Electronic Supplementary Information

Homogenous Thin Layer Coated Graphene via One Pot Reaction with Multidentate Thiolated PMMAs

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Materials

Graphene was purchased from Angstron Materials. For the synthesis of the AcSEMA monomer, potassium thioacetate (98%, Aldrich), 2-bromo-ethanol (99%, Aldrich) and methacryloyl chloride (99%, Aldrich) were employed as received. For the preparation of the polymers, the monomer methyl methacrylate (MMA, 95%, Aldrich) was washed several times with a sodium hydroxide 10 wt % aqueous solution and pure water, dried over sodium sulfate and distillated to remove the radical inhibitor. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA, 99%, Aldrich), N.N.N',N",N"-Pentamethyldiethylenetriamine (PMDETA, 99% Aldrich), ethyl 2-bromoisobutyrate (EBrⁱB, 99%, Aldrich), CuBr (99.999%, Aldrich), CuCl (99.999%, Aldrich), and the solvent benzonitrile (99.6%, Panreac) were used as received. Solvents were dried by standard methods or by elution through a Pure Solv Innovative Technology column drying system. The filter used in the synthesis of Graphene@P(MMA-co-AcSEMA) was a Fluoropore Membrane (Millipore) made from PTFE, hydrophobic, with 0.22 µm pore size. For the preparation of the composites, poly(methyl methacrylate) PMMA (Mw: 25000, 200 micron beads) was purchased from Polyscience, Inc. For surface modification CVD Graphene monolayer grown on Si/SiO₂ substrate (Graphenea) was

utilized.

Methods.

Thin-layer chromatography (TLC) was performed on silica gel pre-coated aluminum foils, Merck 60F 254, 0.25 mm.

¹H- and ¹³C-NMR spectra were registered at room temperature in CDCl₃ solution in Varian INOVA-300 and INOVA-400 spectrometers. Chemical shifts are reported in parts per million (ppm) using as an internal reference the solvent peak. The following abbreviations are used to describe signals: s (singlet), d (doublet), t (triplet), q (quartet), m (complex multiplet). Assignments were based on HSQC and HMBC experiments.

FTIR spectra were recorded on a Perkin–Elmer System 2000 FTIR spectrometer. The samples were mixed with KBr and compressed pellets were prepared for analysis in the spectral range v=4000-500 cm⁻¹ at a resolution of 4 cm⁻¹.

Raman measurements were undertaken in the Raman Microspectroscopy Laboratory of the Characterisation Service in the Institute of Polymer Science & Technology, CSIC using a Renishaw *InVia*-Reflex Raman system (Renishaw plc, Wotton-under-Edge, UK), which employed a grating spectrometer with a Peltier-cooled CCD detector coupled to a confocal microscope. The Raman scattering was excited with an argon ion laser ($\lambda = 514.5$ nm), focusing on the sample with a 100x microscope objective (NA=0.85) with a laser power of approximately 2 mW at the sample. Spectra were recorded in the range between approx. 1200 – 1800 cm⁻¹. All spectral data was processed with Renishaw WiRE 3.2 software.

Several areas were mapped on each sample. The spectral data was analysed by curve-fitting over the region 1250 – 1750 cm⁻¹ using a linear, two point baseline and unsupervised mixed Gaussian-Lorentzian peak profiles to fit the D, G and D' bands of graphene in each sample, with fixed upper and lower limits for band position and bandwidth of each band. Map data was obtained using the Wire 3.2 software package, see Figure S1.

Low resolution mass spectra were registered AutoSpecEQ EI apparatus by electron impact (EI, 70 eV).

Differential scanning calorimetry (DSC) analyses were run in a Perkin Elmer DSC6 model in hermetic aluminum pans under nitrogen flow (50 mL min⁻¹). Tests were performed with ca. 5 mg samples, heating from 30°C to 190°C at a heating rate of 10^oC min⁻¹.

Thermogravimetric analysis (TGA) was performed on a TA Q500 instrument with 3-5 mg samples in platinum pans under helium, heating from 50°C to 800°C at 10°C min⁻¹.

Molecular weights (M_n) and molecular weight distributions (MWD) were determined by size exclusion chromatography (SEC) in a Perkin Elmer GPC equipment provided with a Waters 410 Differential Refractometer detector. All samples were eluted with tetrahydrofuran (THF) as the mobile phase at 1 mL min⁻¹ and 70°C (PMMA standards were employed for the calibration).

Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2100 microscope operating at 200kV equipped with a charged-coupled device (CCD)-camera (Gatan Orius SC1000). Scanning Transmission Electron Microscopy (STEM) images were taken using a FE-SEM apparatus HITACHI SU8000. Samples were prepared by depositing one drop of a diluted solution of modified Graphene onto a holey carbon film supported on a 300 mesh copper grid (3 mm in diameter) from Electron Microscopy Sciences.

Atomic force microscopy (AFM) measurements were conducted on a Multimode Nanoscope IVa, Digital Instrument/Veeco operated in tapping mode at room temperature under ambient conditions. DC-conductivity measurements were carried out on pressed-pellets perfectly dried under vacuum. The measurements were carried out using a four-probe setup equipped with a dc low-current source (LCS-02) and a digital micro-voltmeter (DMV-001) from Scientific Equipment & Services.

The conductivity was calculated by using the following equation:

$$\sigma = \frac{1}{\rho} = 4.5324 \left(\frac{V}{I}\right) f_1 f_2$$

where *t* is the thickness of the sample, f_1 is the finite thickness correction for thick samples on an insulating bottom boundary and f_2 is the finite width correction. The thickness correction is described by the following equation:

$$f_1 = \frac{\ln(2)}{\ln\left[\frac{\sinh(\ell/s)}{\sinh(\ell/2s)}\right]}$$

where s is the probe distance (0.2 cm). The width correction f_2 is a function of the shape of the sample thickness and length (I) for rectangular samples and thickness and diameter for circular samples.

Scheme S1. Synthesis of monomer AcSEMA



Synthesis of the monomer 2-(acetylthio)ethyl methacrylate (AcSEMA). The monomer was synthesized following a previously described method (Scheme S1).¹ To a solution of 2-bromoethanol (14.0 g, 0.11 mol) in 150 mL of dichloromethane, a solution of methacryloyl chloride (11.2 mL, 0.12 mol) in 10 mL of dichloromethane was added gradually over 10 min at 0°C. After addition, the reaction mixture was continuously stirred for 30 min. Triethylamine (8.07 mL, 0.12 mol) was added dropwise in 15 min at 0°C. The solution became slurry after several minutes. The reaction mixture was stirred overnight at room temperature and then filtered. The filtrate was washed thoroughly using 3×100 mL of deionized H₂O and dried by anhydrous magnesium sulphate. The solvent was removed under vacuum providing the temperature lower than 30°C. The work up yielded 17.8 g (85%) of 2-bromoethyl methacrylate (1). ¹H-NMR(400 MHz, CDCl₃): δ (ppm) 6.17 (s, 1H, C*H*H=C(CH₃)-), 5.62 (s, 1H, C*H*H=C(CH₃)-), 4.45 (t, 2H, C*H*₂-O-), 3.56 (t, 2H, C*H*₂-Br), 1.96 (s, 3H CH₂=C(C*H*₃)-).

Potassium thioacetate (11.62 g, 0.102 mol) and 2-bromoethyl methacrylate (17.8 g, 0.093 mol) were dissolved in 200 mL of acetone. The solution was stirred for 24h at room temperature and filtered. Acetone was removed by rota-evaporation at 25°C and the precipitate was redissolved in dichloromethane, washed with water and a saturated NaHCO₃ solution and dried over sodium sulphate. The product was finally vacuum distilled yielding 13.2 g (74%). ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 1.95 (s, 3 H, CH₃C(CH₂)), 2.25 (s, 3 H, CH₃CO), 3.18 (t, 2 H, J = 7.5 Hz, CH₂S), 4.22 (t, 2 H, J = 7.5 Hz, CH₂OCO), 5.48 (m , 1 H, C*H*H=C), 6.04 (m , 1 H, C*H*H=C) (Figure S1, Supporting Information). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 195 (S*C*OCH₃), 167.1 (*C*OO), 136.1 (*C*(CH₃)=CH₂), 126.1 (*C*H₂=), 63.08 (CH₂O), 36.7 (*C*H₂S), 28.0 (*C*H₃CO), 18.39 (CH₃C(=CH₂)CO).

IR (cm⁻¹): 2987.8, 1717 (COO), 1692.9 (COS), 1452, 1295, 1154, 1130, 947. MS (EI), m/z (%) = 162 [nominal mass M⁺] (4), 119 (10), 103 (39), 83 (100).

Scheme S2. Synthesis of P(MMA-co-AcSEMA) (a) and PMMA-SAc (b) and their hydrolysis products



Synthesis of P(MMA-co-AcSEMA) by ATRP. ATRP copolymerizations were carried out in benzonitrile solution (50 wt %) with a constant monomer/initiator/catalyst ratio of 200/1/1. Different amounts of AcSEMA in the feed (2, 6 and 9 mol %) were used to obtain copolymers of different compositions. A typical procedure for the synthesis of these statistical copolymers is described below for 9mol % sample (Scheme S2a). HMTETA (0.034 g, 0.15 mmol), degassed monomers MMA (2.73 g, 27.3 mmol) and AcSEMA (0.50 g, 2.7 mmol) and the solvent benzonitrile (5.5 g) (previously bubbled with nitrogen for at least 15 min) were all added to a dry Pyrex tube ampoule with CuCl (0.014 g, 0.15 mmol). Subsequently the mixture was degassed by bubbling nitrogen during another 20 min, and the initiator EBrⁱB (0.029 g, 0.15 mmol) was introduced into the ampoule using degassed syringes in order to start the polymerization. The ampoules were immediately placed in a thermostatic oil bath maintained at 100°C ± 0.1°C. To stop the polymerization at a selected time (90 min) the reaction mixture was cooled and guenched with chloroform and then passed through a neutral alumina column to remove the catalyst. The solution was concentrated by rota-evaporation and the polymer precipitated by adding the solution to a large excess of hexane. The precipitated products were decanted and dried under high vacuum until constant weight. Total monomer conversions were measured gravimetrically. The samples were denominated P(MMA-co-AcSEMA)x where x denotes the molar percentage of AcSEMA in the feed.

Synthesis of P(MMA)-SAc. The precursor P(MMA)-Br was synthesized by ATRP in benzonitrile solution (50 wt. %) with a constant monomer/initiator/catalyst ratio of 60/1/1 (Scheme S2b). PMDETA (326 μ L, 1.56 mmol), degassed monomer MMA (10 mL, 93.5 mmol) and the solvent benzonitrile (10 mL) (previously bubbled with nitrogen for at least 15 min) were all added to a dry Pyrex tube ampoule with CuBr (0.224 g, 1.56 mmol). Subsequently the mixture was degassed by bubbling nitrogen for a further 20 min, and the initiator EBrⁱB (0.304 g, 1.56 mmol) was introduced into the ampoule using degassed syringes in order to start the polymerization. The ampoules were immediately placed in a thermostatic oil bath at 100 ± 0.1°C. To stop the polymerization at 30 min, the reaction mixture was cooled and quenched with chloroform, then passed through a neutral alumina column to remove the catalyst. The solution was concentrated by rotary-evaporation and the polymer precipitated by adding the solution to a large excess of hexane. The precipitated product was decanted and dried under high vacuum until a constant weight was reached. Total monomer conversion was measured gravimetrically.

The bromine end-functionalized P(MMA)-Br (1g) and potassium thioacetate (3 equiv) were stirred in acetone (25 mL) and refluxed for 4 h. Then, the acetone was removed, and the precipitate was redissolved in dichloromethane, washed with water, and dried with sodium sulfate. The resulting thioacetate end-functionalized P(MMA)-SAc was obtained as a pale-yellow solid. Yield: 99%

Table S1. Experimental synthetic conditions and characterization^a of P(MMA-*co*-AcSEMA) copolymers synthesized by ATRP (entries 1 to 3) and P(MMA)-Br synthesized by ATRP and afterward transformed in P(MMA)-Ac (entry 4).

əntry	Time (min)	F _{AcSEMA}	Conv.(%)	$M_{\rm nSEC}$ (g.mol ⁻¹)	∕l _{wSEC} (g.mol⁻¹	M _w /M _n	T _{max.} (°C)	<i>T</i> _g (°C)
1	90	0.02	56	22813	21750	1.19	381	85
2	90	0.06	46	15237	17950	1.18	404	71
3	90	0.09	35	12983	13730	1.30	399	60
4	30		19	8136	11318	1.14	395	85

 F_{ACSEMA} : experimental molar fraction composition in the copolymer (calculated by ¹H-NMR), Conv: conversion (%), $M_{n SEC}$: number average, $M_{w SEC}$: weight average molecular weight (calculated by SEC), M_w/M_n : polydispersity index, T_{max} : decomposition temperature and T_g : glass transition temperature.

Additional information on the chacracterization of graphene@P(MMA-co-SEMA)x.

The materials were characterized spectroscopically. The infrared spectra of pristine graphene and all the polymer covered samples are shown in Figure S1.



Figure S1. A) FTIR spectra of starting graphene (black line), graphene@P(MMA-co-SEMA)-2 (pink), -6 (green), -9 (red) and graphene@P(MMA)-SH (blue) B) FTIR spectra of P(MMA-co-AcSEMA)-2, -6 and -9, the inset show the different intensity of thioester carbonyl band.

The Raman spectra of the polymer-modified graphene are shown in Figure S2, where the spectrum of the starting graphene is also included for comparison. The most important features observed for all samples are the G band appearing between 1590-1598 cm⁻¹, the disorder-induced D band at 1350 cm⁻¹, the second order 2D band at around 2700 cm⁻¹ and the D+G band near 2940 cm⁻¹. In comparison with the starting graphene, only slight changes are observed. The D/G ratio, which is normally used as a marker of covalent modification of graphene, did not change from one sample to another probably due to the nature of the starting graphene employed in this study, which is already highly defective. Thus the sheets can be considered laminates with internal holes or vacancies that largely contribute to increase the D band. When reacting with the polymers the edges of these vacancies are more reactive and the polymer may bind to the graphene at these sites, reason why the intensity of the D band did not change much after the reaction. However, the full-width half-maximum (FWHM) of the D band is slightly broader in all polymer-modified graphene evidencing some disorder^{2,3} created by the linking of the polymers. In fact, the FWHM(D) is higher for the samples prepared from copolymers with the highest content of thiol groups, while the brushlike material and the copolymer with the lowest amount of thiol groups displayed the lowest FWHM values (Figure S2). This result indicates that the chains of the copolymer are connected to the graphene at several sites in a multidentate manner since a correlation exists between the multidentate effects with the concentration of linkable thiol groups.



Figure S2. Raman spectra of starting graphene (black line), graphene@P(MMA-co-SEMA)-2 (pink), -6 (green), -9 (red) and graphene@P(MMA)-SH (blue).

For comparison purposes, the TGA curve of the starting graphene is shown in Figure S3, where it can be seen that the pristine material shows a weight loss lower than 1 %.



Figure S3. TGA curve for starting graphene collected at a heating scan of 10°C.min⁻¹ under nitrogen atmosphere. Note: total loss of mass at 800° C is less than 1%. The signal is very noisy due to the low density of the graphene makes the mass of material that can be loaded into the crucible is very low, even after compressing.

Figure S4 shows the FESEM image of a pressed-pellet of graphene@P(MMA-co-SEMA)-9 (a) and the EDAX mapping analysis of C, S and O, demonstrating the presence of the covering polymer on the graphene surface.



Figure S4. a) FESEM image of graphene@P(MMA-co-SEMA)-9 and elemental mapping of b) Sulfur (Blue dots), c) Carbon (Red dots) and d) Oxygen (Green dots).

The modification of CVD graphene was monitored with Raman spectroscopy since it is highly sensitive to the changes of hybridization of carbon atoms (sp² to sp³) in graphene due to covalent modification.



Figure S5. Averaged Raman spectra of CVD graphene (black), and copolymer-modified CVD graphene prepared by brush-like (green) and multidentate (red) approaches.

An initial analysis from randomly selected points of the CVD graphene revealed that the multidentate approach leads to a stronger D band (Figure S5). This band is related to defect sites and its greater intensity indicates higher degree of polymer bonding in the multidentate copolymer-modified graphene.

We focused on the multidentate copolymer-modified graphene and collected a 2D mapping of a larger region of the substrate to have a more representative picture about the distribution of modification (Figure S6). On the left hand side of Figure S6, a visible image of a region analysed on the sample graphene@P(MMA-co-SEMA)-9 is shown. On the right hand side the maps generated from curve fitting of the intensity of the D and G modes are shown over the visible image. The central image is a superimposition of these maps. Spectra from three different points are shown to illustrate the curve fitted D, G and D' bands. The maps were exported in ASCII format to Origin, and D/G maps were constructed. In the calculation of the D/G ratio, the contribution of D' was removed. Regions where no spectral data was observed were eliminated from the map matrix. The maps obtained for each sample are compared in Figure 6 in the manuscript.



Figure S6. Raman mapping analysis of the graphene@P(MMA-co-SEMA)-9 sample.

The electrical conductivity values for all samples, measured by the four-probe in line method are shown in Table S2.

Table S2. DC-Conductivity values of all samples studied.

Sample	DC-Conductivity (S.cm ⁻¹)
Graphene	~ 30
graphene@P(MMA-co-SEMA)-2	22.8
graphene@P(MMA-co-SEMA)-6	24.8
graphene@P(MMA-co-SEMA)-9	24.2
graphene@PMMA-SH	22.4

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