Supplementary Information

Lewis acid ionic liquid catalysed synthesis of bioderived surfactants from β-pinene

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Table S1: Synthetic details for the preparation of ILs.

IL	1-Methylimidazole	Alkyl chloride	Alkyl chloride	Acetonitrile (mL)	^{1}H NMR conversion
[bmim]-Cl	1.00 equiv., 3.68 mL, 46.30 mmol	1-Chlorobutane	1.30 equiv., 6.27 mL, 60.13 mmol	5	70
[pmim]-Cl	1.00 equiv., 7.36 mL, 95.50 mmol	1-Chloropentane	1.26 equiv., 14.54 mL, 120.25 mmol	3	70[a]
[omim]-Cl	1.00 equiv., 7.36 mL, 95.50 mmol	1-Chlorooctane	1.26 equiv., 20.43 mL, 120.25 mmol	3	51[b]

[a] ^{1}H NMR conversion: 70% determined by comparing the integral of unreacted 1-methylimidazole at 6.91 ppm with that of 1-pentyl-3-methylimidazolium at 7.41 ppm. [b] ^{1}H NMR conversion: 51%, determined by comparing the integral of unreacted 1-methylimidazole at 6.92 ppm with that of 1-octyl-3-methylimidazolium chloride at 7.40 ppm.

[pmim]-Cl: ^{1}H-NMR: ($CDCl_3$, δ in ppm): 0.88 (3H, t, $N(CH_2)_4C\mathbf{H_3}$), 1.32 (4H, m, $N(CH_2)_2C\mathbf{H_2}C\mathbf{H_2}CH_3$), 1.91 (2H, m, $NCH_2C\mathbf{H_2}(CH_2)_2CH_3$), 4.12 (3H, s, $NC\mathbf{H_3}$), 4.33 (2H, t, $NC\mathbf{H_2}(CH_2)_3CH_3$), 7.41 (1H, s, $CH_3NC\mathbf{H}CHN$), 7.58 (1H, s, $CH_3NCHC\mathbf{H}N$), 10.75 (1H, s, $NC\mathbf{H}N$). These data are in agreement with that of Yang *et al.*[1]

[omim]-Cl: ^{1}H-NMR: ($CDCl_3$, δ in ppm): 0.77 (3H, t, $N(CH_3)_7C\mathbf{H_3}$), 1.16 (10H, m, $N(CH_3)_2(C\mathbf{H_2})_5CH_3$, 1.82 (2H, m, $NCH_2C\mathbf{H_2}(CH_2)_5CH_3$), 4.04 (3H, s, $NC\mathbf{H_3}$), 4.22 (2H, t, $NC\mathbf{H_2}(CH_2)_6CH_3$), 7.40 (1H, s, $CH_3NC\mathbf{H}CHN$), 7.63 (1H, s, $CH_3NCHC\mathbf{H}N$), 10.55 (1H, s, $NC\mathbf{H}N$). These data are in agreement with that of Gómez *et al.*[2] Mass spectrometry: calculated *m/z* 195.1856, found *m/z* 195.1868 (M+, 100%).

Table S2: Synthetic details for the preparation of LA-ILs.

LA-IL	LA	$FeCl_3$
[bmim]-Fe_2Cl_7	3.00 g, 17.23 mmol	5.5902 g, 34.46 mmol
[pmim] -Fe_2Cl_7	3.00 g, 15.95 mmol	5.17 g, 31.89 mmol
[omim] -Fe_2Cl_7	3.00 g, 13.03 mmol	4.23 g, 26.07 mmol

Table S3: Synthetic details for the preparation of epoxidized PBP *via* mCPBA route.

Polymer	PBP	mCPBA	DCM	Degree of epoxidation of alkenes (%)
EPBP-10	20 g, 0,147 mol	3.04 g, 0.018 mol	200 mL	13
EPBP-50	20 g, 0.147 mol	15.22 g, 0.088 mol,	200 mL	54

Table S4: Synthetic details for the preparation of hydrolysis of EPBP.

Polymer	Starting material (g)	*p*-TsOH (10 mol %)	Toluene (mL)	Water (mL)	Degree of alkene functionalisation to diols (%)[a]
PBP-OH-10	EPBP-10, 9.00 g (0.90 g epoxidized polymer, 5.96 mmol)	0.60 mmol, 0.10 g	200	20	13
PBP-OH-50	EPBP-50, 9.00 g (4.50 g epoxidized polymer, 29.80 mmol)	2.80 mmol, 0.51 g	270	90	54
PBP-OH-80	EPBP-80, 2.00 g, 0132 mmol	0.0013 mmol, 0.22 g	50	30	84

[a]Assuming complete hydrolysis of epoxides.

Supplementary Figures

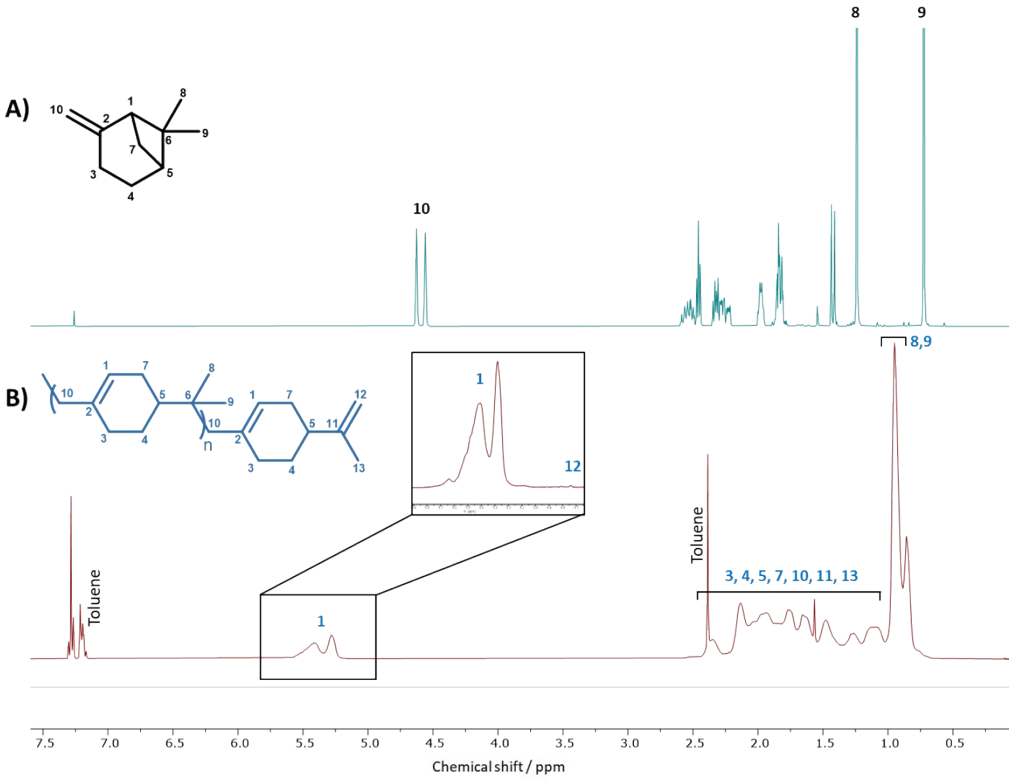

Figure S1: *^{1}H NMR spectra of βP (upper) and PBP (lower) demonstrating the successful polymerisation. Full assignment of the ^{1}H NMR spectrum of βP has been reported by Kolehmainen et al.[3]*

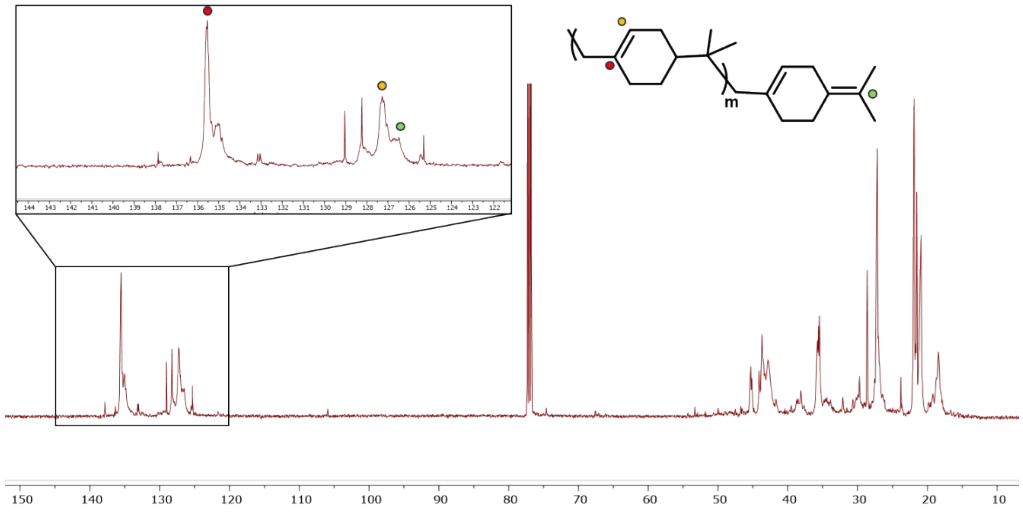

Figure S2: *^{13}C NMR spectrum of PBP, synthesised using [bmim]-Fe_2Cl_7, demonstrating the predominantly endo-olefin end group of the polymer.*

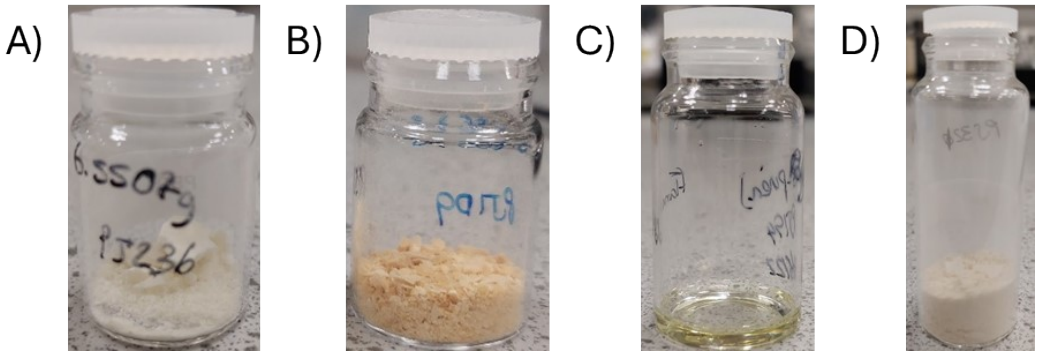

***Figure S3**: PBP A) synthesised using [bmim]-Fe_2Cl_7 after purification with activated charcoal and extracted using $scCO_2$ B) synthesised using [bmim]-Fe_2Cl_7 and purified by aqueous washing and precipitation C) synthesised using $FeCl_3$ and purified using activated charcoal D) synthesised using $FeCl_3$ and purified with activated charcoal and extracted using $scCO_2$.*

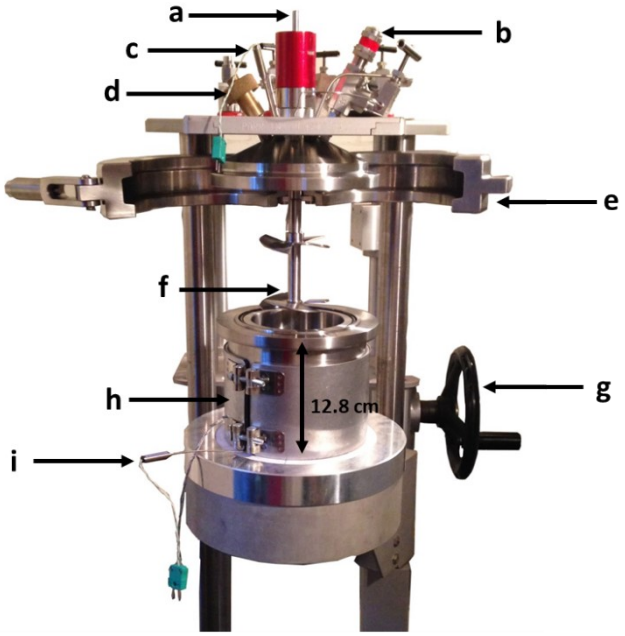

***Figure S4**: 1 L $scCO_2$ autoclave.*

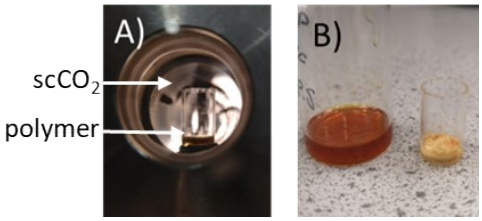

***Figure S5:** A) Solubility testing of PBP in $scCO_2$ at 45 °C and 193 bar. Polymer can clearly be seen in the vial, unable to enter the $scCO_2$ phase due to insolubility. B) PBP before (left) and after (right) exposure to $scCO_2$. After exposure to CO_2 the polymer is no longer tacky, and bubbles can be seen in the polymer showing where CO_2 has swollen the polymer matrix.*

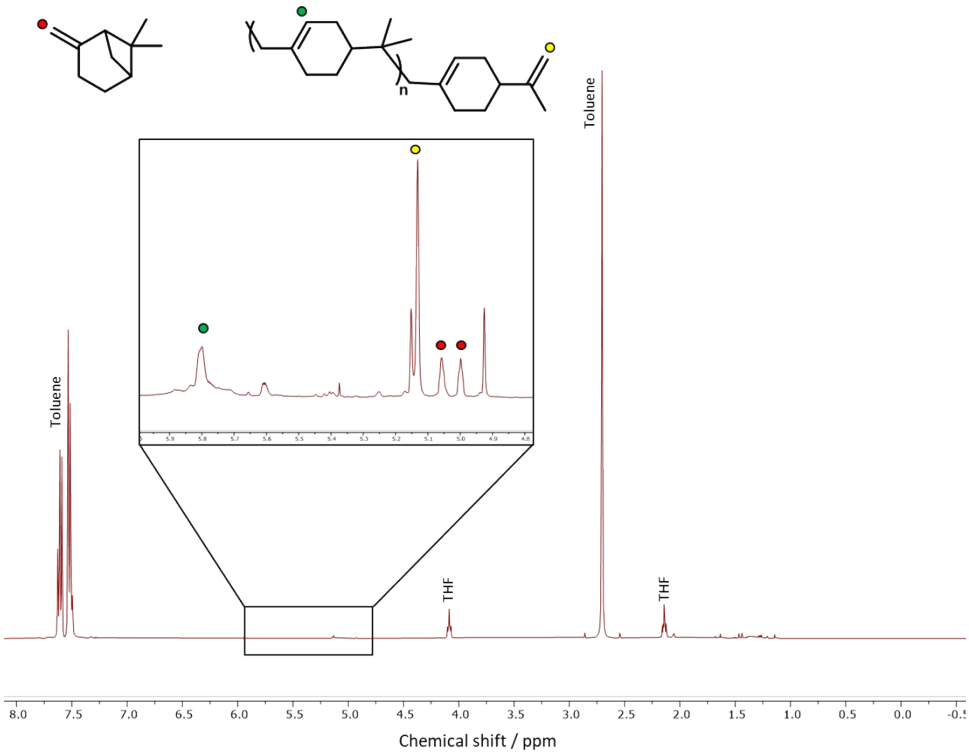

***Figure S6**: [1]H NMR spectrum of the collected extract of PBP purification by $scCO_2$ extraction.*

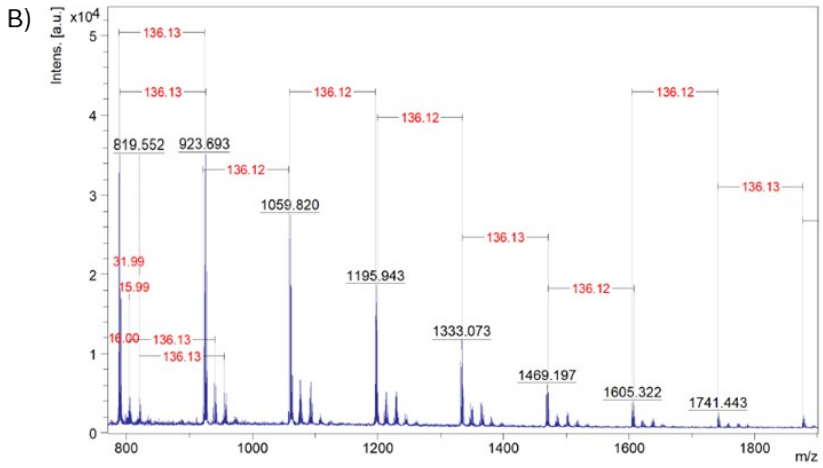

***Figure S7:** MALDI-ToF MS of PBP synthesised using [bmim]-Fe_2Cl_7. Silver trifluoroacetate was used as a cationisation agent and DCTB as a matrix. Note, as the reaction was quenched by adding NaOH, smaller peaks with an m/z difference of 16 are observed in addition to the major population.*

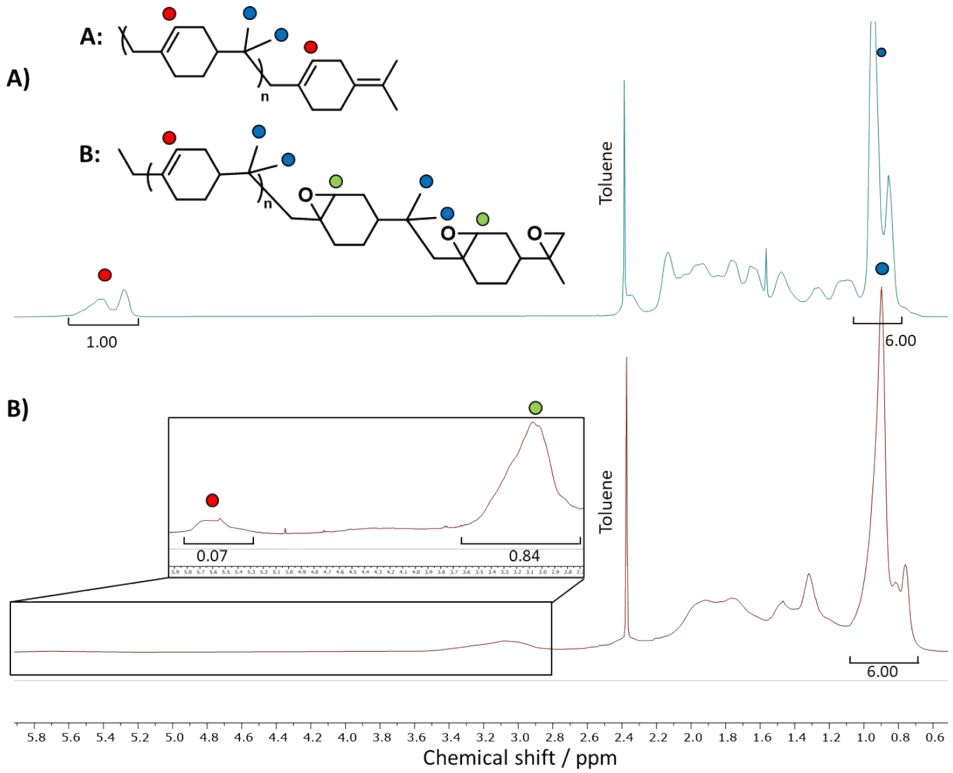

Figure S8: *^{1}H NMR spectra of A) PBP and B) EPBP-80.*

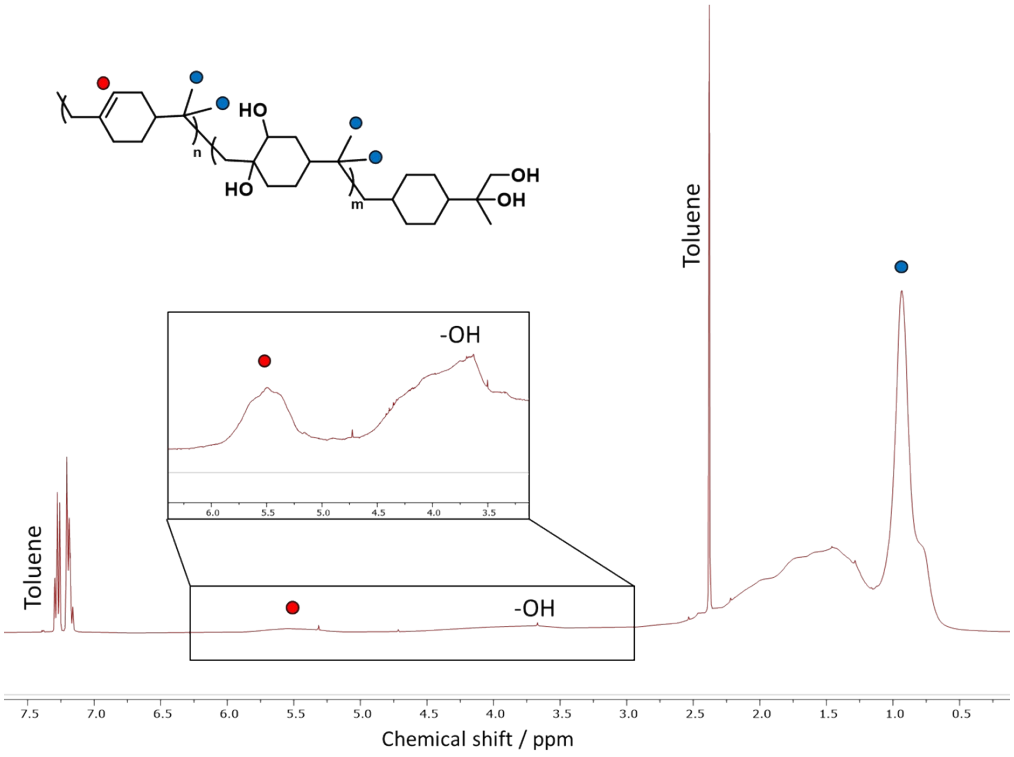

Figure S9*: ^{1}H NMR spectrum of PBP-OH-80.*

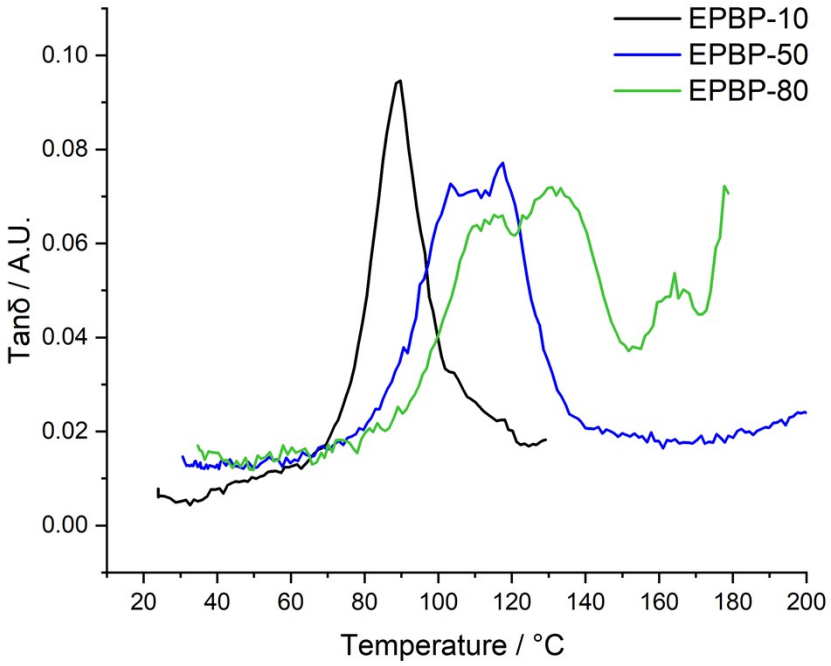

Figure S10: *DMA of EPBPs, demonstrating increasing T_gs with increasing degrees of epoxidation. The second peak in the tanδ trace of EPBP-80 is likely the result of epoxide curing.*

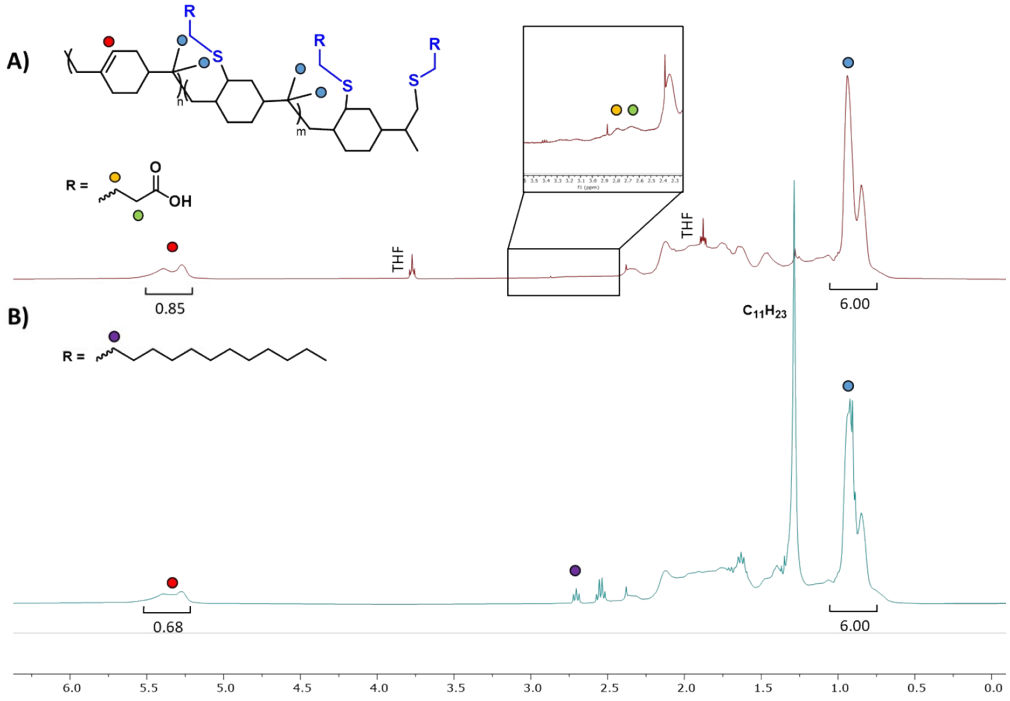

Figure S11: *^{1}H NMR spectra of A) 3-mercaptopropionic acid functionalised PBP and B) dodecanethiol functionalised PBP.*

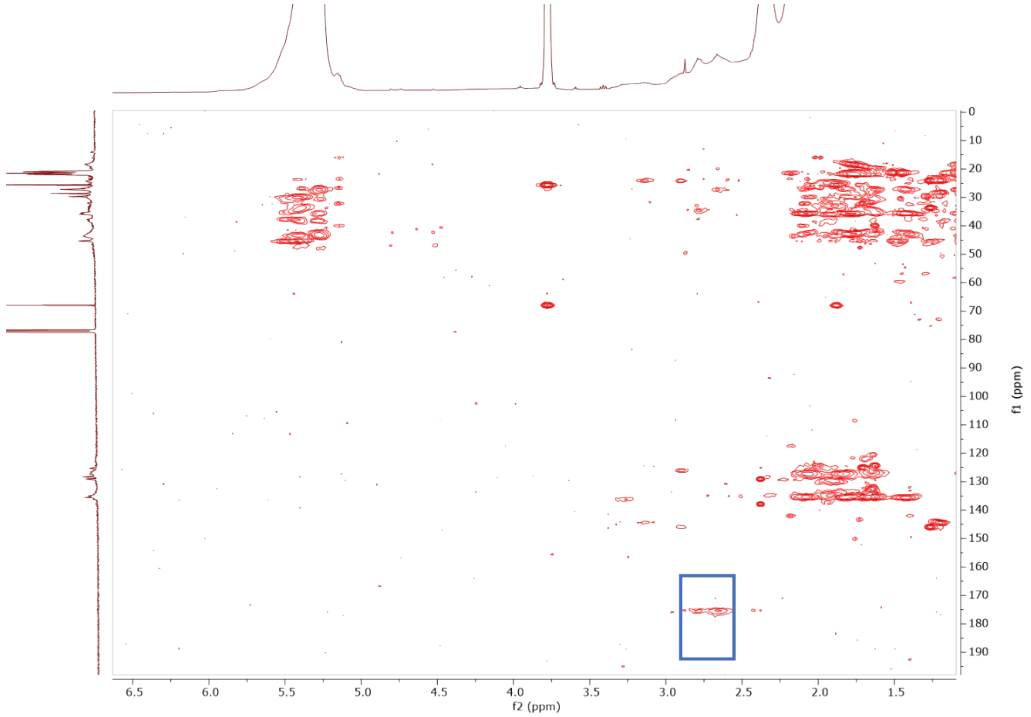

Figure S12: *HMBC analysis of PBP-3-mercaptopropionic acid demonstrating the coupling of peaks between 2.80 and 2.65 ppm with a peak at 175 ppm.*

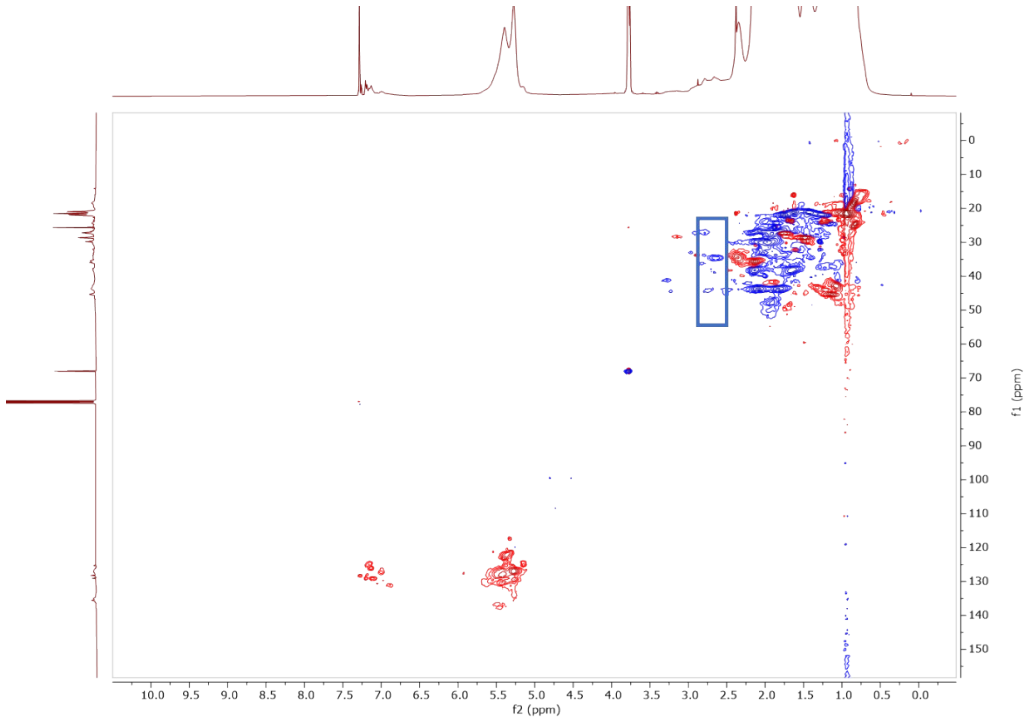

Figure S13 *Multiplicity edited HSQC analysis of PBP-3-mercaptopropionic acid demonstrating the presence of two -CH_2 groups in blue. -CH_2 groups are shown in the blue box, -CH and -CH_3 groups are shown in red.*

References:

1. J.-Z. Yang, W. Guan, J. Tong, H. Wang and L. Li, *J. Solution Chem.*, 2006, **35**, 845-852.
2. E. Gómez, B. González, Á. Domínguez, E. Tojo and J. Tojo, *Journal of Chemical & Engineering Data*, 2006, **51**, 696-701.
3. E. Kolehmainen, K. Laihia, R. Laatikainen, J. Vepsäläinen, M. Niemitz and R. Suontamo, *Magn. Reson. Chem.*, 1997, **35**, 463-467.