

Electronic Supplementary Information

Radical Polymerisation and Thiol-Ene Post-Polymerisation Functionalisation of Terpenoid Acrylates in Conventional and Renewably Sourced Organic Solvents

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Experimental Section

Materials

Geraniol (97%), triethylamine (99%), acryloyl chloride (97%), basic aluminium oxide, hydrochloric acid (HCl, 37%), sodium hydrogen carbonate (NaHCO₃), 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99%), magnesium sulphate (MgSO₄), dimethyl 2,2'-azobis(2-methylpropionate) (V-601), ethyl α -bromoisobutyrate (EBiB, 98%), copper(II) bromide (CuBr₂, 99%), methyl thioglycolate (95%), 2-mercaptoethanol (99%), 3-mercaptopropionic acid (99%), 2,2-dimethoxy-2-phenyl acetophenone (DMPA, 99%), dichloromethane (DCM), cyclohexane, dihydrolevoglucosenone (Cyrene, 99%), trifluoroethanol (TFE, 99%), methanol (MeOH), isopropanol (IPA), acetonitrile (ACN), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP) and toluene were all purchased from Sigma-Aldrich and used as received. Cu⁰ wire (gauge 0.25 mm) was purchased from Comax Engineered Wires and pre-activated by immersion in concentrated HCl, rinsed with water and dried before use. Tris(2-(dimethylamino)ethyl)amine (Me₆TREN) was prepared following the literature,^{1,2} and stored under a nitrogen atmosphere. Deionised water (DI water) was used for the purification step of geraniol acrylate monomer (15.6 M Ω , VEOLIA Elga Purelab).

Instrumentals and analysis

NMR spectroscopy

NMR spectra were obtained on a Bruker DPX-400 and Bruker AV III-500 spectrometers. Polymer samples were dissolved in deuterated chloroform (CDCl₃) obtained from Sigma-Aldrich, with ca. 100 mg/mL used for the branching analysis. All chemical shifts are reported in ppm (δ). Data was processed and analysed using the ACD/NMR software.

Size exclusion chromatography (SEC)

Molar mass distribution and molecular weight were measured using size exclusion chromatography (SEC). All samples, except that of poly(geranyl acrylate) functionalized with 3-mercaptopropionic acid, were run on an Agilent Infinity II MDS instrument equipped with differential refractive index (DRI), viscometry (VS) dual angle light scatter (LS), multiple

wavelength UV detectors. The system was equipped with 2 x PLgel Mixed C columns (300 x 7.5 mm) and a PLgel 5 μm guard column. The eluent used was tetrahydrofuran (THF) with 2 % trimethylamine (TEA) and 0.01 % butylated hydroxytoluene additives. Samples were run at 1 mL/min at 30 °C. Narrow dispersity poly(methyl methacrylate) and polystyrene standards were applied for calibration, (Agilent EasyVials). All samples were filtered through a GVHP membrane with 0.22 μm pore size before injection. Experimental molar mass ($M_{n,SEC}$) and dispersity (\mathcal{D}) values were determined by conventional calibration using the Agilent GPC/SEC software.

The molar mass distribution and molecular weight of poly(geranyl acrylate) functionalized with 3-mercaptopropionic acid were measured on an Agilent Infinity II MDS instrument equipped with differential refractive index (DRI), viscometry (VS), dual angle light scatter (LS) and variable wavelength UV detectors. The system was equipped with 2 x PLgel Mixed D columns (300 x 7.5 mm) and a PLgel 5 μm guard column. The eluent was DMF with 5 mmol NH_4BF_4 additive. Samples were run at 1ml/min at 50 °C. Poly(methyl methacrylate) standards (Agilent EasiVials) were used for calibration between 550 – 955,000 g/mol. Analyte samples were filtered through a nylon membrane with 0.22 μm pore size before injection. Experimental molar mass ($M_{n,SEC}$) and dispersity (\mathcal{D}) values were determined by conventional calibration using the Agilent GPC/SEC software.

Fourier-transform infrared spectroscopy (FT-IR)

FT-IR measurements were performed on a Shimadzu Spirit IR equipped with a SpecAc Golden Gate ATR. The wavelength range was from 500 to 4000 cm^{-1} , for 40 scans at 4 cm^{-1} resolution.

Differential scanning calorimetry (DSC)

DSC measurements were performed on a TA Discovery DSC 2500 with autosampler. Measurements were carried out under N_2 , from -100 to 220 °C at a rate of 10 K/min in aluminium pans.

Experimental procedures

Esterification of geraniol using acryloyl chloride

Geraniol (1 equiv., 0.128 mol), triethylamine (1.9 equiv.) and dichloromethane (DCM) (200 mL) were added to a round bottom flask. A mixture of acryloyl chloride (1.5 equiv.) and DCM (50 mL), kept at 0 °C, was added dropwise over 1 hour to the reaction vessel. The reaction proceeded overnight, at room temperature, with stirring. The resulting salt was vacuum filtered, and the collected solution washed with 1 M hydrochloric acid (HCl) (3 x 100 mL), saturated sodium hydrogen carbonate (NaHCO₃) (3 x 100 mL) and DI water (3 x 100 mL) and dried with magnesium sulphate (MgSO₄). DCM was then removed under vacuum. Butylated hydroxytoluene (BHT) (0.1 mg) was added to the solution as a radical stabiliser, and the product purified by vacuum distillation at 67 °C, at 6 x 10⁻² mbar. The product was obtained as a colourless liquid. The purity of geranyl acrylate monomer was evaluated by NMR, FT-IR, and LC-MS.

Geraniol

¹H NMR (CDCl₃, 400 MHz) δ (ppm): 5.38 – 5.42 (m, 1H, -CH=C(CH₃)-CH₂-), 5.07 – 5.12 (m, 1H, -CH=C(CH₃)CH₃), 4.12 (d, J = 6.85 Hz, 2H, OH-CH₂-), 2.25 (s, 1H, HO-CH₂-), 2.00 – 2.13 (m, 4H, -CH₂-CH₂-), 1.67 – 1.68 (m, 6H, -CH=C(CH₃)-CH₂-; -CH=C(CH₃)CH₃), 1.60 (s, 3H, -CH=C(CH₃)CH₃).

¹³C NMR (CDCl₃, 400 MHz) δ (ppm): 139.19 (C), 131.60 (C), 123.93 (CH), 123.49 (CH), 59.13 (CH₂), 39.53 (CH₂), 26.38 (CH₂), 25.60 (CH₃), 17.60 (CH₃), 16.18 (CH₃).

FT-IR (cm⁻¹): 3300 (O-H stretching, weak, broad, alcohol), 2916 (C-H, medium, alkane), 1660 (C=C, medium, alkene), 1436 (CH₂ & CH₃ deformation, medium, bending, alkane), 1373 (CH₃ deformation, medium, bending, alkane), 992 (C=C bending, strong, alkene).

Geranyl acrylate

¹H NMR (CDCl₃, 400 MHz) δ (ppm): 6.37 (dd, J = 17.36, 1.10 Hz, 1H, H-C(H)=CH-), 6.13 (dd, J = 17.36 Hz, 10.39 Hz, 1H, H-C(H)=CH-), 5.80 (dd, J = 10.52 Hz, 1.10 Hz, 1H, H-C(H)-CH-), 5.37 (t, J = 7.09 Hz, 1H, -CH₂-CH=C(CH₃)CH₂-), 5.08 (t, J = 5.75 Hz, 1H, -CH₂-CH=C(CH₃)CH₃-), 4.68 (d, J = 7.09 Hz, 2H, -O-CH₂-),

2.04 - 2.11 (m, 4H, $-\text{CH}_2-\text{CH}_2-$), 1.67-1.71 (m, 6H, $-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2-$; $-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)\text{CH}_3-$), 1.59 (s, 3H, $-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)\text{CH}_3-$).

^{13}C NMR (CDCl_3 , 400 MHz) δ (ppm): 166.15 (C), 142.26 (C), 131.73 (C), 130.38 (CH_2), 128.61 (CH), 123.71 (CH), 118.24 (CH), 61.37 (CH_2), 39.50 (CH_2), 26.25 (CH_2), 25.61 (CH_3), 17.62 (CH_3), 16.42 (CH_3).

FT-IR (cm^{-1}): 2912 (C-H, medium, alkane), 1725 (C=O, strong, ester), 1636 (C=C, medium, alkene), 1404 (CH_2 & CH_3 deformation, medium, bending, alkane), 1178 (C-O, strong, ester), 963 (C=C, strong, bending, alkene), 810 (C-H, strong, bending, alkane).

LC-MS (g/mol): $m/z = 208.3$

General procedure for the free radical polymerisation of geranyl acrylate

Geranyl acrylate, cyclohexane (3 mL, 0.01 mol), cyclohexane (7 mL) and dimethyl 2,2'-azobis(2-methylpropionate) (V-601) (0.044 g, 1.5 mol% with respect to monomer) were introduced in a round-bottom flask with a magnetic stir bar. The flask was sealed with a suba-seal and purged with nitrogen gas for 1 hour. The reaction was carried out at 66 °C in an oil bath, with stirring, and was monitored by regular sampling using 1 mL degassed syringes, until full conversion was obtained after 21 hrs.

Poly(geranyl acrylate)

^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 5.32 (s, 1H, repeat unit, $-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2-$), 5.08 (s, 1H, repeat unit, $-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)\text{CH}_3-$), 4.55 (s, 2H, repeat unit, $-\text{O}-\text{CH}_2-$), 2.32 (s, 1H, repeat unit, $-\text{CH}_2-\text{CH}-$), 2.04 (d, $J = 14.55$ Hz, 4H, repeat unit, $-\text{CH}_2-\text{CH}_2-$), 1.59 – 1.67 (m, 11H, repeat unit, $-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2-$; $-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)\text{CH}_3-$; $-\text{CH}_2-\text{CH}-$).

^{13}C NMR (CDCl_3 , 400 MHz) δ (ppm): 174.42 (C), 141.71 (C), 131.57 (C), 123.89 (CH), 118.58 (CH), 61.48 (CH_2), 41.3 (CH), 39.61 (CH_2), 26.43 (CH_2), 25.67 (CH_3), 17.67 (CH_3), 16.42 (CH_3).

FT-IR (cm^{-1}): 2912 (C-H, medium, alkane), 1725 (C=O, strong, ester), 1636 (C=C, medium, alkene), 1404 (CH_2 & CH_3 deformation, medium, bending, alkane), 1178 (C-O, strong, ester), 963 (C=C, strong, bending, alkene), 810 (C-H, strong, bending, alkane).

General procedure for the Cu⁰ wire-mediated reversible deactivation radical polymerization (RDRP) of geranyl acrylate

Geranyl acrylate (DP equiv.), pre-activated copper wire (5 cm), ethyl α -bromoisobutyrate (EBiB) (1 equiv.), CuBr₂ (0.05 equiv.), tris[2-(dimethylamino)ethyl] amine (Me₆TREN) (0.18 equiv.) and Cyrene (1:1 to the volume of monomer) were loaded in a vial with a magnetic stir bar. The copper wire was wrapped around the stir bar. The vial was then fitted with a suba-seal and purged with nitrogen gas for 30 minutes. The reaction was carried out at ambient temperature for 24 hrs with stirring and monitored by periodical sampling using 1 mL degassed syringes and passing the samples through a neutral alumina column to remove dissolved copper salts. The samples were analysed by NMR and SEC.

General procedure for the Cu^{II}-mediated photoinduced reversible deactivation radical polymerization (RDRP) of geranyl acrylate

Geranyl acrylate (DP equiv.), EBiB (1 equiv.), CuBr₂ (0.02 equiv.), Me₆TREN (0.12 equiv.) and Cyrene (1:1 to the volume of monomer) were loaded in a vial which was then fitted with a suba-seal and purged with nitrogen gas for 30 minutes. The degassed solution was then transferred into a UV box ($\lambda_{\text{max}} \approx 360$ nm) and left to react for 21 hrs, with stirring. The reaction was monitored by regular sampling under nitrogen and, prior to analysis by NMR and SEC, samples were passed through a neutral alumina column to remove dissolved copper salts.

General procedure for the thiol-ene reaction of poly(geranyl acrylate)

Poly(geranyl acrylate) was precipitated in methanol and volatiles removed in a vacuum oven. Purified poly(geranyl acrylate) (200 mg, 1 equiv.), thiol (10 equiv.), and DMPA photoinitiator (0.1 equiv.) were dissolved in toluene (4 mL) and added to a vial fitted with a suba-seal which was purged with nitrogen gas for 30 minutes. The degassed solution was placed in a UV box ($\lambda_{\text{max}} = 365$ nm) and left to react for 24 hours, with stirring. The final product was analysed by NMR, FT-IR, and SEC. Poly(geranyl acrylate) functionalized with methyl thioglycolate was purified by precipitation in methanol while those functionalized with 2-mercaptoethanol and 3-mercaptopropionic acid were precipitated in water. All polymers were then dried in a vacuum oven.

Functionalisation of poly(geranyl acrylate) with methyl thioglycolate

$^1\text{H NMR}$ (Toluene- d_8 , 400 MHz) δ (ppm): 4.51 (br s, 2H, $-\text{CH}_2-\text{CH}(\text{SR})-$), 3.60 – 3.70 (m, 6H, $-\text{COO}-\text{CH}_3$), 3.20 – 3.34 (m, 4H, $-\text{H}_3\text{COOC}-\text{CH}_2-\text{SR}-$), 2.74 (br s, 1H, $-\text{RS}-\text{CH}(\text{CH}(\text{CH}_3)\text{CR})-$), 1.65 – 2.14 (m, 9H, $-\text{CH}_2-$; $-\text{CH}(\text{CH}_3)-$), 1.08 – 1.40 (m, 9H, $-\text{CH}_3$).

Functionalisation of poly(geranyl acrylate) with 2-mercaptoethanol

$^1\text{H NMR}$ (DMSO- d_6 , 400 MHz) δ (ppm): 5.03 (br s, 2H, $-\text{HO}-\text{CH}_2-\text{R}$), 4.50 ($-\text{CH}_2-\text{CH}(\text{SR})-$), 3.36 (t, 4H, $J = 6.48$ Hz, $-\text{HO}-\text{CH}_2-\text{R}$), 2.55 (t, 1H, $J = 6.60$ Hz, $-\text{CH}_2-\text{CH}(\text{SR})-$), 2.27-2.37 (m, 4H, $\text{HO}-\text{CH}_2-\text{CH}_2-\text{SR}$), 2.17 (bs, 2H, $\text{RS}-\text{CH}(\text{CH}_2-\text{R})-$; $-\text{H}_2\text{C}-\text{CH}(\text{COOR})-$), 1.11-1.61 (m, 6H, $-\text{CH}(\text{CH}_3)\text{CH}_3$; $-\text{CH}_2-$), 0.96 (s, 2H, $-\text{CH}_2-$), 0.58-0.70 (m, 9H, $-\text{CH}_3$).

Functionalisation of poly(geranyl acrylate) with 3-mercaptopropionic acid

$^1\text{H NMR}$ (DMSO- d_6 , 400 MHz) δ (ppm): 4.14 (br s, 2H, $-\text{CH}_2-\text{CH}(\text{SR})-$), 3.59-3.63 (m, 1H, $J = -\text{CH}_2-\text{CH}(\text{SR})-$), 2.46-2.89 (m, 8H, $\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{SR}$), 2.31 (s, 2H, $\text{RS}-\text{CH}(\text{CH}_2-\text{R})-$; $-\text{H}_2\text{C}-\text{CH}(\text{COOR})-$), 1.21-1.87 (m, 8H, $-\text{CH}(\text{CH}_3)\text{CH}_3$; $-\text{CH}_2-$), 0.88-0.93 (m, 9H, $-\text{CH}_3$).

Supplementary data for geraniol and geranyl acrylate

Geraniol

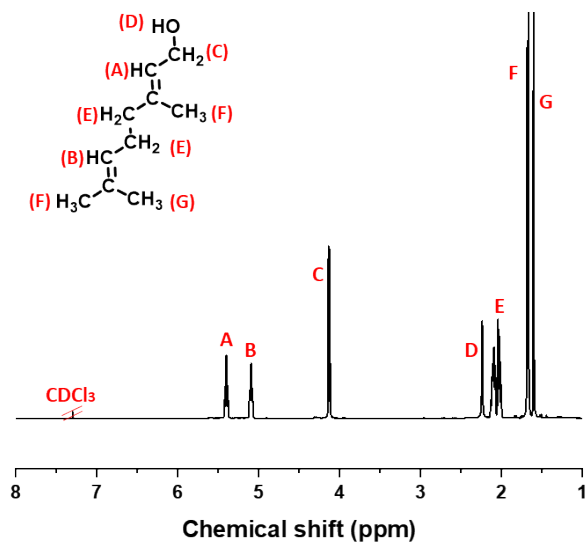


Figure S1. ¹H NMR (400 MHz, CDCl₃) spectrum of geraniol.

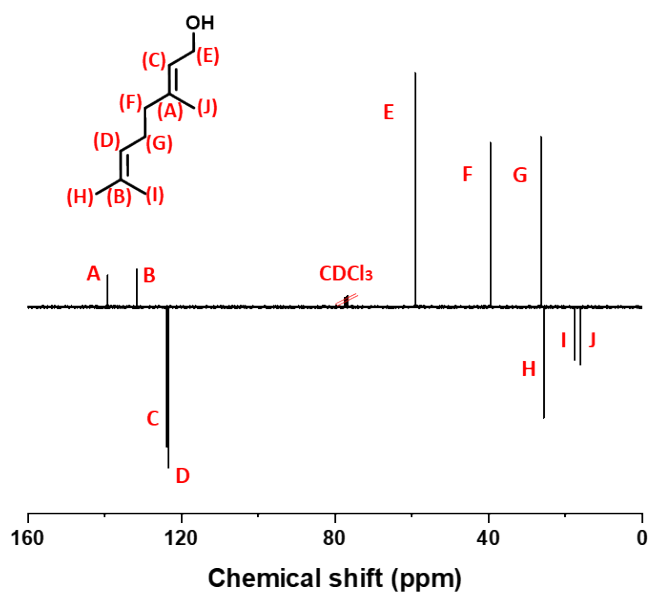


Figure S2. ¹³C DEPT NMR (400 MHz, CDCl₃) spectrum of geraniol.

Geranyl acrylate

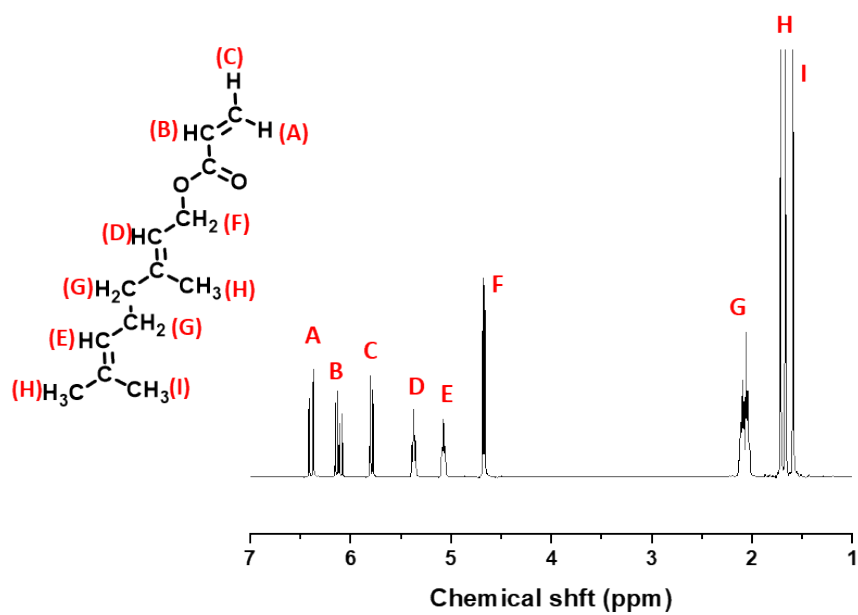


Figure S3. ¹H NMR (400 MHz, CDCl₃) spectrum of geranyl acrylate.

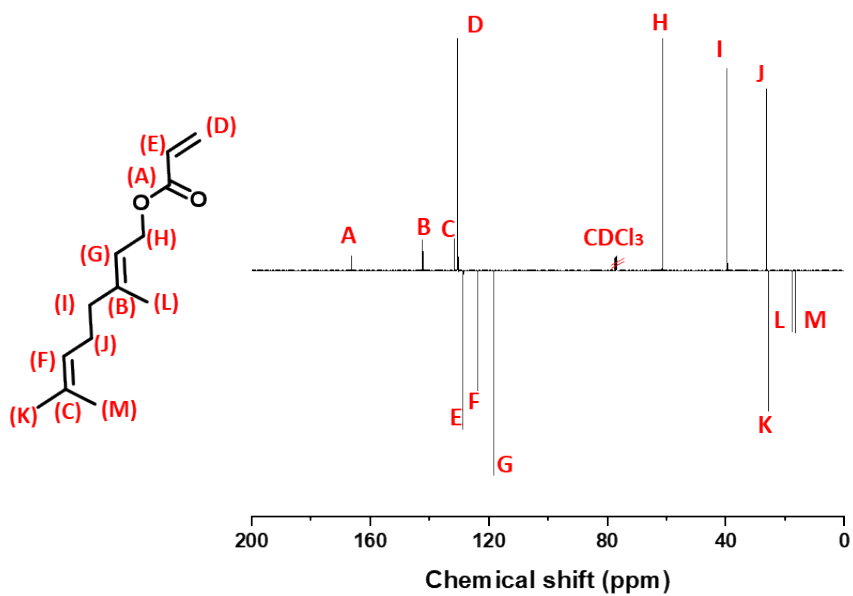


Figure S4. ¹³C DEPT NMR (400 MHz, CDCl₃) spectrum of geranyl acrylate.

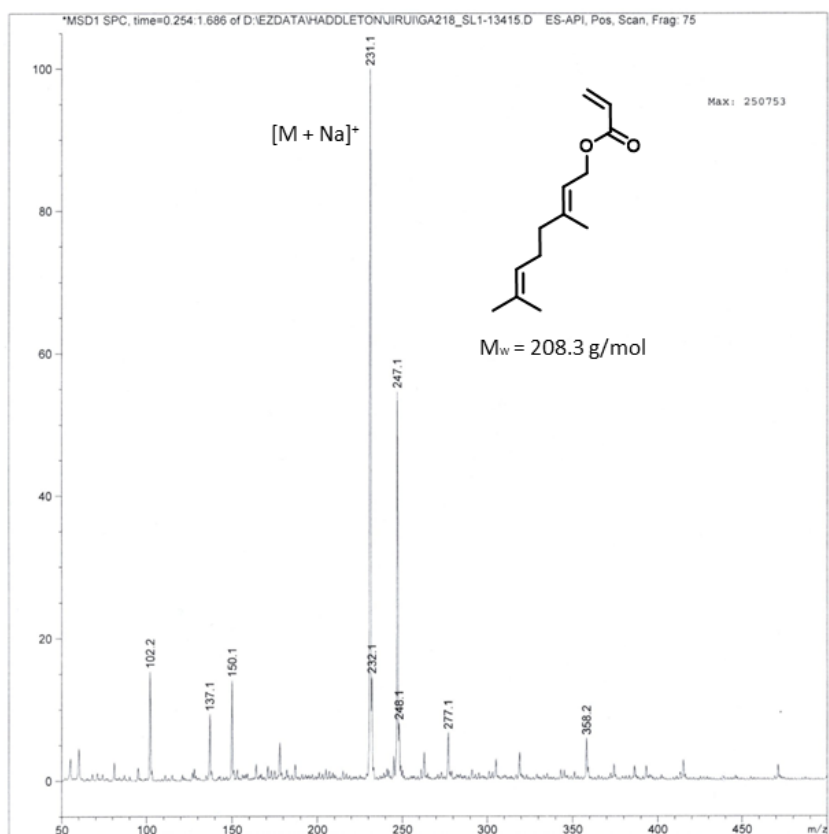


Figure S5. Mass spectrum of geranyl acrylate.

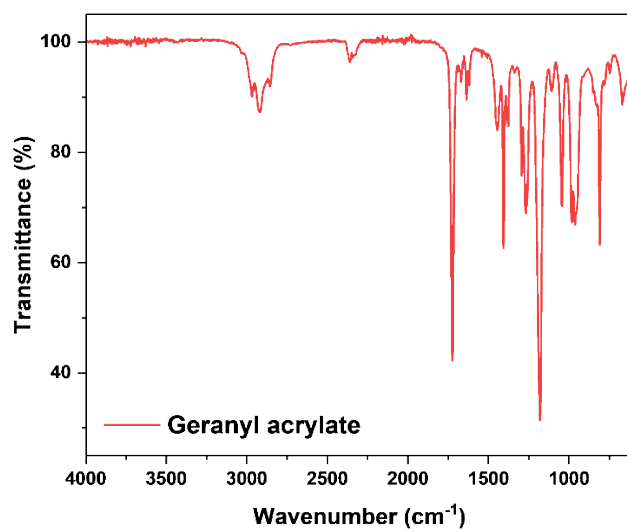


Figure S6. FT-IR spectrum of geranyl acrylate.

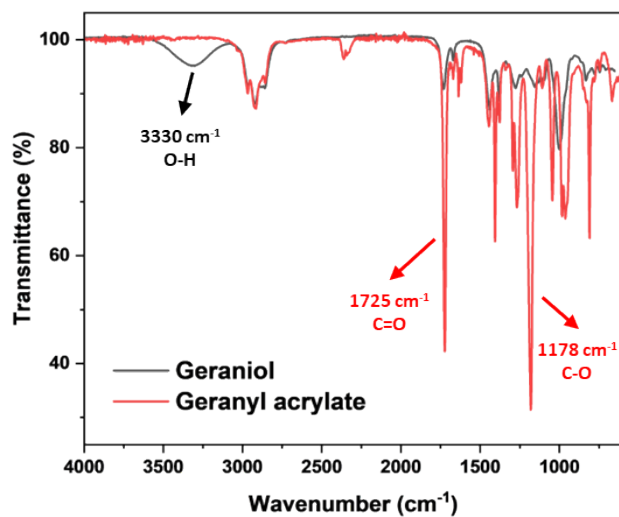


Figure S7. Overlaid FT-IR spectra of geraniol and geranyl acrylate.

Supplementary data for the free radical polymerization of geranyl acrylate

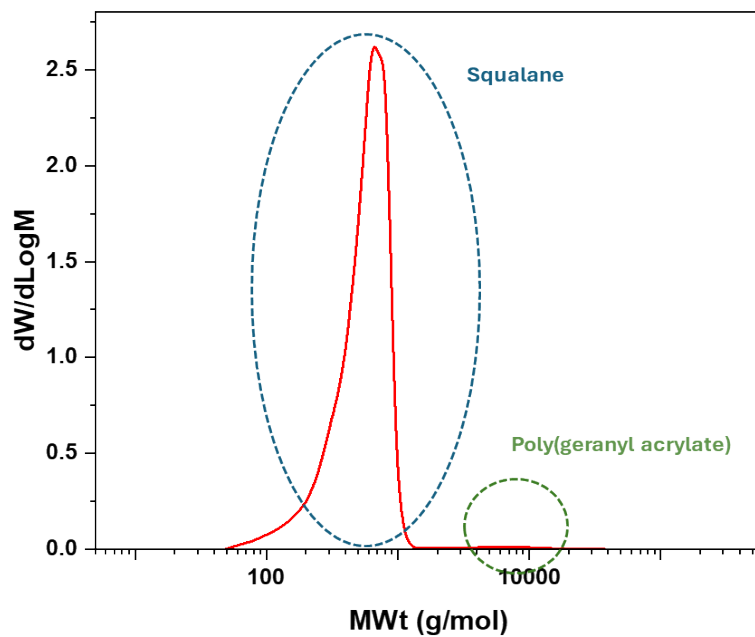


Figure S8. SEC analysis of poly(geranyl acrylate) in squalane. RI detection in THF using pMMA standards.

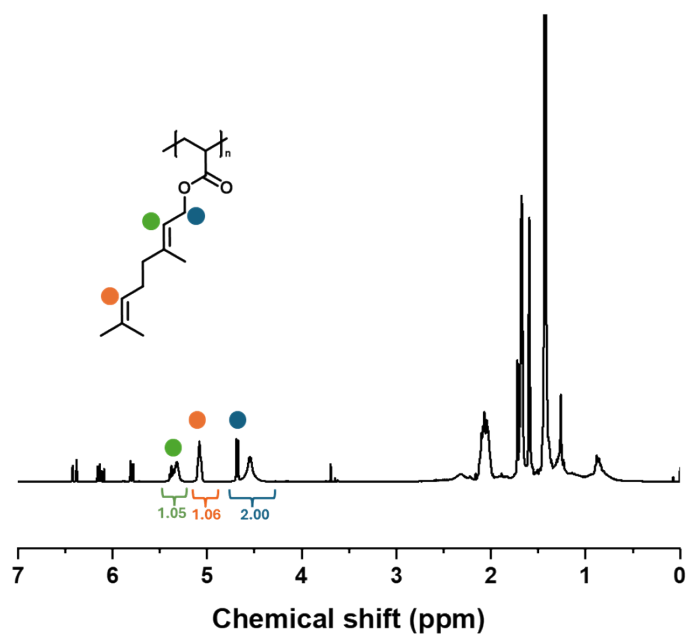


Figure S9. ^1H NMR (MHz, CDCl_3) of FRP of geranyl acrylate in cyclohexane with 20 wt% monomer:solvent and 2.0 mol% [V-601].

Supplementary data for purified poly(geranyl acrylate)

Cyrene

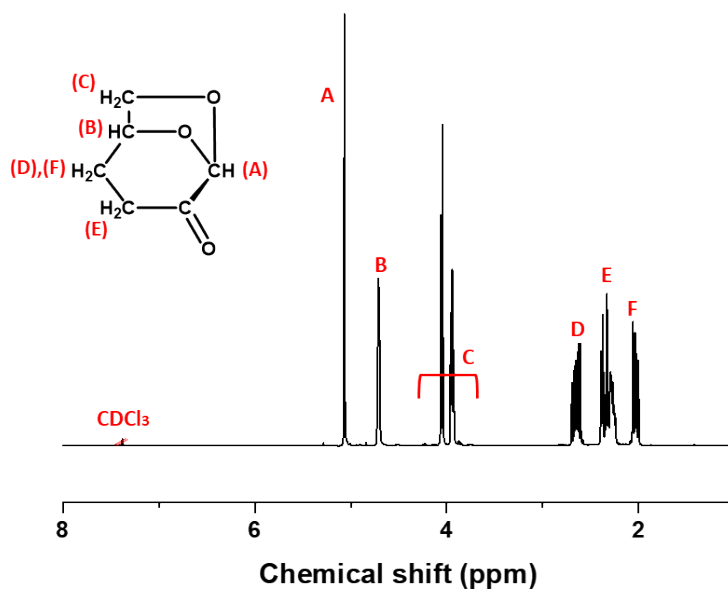


Figure S10. ^1H NMR (400 MHz, CDCl_3) spectrum of Cyrene.

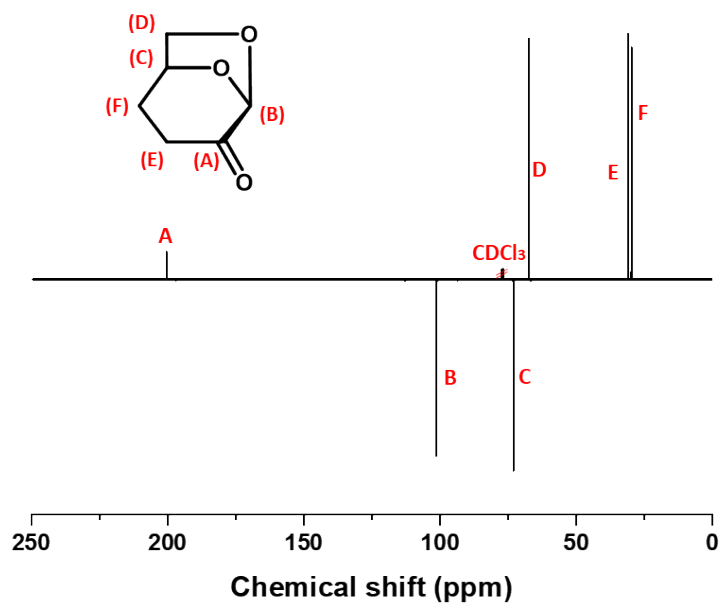


Figure S11. ^{13}C DEPT NMR (400 MHz, CDCl_3) spectrum of Cyrene.

Poly(geranyl acrylate)

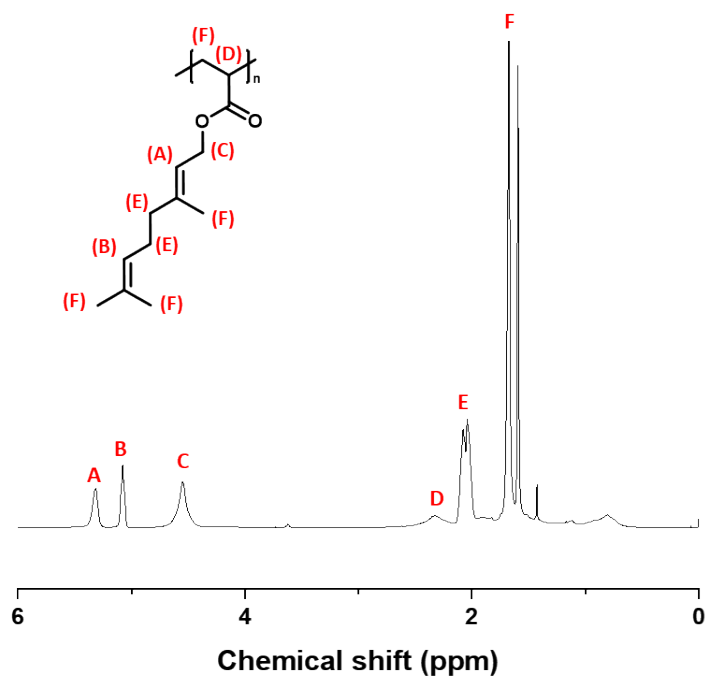


Figure S12. ^1H NMR (400 MHz, CDCl_3) spectrum of poly(geranyl acrylate).

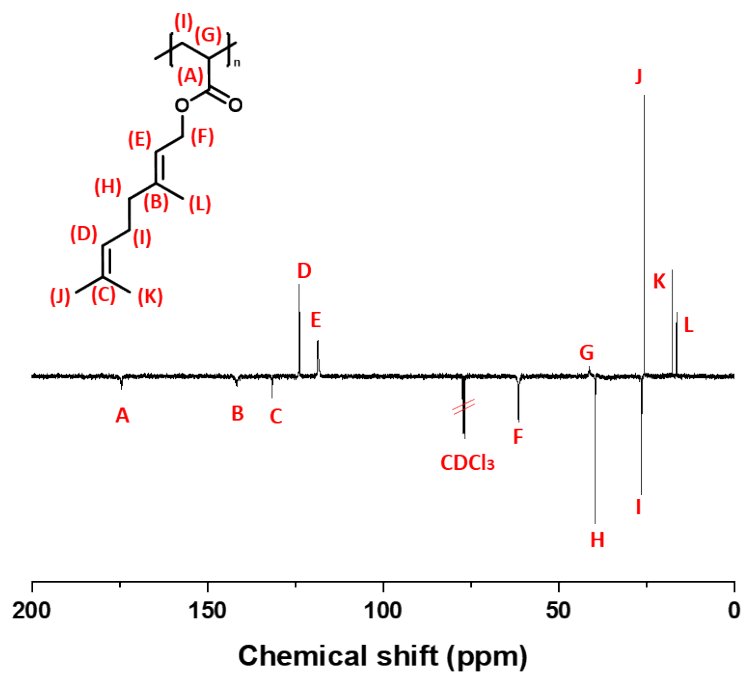


Figure S13. ¹³C DEPT NMR (400 MHz, CDCl₃) spectrum of poly(geranyl acrylate).

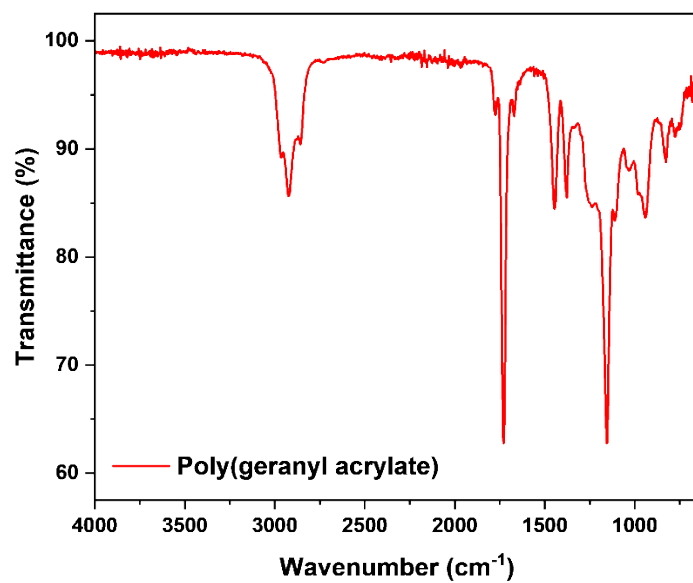


Figure S14. FT-IR spectrum of poly(geranyl acrylate).

Supplementary data for the Cu⁰ wire-mediated RDRP of geranyl acrylate

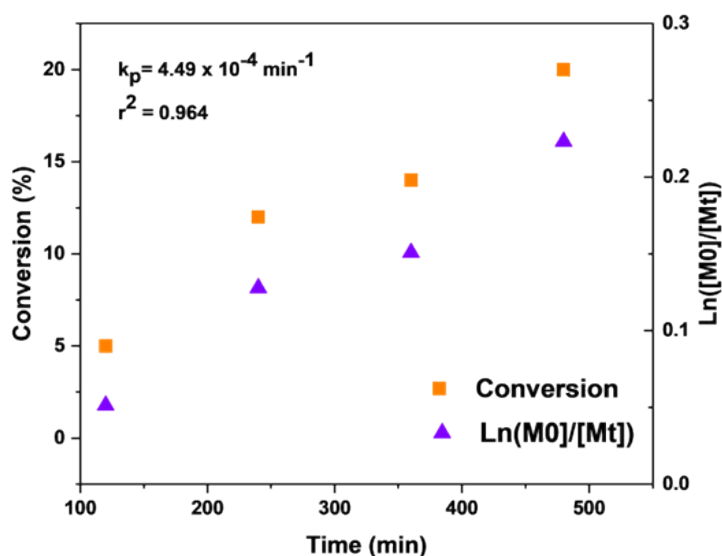


Figure S15. Plot of percentage conversion vs time for the Cu⁰ wire-mediated RDRP of geranyl acrylate in Cyrene, [GA]:[EBiB]:[Me₆TREN]:[CuBr₂] = 50 : 1 : 0.18 : 0.05, V_{Cyrene} = 50% v/v to monomer, at RT.

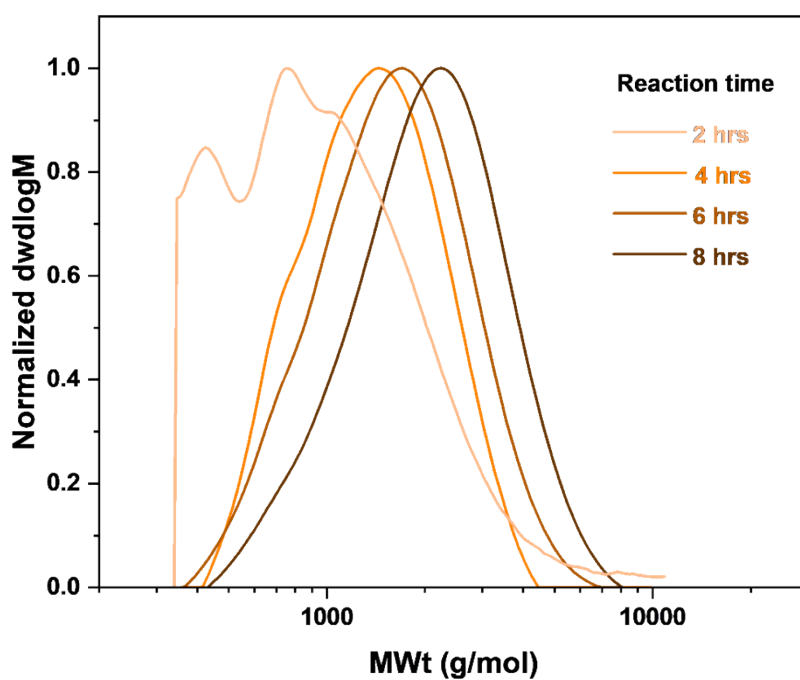


Figure S16. SEC curves of poly(geranyl acrylate) synthesised by Cu⁰ wire-mediated RDRP in Cyrene at different reaction times. RI detection in THF using pMMA standards. Conditions: [GA]:[EBiB]:[Me₆TREN]:[CuBr₂] = 50 : 1 : 0.18 : 0.05, V_{Cyrene} = 50% v/v to monomer, at RT.

Table S1. Characterisation data for poly(geranyl acrylate) synthesised by Cu⁰ wire-mediated RDRP in Cyrene, from 2h to 8h.

Time (min)	Monomer conversion (%)	M _{n, theoretical} (g/mol)	M _{n, SEC} (g/mol)	M _{w, SEC} (g/mol)	Đ	Ln([M0]/[Mt])
120	5	540	800	1200	1.52	0.05
240	12	1300	1200	1500	1.24	0.13
360	14	1500	1400	1800	1.31	0.15
480	20	2190	1700	2300	1.34	0.22

Supplementary data for the functionalisation of poly(geranyl acrylate) by thiol-ene chemistry

Functionalisation with 2-mercaptoethanol

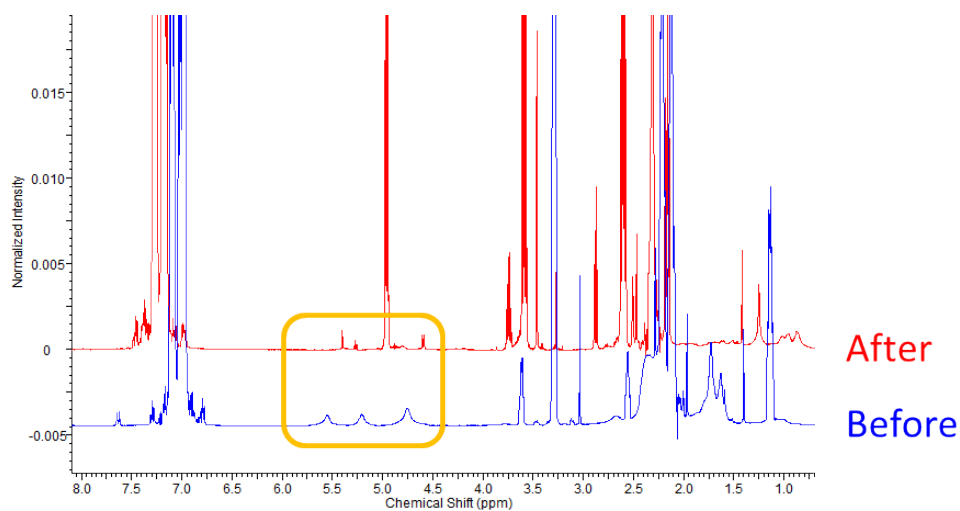


Figure S17. ¹H NMR (400 MHz, DMSO-d₆) spectra of poly(geranyl acrylate), before and after functionalisation with 2-mercaptoethanol.

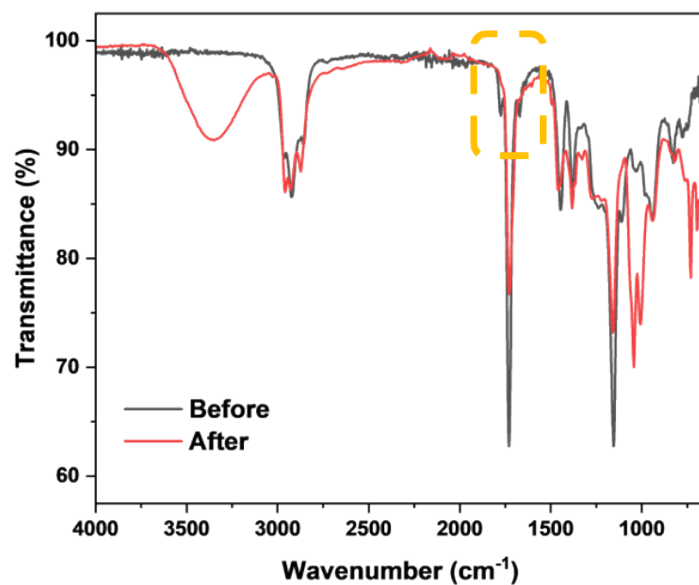


Figure S18. FT-IR spectra of poly(geranyl acrylate), before and after functionalisation with 2-mercaptoethanol.

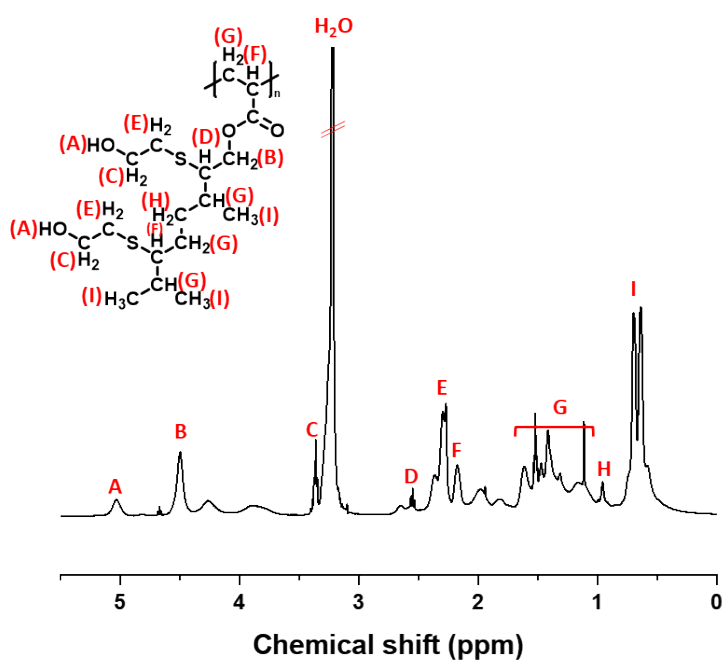


Figure S19. ^1H NMR (400 MHz, DMSO-d_6) spectrum of 2-mercaptoethanol functionalised poly(geranyl acrylate).

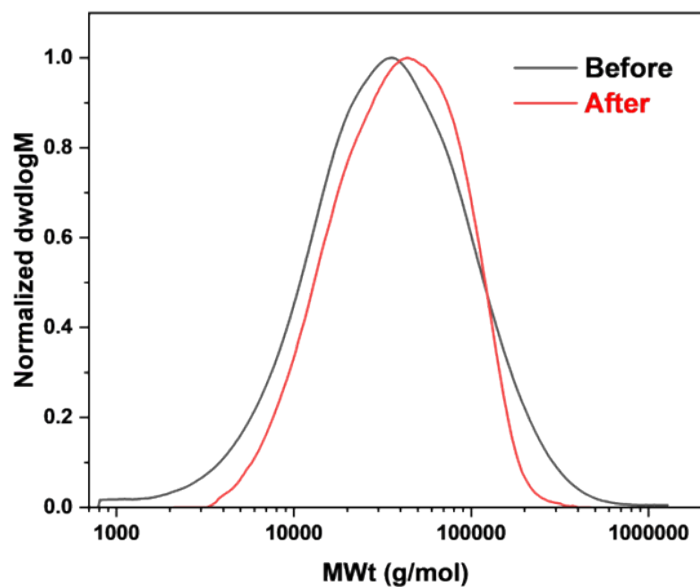


Figure S20. SEC curves of poly(geranyl acrylate), before and after functionalisation with 2-mercaptoethanol. RI detection in THF using pMMA standards.

Functionalisation with 3-mercaptopropionic acid

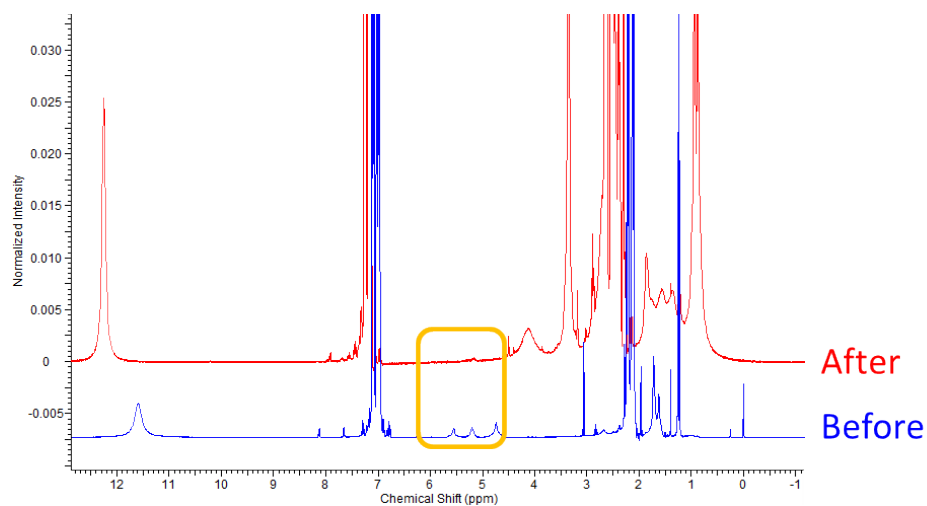


Figure S21. ^1H NMR (400 MHz, DMSO-d_6) spectra of poly(geranyl acrylate), before and after functionalisation with 3-mercaptopropionic acid.

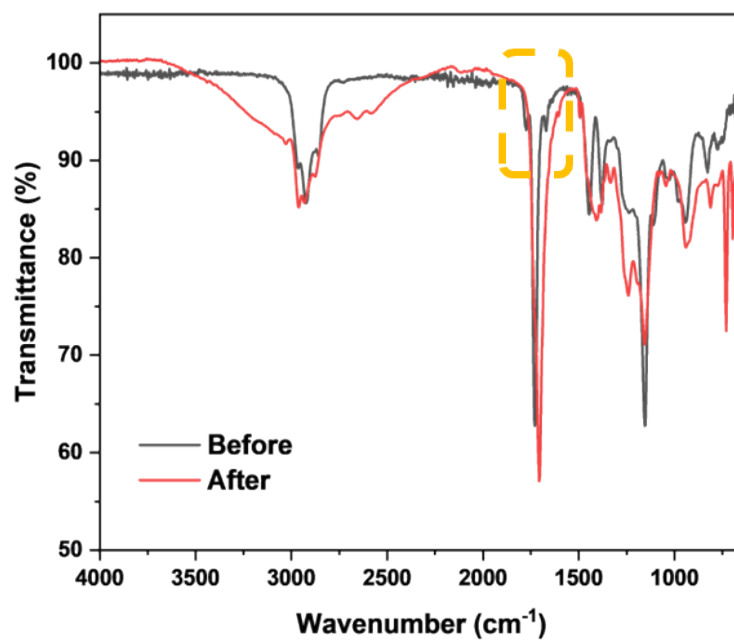


Figure S22. FT-IR spectra of poly(geranyl acrylate), before and after functionalisation with 3-mercaptoacrylic acid.

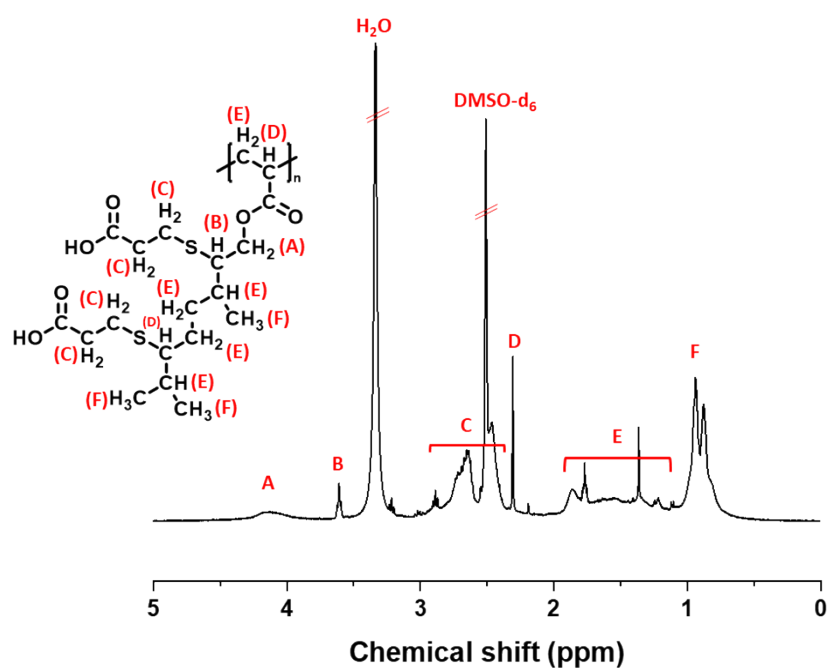


Figure S23. ^1H NMR (400 MHz, DMSO-d_6) spectrum of 3-mercaptoacrylic acid functionalised poly(geranyl acrylate).

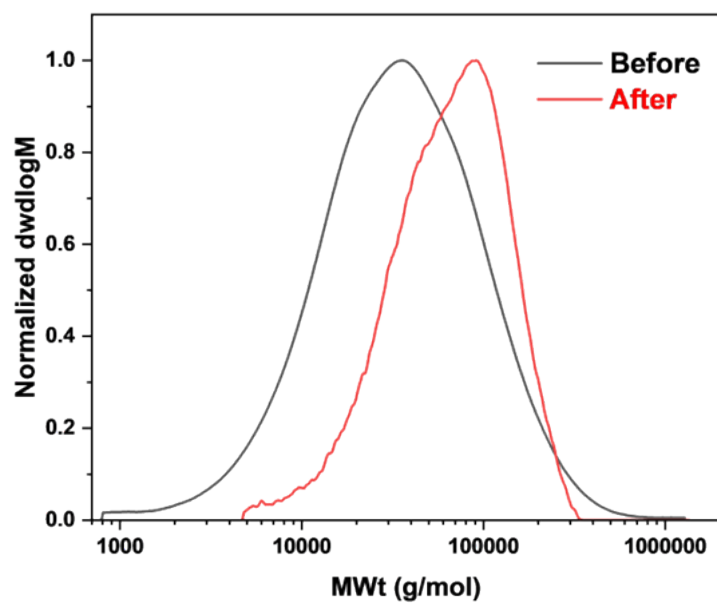


Figure S24. SEC curves of poly(geranyl acrylate), before and after functionalisation with 3-mercaptopropionic acid. RI detection in DMF using pMMA standards.

References

1. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41-44.
2. Q. Zhang, P. Wilson, Z. Li, R. McHale, J. Godfrey, A. Anastasaki, C. Waldron and D. M. Haddleton, *J. Am. Chem. Soc.*, 2013, **135**, 7355-7363.