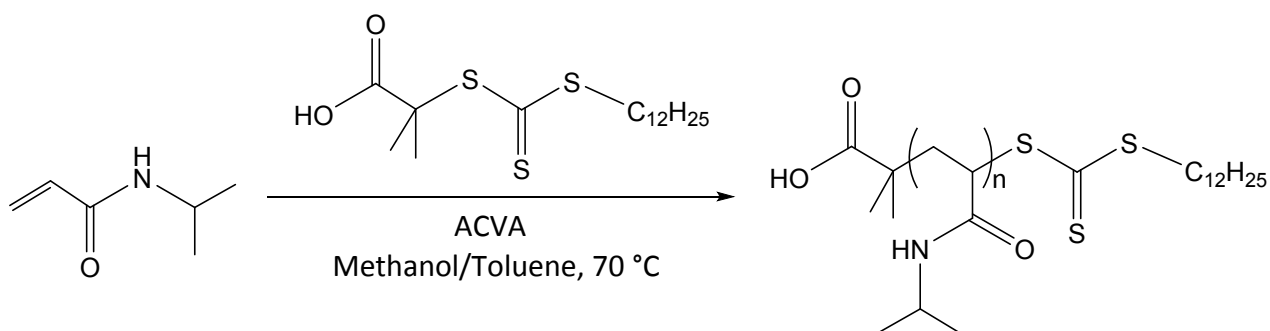
Polymerisation of *N*-isopropylacrylamide

General

All chemicals were used as supplied. Methanol, toluene, tetrahydrofuran and diethyl ether were all purchased from Fisher Scientific at laboratory reagent grade. Deuterated chloroform (99.8 atom % D), *N*-isopropylacrylamide (97.0 %), 4,4'-azobis(4-cyanovaleric acid) (≥ 98.0 %) and mesitylene (97.0 %) were purchased from Sigma Aldrich. 2-(Dodecylthiocarbonothioylthio)-2-methylpropanoic acid was synthesised as described elsewhere (Phillips, D. J.; Gibson, M. I. *Biomacromolecules* **2012**, *13*, 3200-3208).

NMR spectroscopy (^1H , ^{13}C) was conducted on a Bruker AV-250 spectrometer using deuterated chloroform as solvent. SEC analysis was performed on a Varian 390-LC MDS system equipped with a PL-AS RT/MT autosampler, a PL-gel 3 μm (50 x 7.5 mm) guard column, two PL-gel 5 μm (300 x 7.5 mm) mixed-D columns using DMF containing 5 mM NH_4BF_4 at 50 $^\circ\text{C}$ as the eluent at a flow rate of 1.0 $\text{mL}\cdot\text{min}^{-1}$. The system was equipped with ultraviolet (set at 280 nm) and differential refractive index (DRI) detectors. Narrow molecular weight PMMA standards (200 – 1.0 x 10⁶ $\text{g}\cdot\text{mol}^{-1}$) were used for calibration using a second order polynomial fit.

Synthesis



Scheme 1SI Synthetic scheme for the preparation of pNIPAM samples used in this study.

In a typical procedure *N*-isopropylacrylamide (0.50 g, 4.42 mmol), 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid (26.85 mg, 73.64 μmol) and 4,4'-azobis(4-cyanovaleric acid) (4.13 mg, 14.74 μmol) were dissolved in methanol: toluene (1:1) (2 mL) in a glass vial containing a stir bar. Mesitylene (100 μL) was added as an internal reference and the mixture stirred (5 mins). An aliquot of this starting mixture was removed for ^1H NMR spectroscopic analysis. The vial was fitted with a rubber septum and degassed by bubbling with nitrogen gas (30 mins). The vial was then placed in an oil bath thermostated at 70 $^\circ\text{C}$ for 30 mins, after which time the reaction mixture was opened to air and quenched in liquid nitrogen. An aliquot was removed and conversion determined by ^1H NMR spectroscopy. The product was purified three times by precipitation from tetrahydrofuran into cold diethyl ether, isolated by centrifugation and dried under vacuum overnight.

to give a yellow solid. The overall monomer conversion was determined from the ^1H NMR spectrum by measuring the decrease in intensity of the vinyl peaks associated with the monomer relative to mesitylene. Conversion (NMR): 50.4 %; M_n (theoretical): 3400 $\text{g}\cdot\text{mol}^{-1}$; M_n (SEC) 4600 $\text{g}\cdot\text{mol}^{-1}$; M_w/M_n (SEC): 1.09.

Table 1SI Characterisation of pNIPAM samples prepared in this study

Polymer	[M]:[CTA]	Conversion (%) ^a	$M_n(\text{th})$ ($\text{g}\cdot\text{mol}^{-1}$) ^a	$M_n(\text{SEC})$ ($\text{g}\cdot\text{mol}^{-1}$) ^a	M_w/M_n ^b
pNIPAM ₃₀	60	50.4	3400	4600	1.09
pNIPAM ₂₀₀	600	33.3	22400	22600	1.14
pNIPAM ₄₄₀	600	73.8	46800	50100	1.14

^aDetermined by ^1H NMR relative to an internal standard (mesitylene); ^bDetermined by SEC (DMF inc. 5 mM NH_4BF_4) relative to PMMA standards.

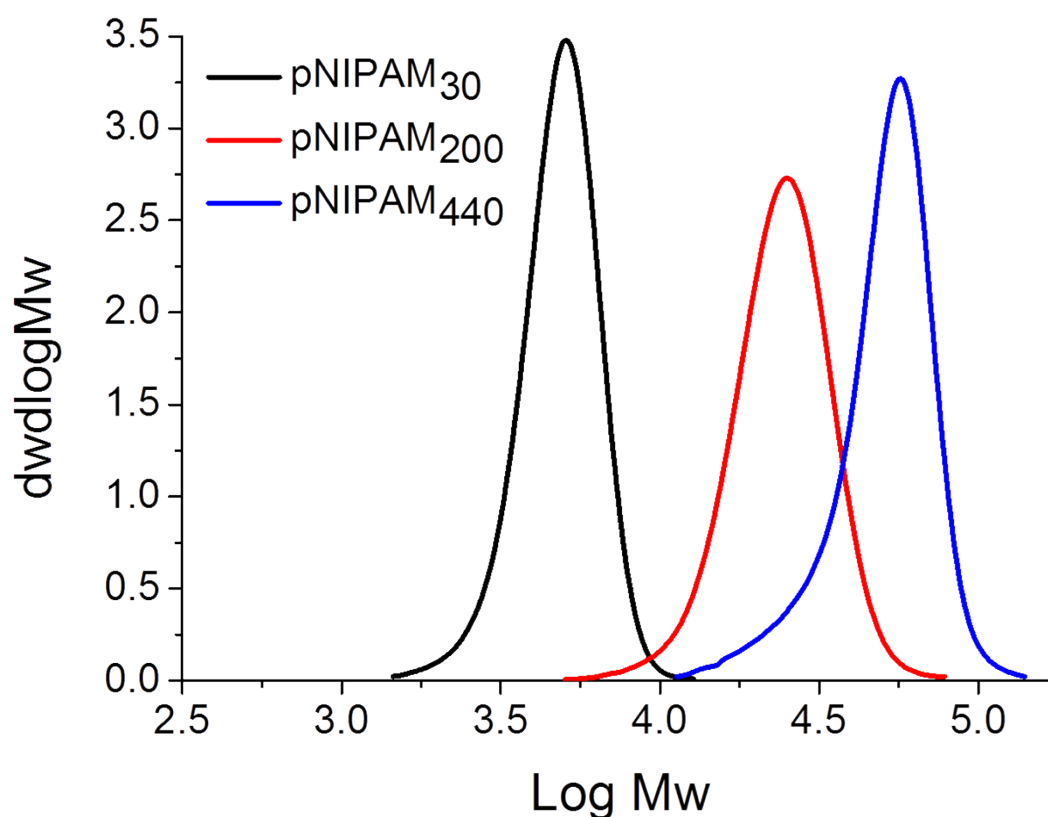
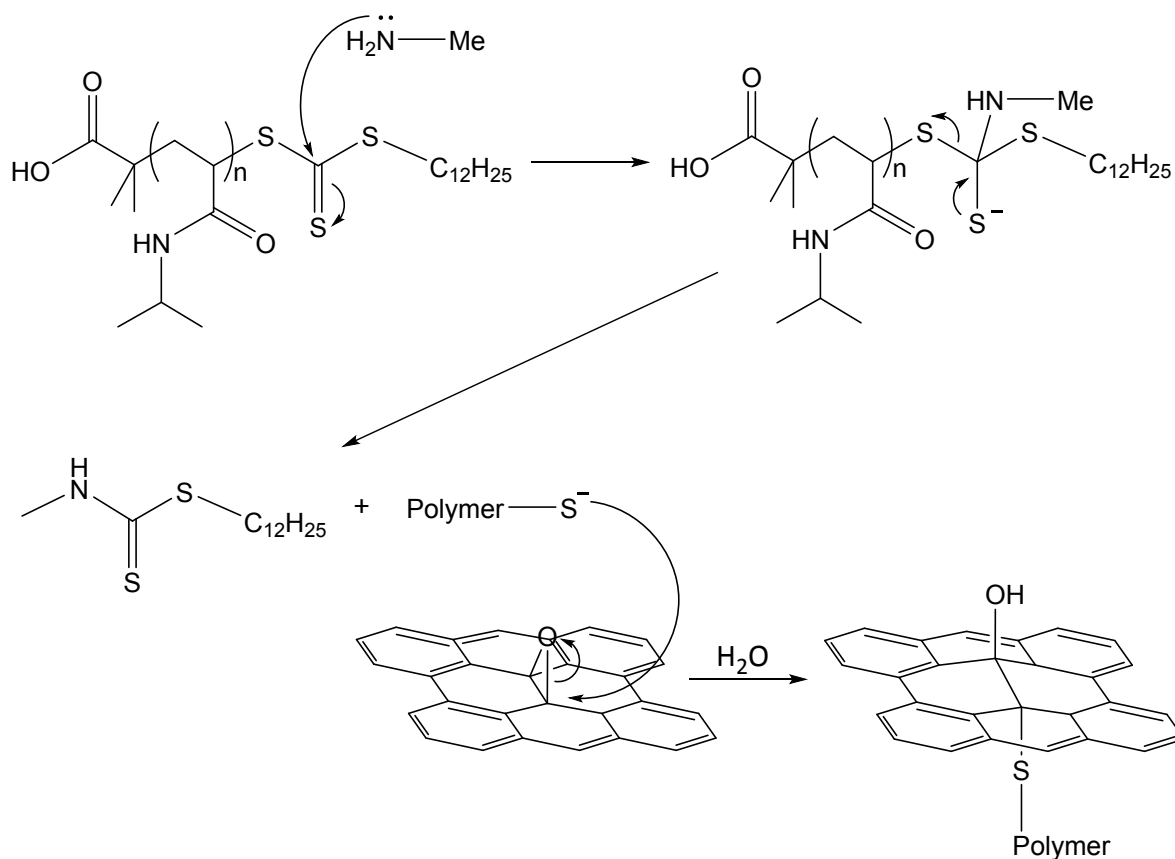


Figure 1SI SEC characterisation of pNIPAM samples prepared in this study.

Synthesis of GO-pNIPAM

The bwGO material used in this study was prepared via the Hummers synthesis and a NaOH wash, as described elsewhere. (Thomas, H. R.; Day, S. P.; Woodruff, W. E.; Vallés, C.; Young, R. J.; Kinloch, I. A.; Morley, G. W.; Hanna, J. V.; Wilson, N. R.; Rourke, J. P. *Chem. Mater.* **2013**, *25*, (18), 3580-3588; Rourke, J. P.; Pandey, P. A.; Moore, J. J.; Bates, M.; Kinloch, I. A.; Young, R. J.; Wilson, N. R. *Angew. Chem., Int. Ed.* **2011**, *50*, (14), 3173-3177.)



Scheme 2SI Synthetic scheme for the preparation of GO-pNIPAM samples used in this study.

The reaction was carried out using standard Schlenk conditions, operating under a dinitrogen atmosphere. Methylamine (3ml) was added to a solution of pNIPAM (20mg) in DMF (3 ml) together with a catalytic amount of glacial ethanoic acid, generating effervescence. This mixture was then immediately transferred into a solution of bwGO (60mg) in DMF (120ml). The GO/pNIPAM mixture was heated to 50 °C for one hour, before being allowed to cool to room temperature and left to stir under N₂ overnight (16hr).

The product was collected via centrifugation (12500 rpm), and was washed with acetone (20 minutes, x2), methanol (30 minutes, x2) and water (1 hour, x5) before being dried under vacuum to give a black solid (85.5 mg).

A control experiment, treating the bwGO with methylamine in DMF (no pNIPAM) was carried out. No nitrogen incorporation was seen (see XPS data in Table 2SI).

Characterisation data

FTIR

FTIR spectra were recorded on an Avatar 320 FTIR spectrometer as solids on a total internal reflectance device. Baseline corrections were applied using the supplied software

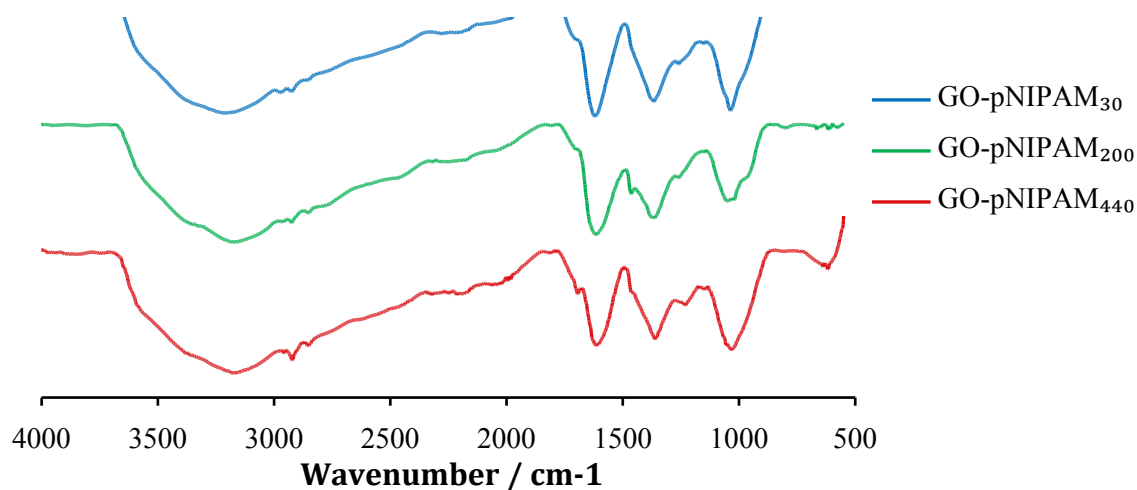


Fig 2SI FTIR spectra of the three p(NIPAM) functionalised GO materials.

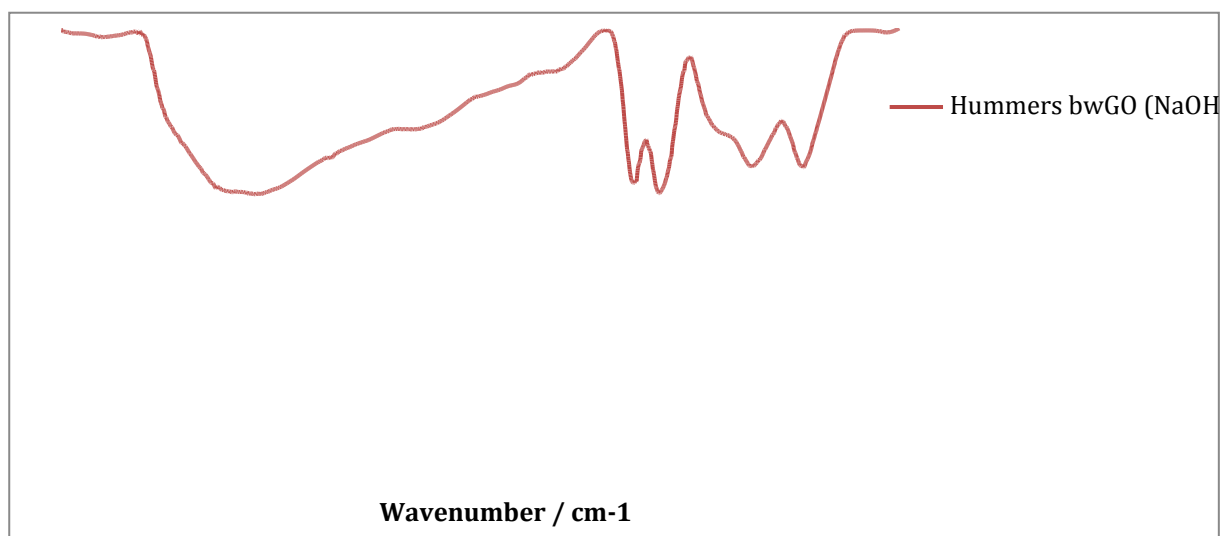


Fig 3SI FTIR spectra of the bwGO material.

EDX

EDX were recorded on a Zeiss SUPRA 55-VP FEGSEM with an EDAX Genesis analytical system, readings were taken at least four random spots across a sample with the standard deviations from the mean values noted in parentheses.

Table 2SI EDX atomic % of all three GO-pNIPAM materials with standard deviation in parentheses.

Sample	atomic % (standard deviation)				Calculated relative grafting density
	C	O	N	C/O	(chains/area)
GO-pNIPAM ₃₀	75 (1)	24 (1)	1.3 (0.8)	3:1	0.43
GO-pNIPAM ₂₀₀	76 (1)	20 (1)	2.9 (0.2)	4:1	0.015
GO-pNIPAM ₄₄₀	79 (2)	18 (2)	2.7 (0.4)	4:1	0.006
Control*	77 (1)	23(2)	0.1 (0.4)	3:1	

* control experiment, treating the bwGO with methylamine in DMF (no pNIPAM).

We know that the polymer repeat unit has atomic ratios, C:N:O of 6:1:1. Therefore we can separate the polymer and non-polymer C and O atomic percentages:

Table 3SI EDX atomic % attributed to the GO and polymer components

	GO C	GO O	Polymer C	Polymer O	Polymer N	% C in polymer
GO-pNIPAM ₃₀	67	23	8	1.3	1.3	11
GO-pNIPAM ₂₀₀	59	17	17	2.9	2.9	22
GO-pNIPAM ₄₄₀	63	15	16	2.7	2.9	20

We can then calculate the number of carbon atoms in the basal GO per polymer chain and arrive a polymer chain per ~1100 C atoms in GO for the pNIPAM₃₀, and 1 per ~3200 and ~8300 respectively for the 200 and 440 pNIPAM polymers.

SSNMR

Solid-state MAS NMR data were measured at an external field B_0 of 9.4 T using a Varian VNMRS 400 spectrometer operating at a ^{13}C Larmor frequency of 100.562 MHz. Both single pulse magic angle- spinning (MAS) and cross-polarisation, magic-angle-spinning (CPMAS) were recorded with a 1 s recycle time, and the CPMAS spectra were recorded with a 1 ms contact time. All ^{13}C chemical shifts are calibrated against external TMS (δ 0 ppm).

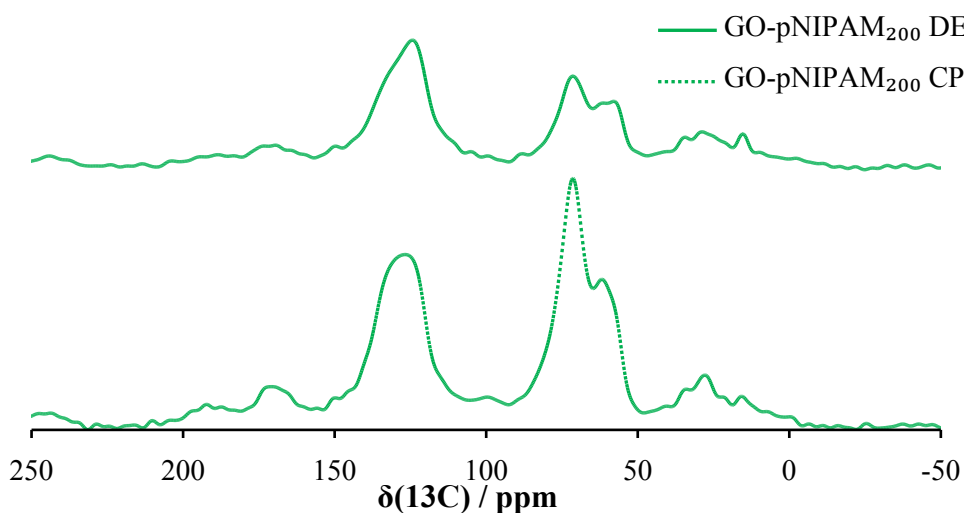


Fig 4SI ^{13}C MAS ssNMR spectra of GO-pNIPAM₂₀₀, both the direct excitation spectrum (solid) and the cross polarised spectrum (dashed) are shown.

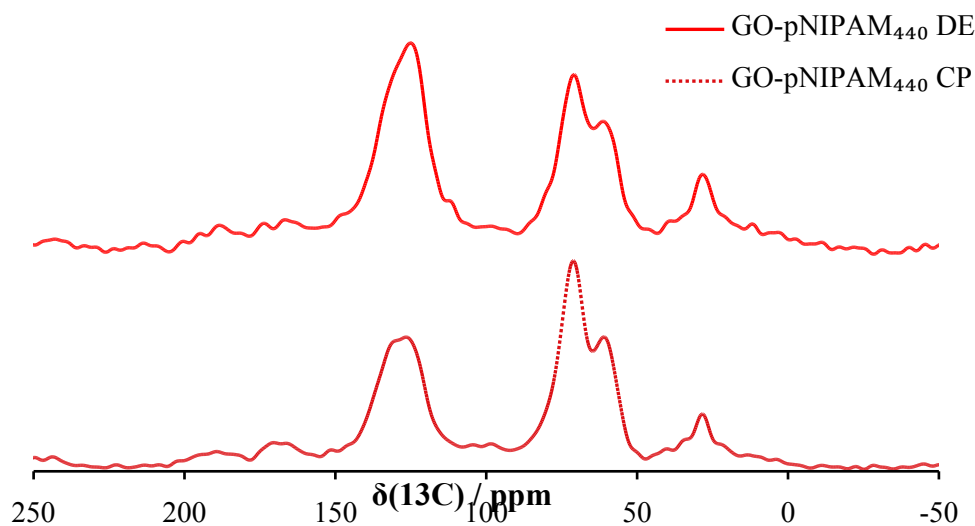


Fig 5SI ^{13}C MAS ssNMR spectra of GO-pNIPAM₄₄₀, both the direct excitation spectrum (solid) and the cross polarised spectrum (dashed) are shown.

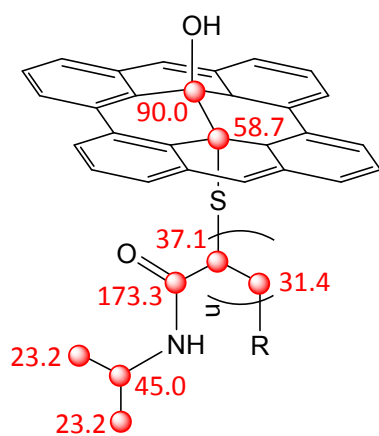


Fig 6SI ^{13}C ssNMR chemical shift prediction for the new signals in GO-pNIPAM. The red spheres indicate carbons of interest, with predicted chemical shifts as labelled.

Raman

Raman spectra were recorded on a Renishaw 2000 spectrometer under 514 nm excitation.

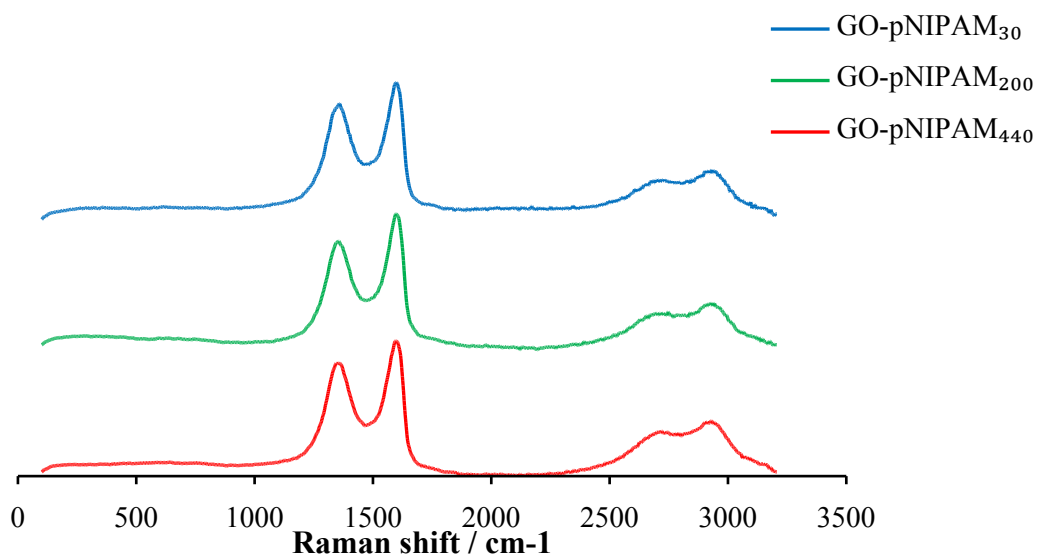


Fig 7SI Raman spectrum of all three GO- pNIPAM materials

XPS

The x-ray photoemission spectroscopy (XPS) data were collected at the Science City Photoemission Facility, University of Warwick, more details of which are available at <http://go.warwick.ac.uk/XPS>. The samples investigated in this study were mounted on Omicron sample plates using electrically conducting carbon tape and loaded in to the vacuum chamber. During the experiments the samples were stored in a 12-stage storage carousel, located between the preparation and main analysis chambers, for storage at pressures of less than 2×10^{-10} mbar.

XPS measurements were conducted in the main analysis chamber (base pressure 2×10^{-11} mbar), with the sample being illuminated using an XM1000 monochromatic Al $K\alpha$ x-ray source (Omicron Nanotechnology). The measurements were conducted at room temperature and at a take-off angle of 90° with respect to the surface parallel. To ensure a complete coverage of the carbon tape, the Si 2p region was monitored as Si is a component of the adhesive in the carbon tape used to mount the samples. No Si was observed in the survey spectra and thus all of the core levels observed in the data must originate from the given sample. The photoelectrons were detected using a Sphera electron analyser (Omicron Nanotechnology), with the core levels recorded using a pass energy of 10 eV (resolution approx. 0.47 eV). The spectrometer work function and binding energy scale were calibrated using the Fermi edge and 3d_{5/2} peak recorded from a polycrystalline Ag sample immediately prior to the commencement of the experiments. The data were analysed using the CasaXPS package, using Shirley backgrounds, mixed Gaussian-Lorentzian (Voigt) lineshapes and asymmetry parameters for the sp² graphitic components [<http://www.xpsfitting.com/2008/12/graphite.html>]. For compositional analysis, the analyser work function has been determined using Ag, Au and Cu foils to determine the detection efficiency across the full binding energy range.

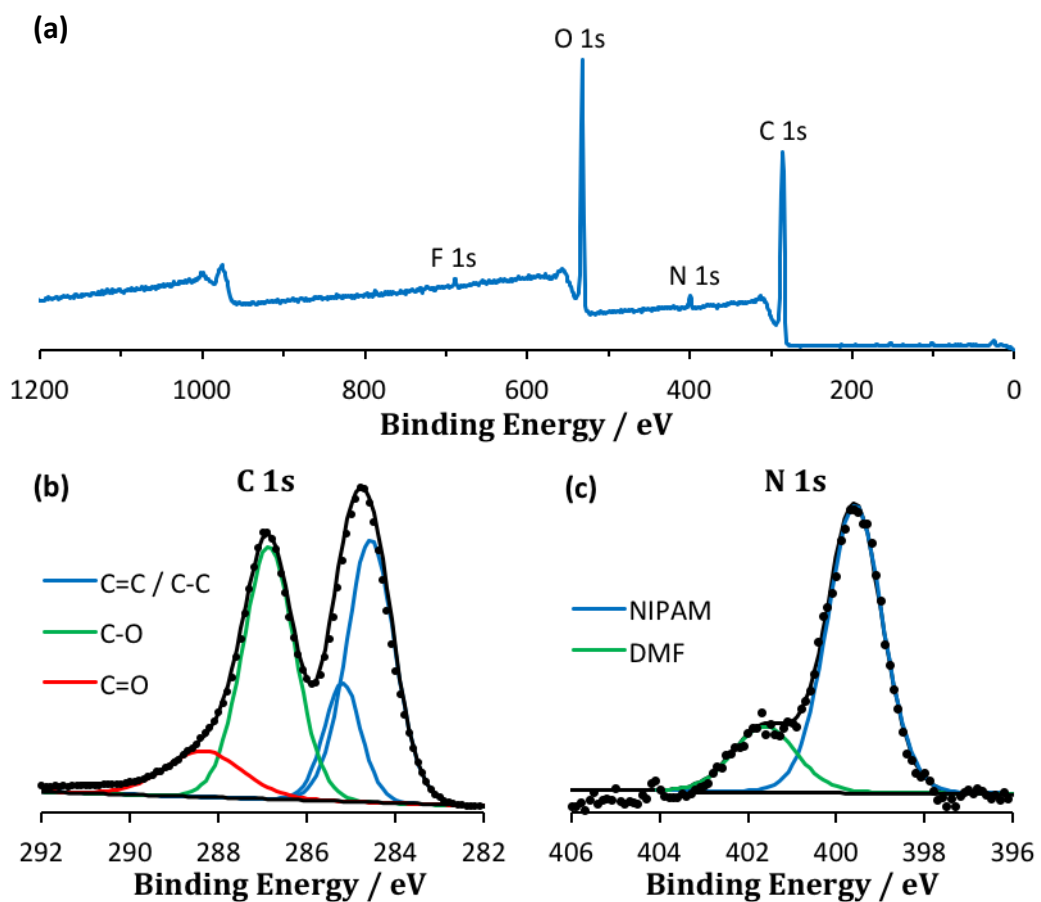


Fig 8 SI XPS analysis of GO-NIPAM₃₀, complete with survey scan (a), and core level spectra C 1s (b) and N 1s (c). The experimental data is shown as points with the underlying lines showing the fitted peaks (assignments as labelled).

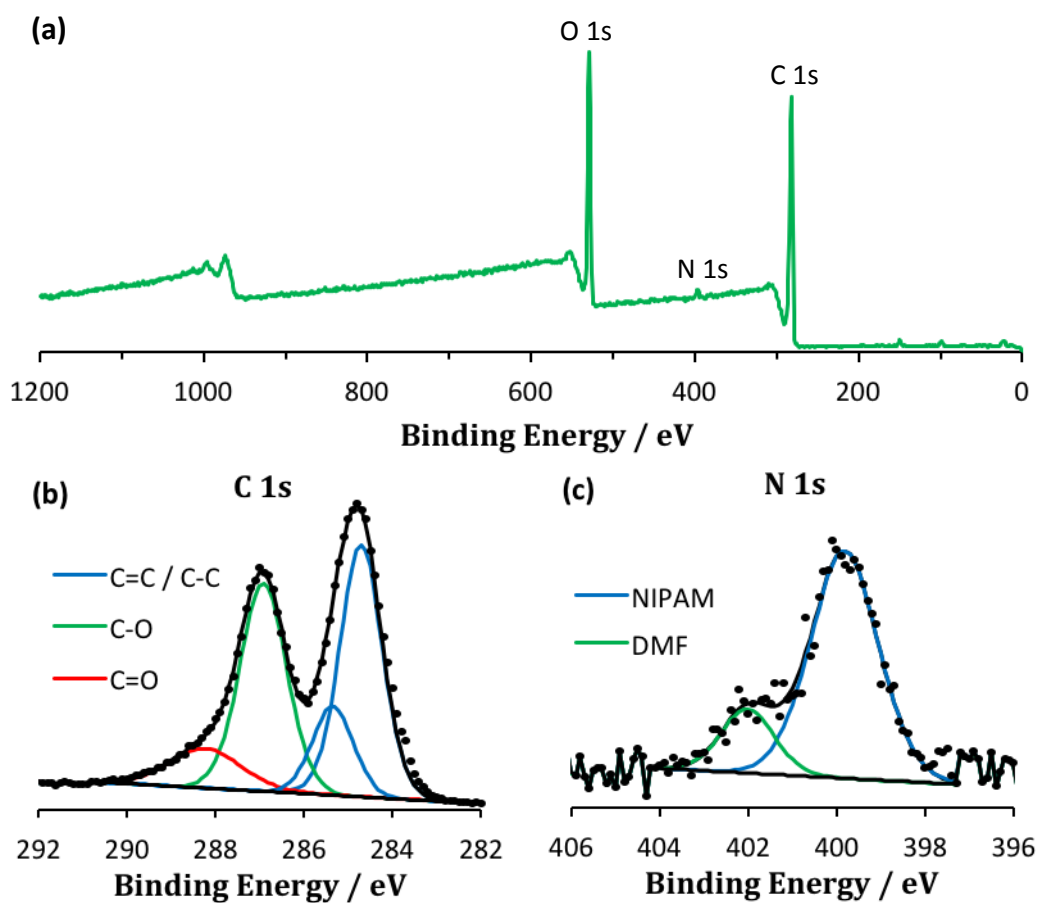


Fig 9SI XPS analysis of GO-NIPAM₂₀₀, complete with survey scan (a), and core level spectra C 1s (b) and N 1s (c). The experimental data is shown as points with the underlying lines showing the fitted peaks (assignments as labelled).

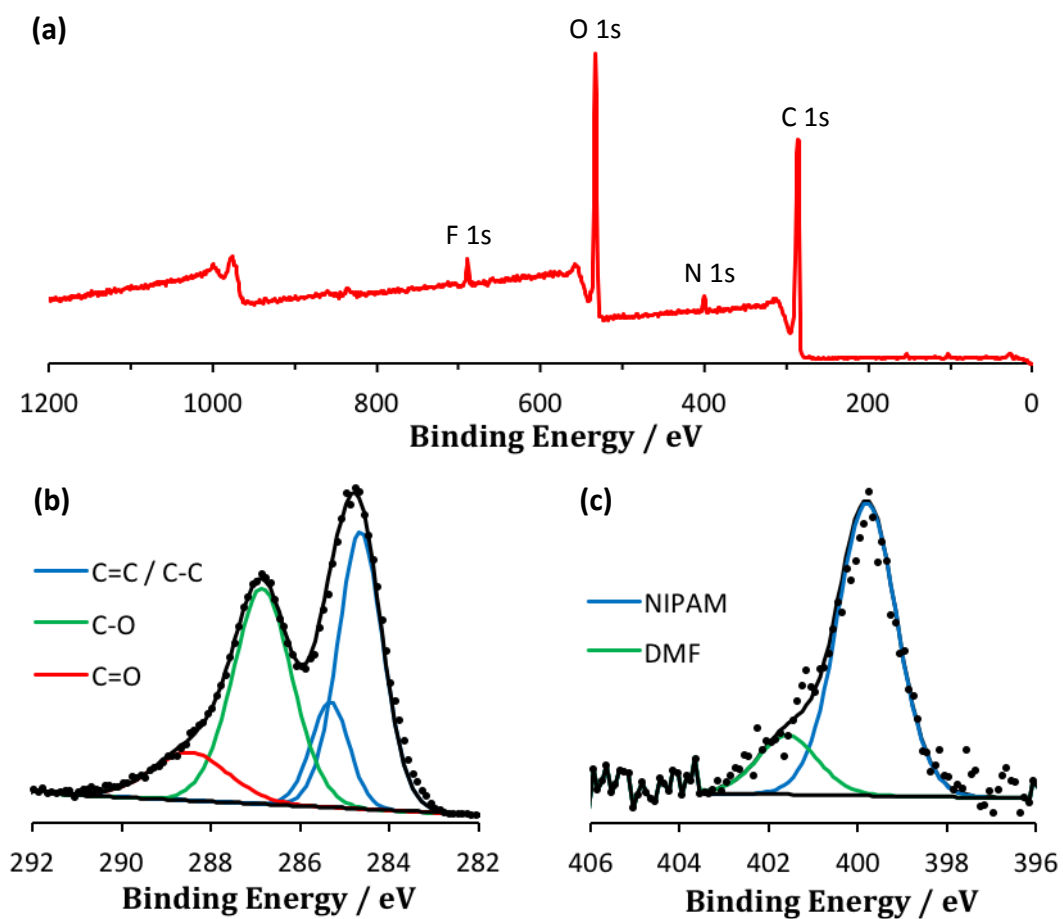


Fig 10SI XPS analysis of GO-NIPAM₄₀₀, complete with survey scan (a), and core level spectra C 1s (b) and N 1s (c). The experimental data is shown as points with the underlying lines showing the fitted peaks (assignments as labelled).

TGA

All TGA were recorded on a Mettler-Toledo TGA/DSC1 system at a heating rate of 10 K/min from 25-800 °C under air.

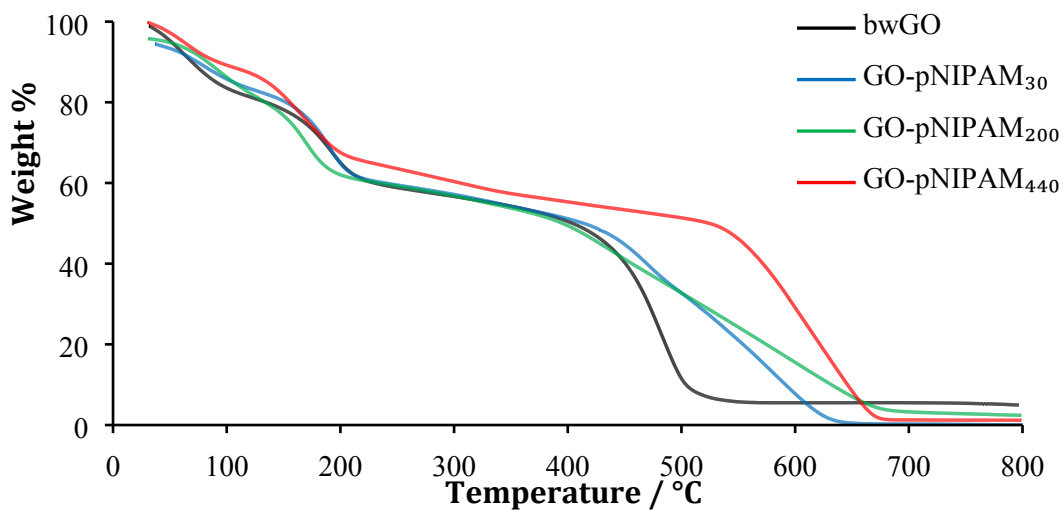


Fig 11SI TGA profiles of bwGO and all three GO-pNIPAM materials.

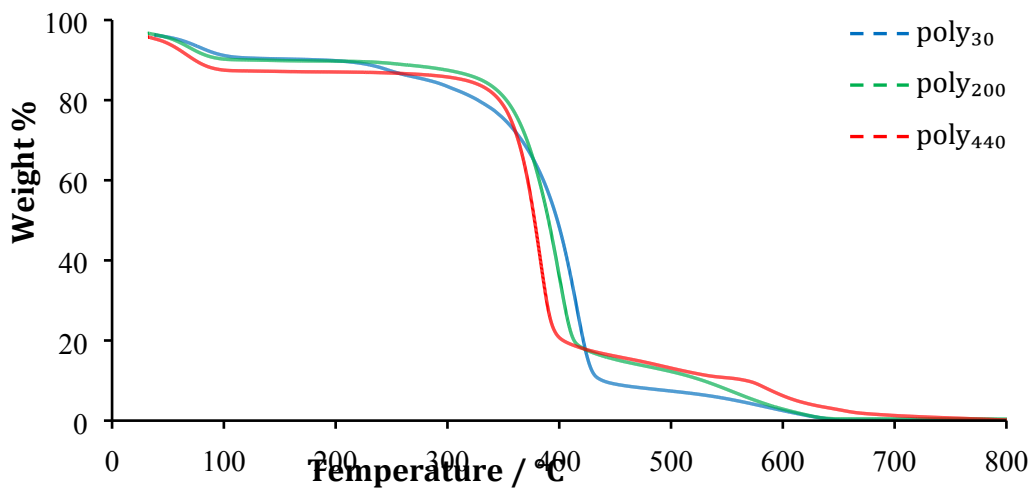


Fig 12SI TGA profiles of all three pNIPAM polymers.

Contact Angle

Contact angle measurements were carried out on a DSA100 Contact Angle Measuring System with DAS3 software.

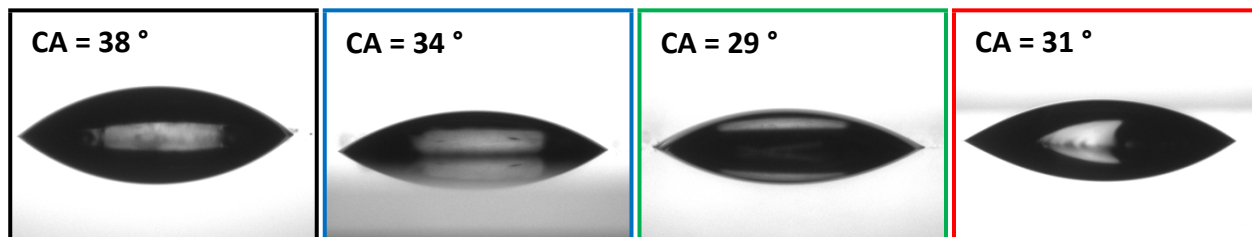


Fig 13SI Drop shape analysis of bwGO (black), GO-pNIPAM₃₀ (blue), GO-pNIPAM₂₀₀ (green) and GO-pNIPAM₄₄₀ (red).