Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Solvent-free Manufacture of Methacrylate Polymers from Biomass Pyrolysis Products

J. Ryan, M.T. Elsmore, E.R. Binner, D.S.A. De Focatiis, D.J. Irvine and J.P. Robinson

Coates building, Faculty of Engineering, University of Nottingham, NG7 2RD, UK

Number of pages:	10
Number of figures:	11
Number of tables:	3

E-mail: John.robinson@nottingham.ac.uk
Telephone: 0115 95 14092

Supporting Information

Figure S1: Example ^{31}P-NMR spectra. The peak marked with * is used as integral reference for OH group quantification.

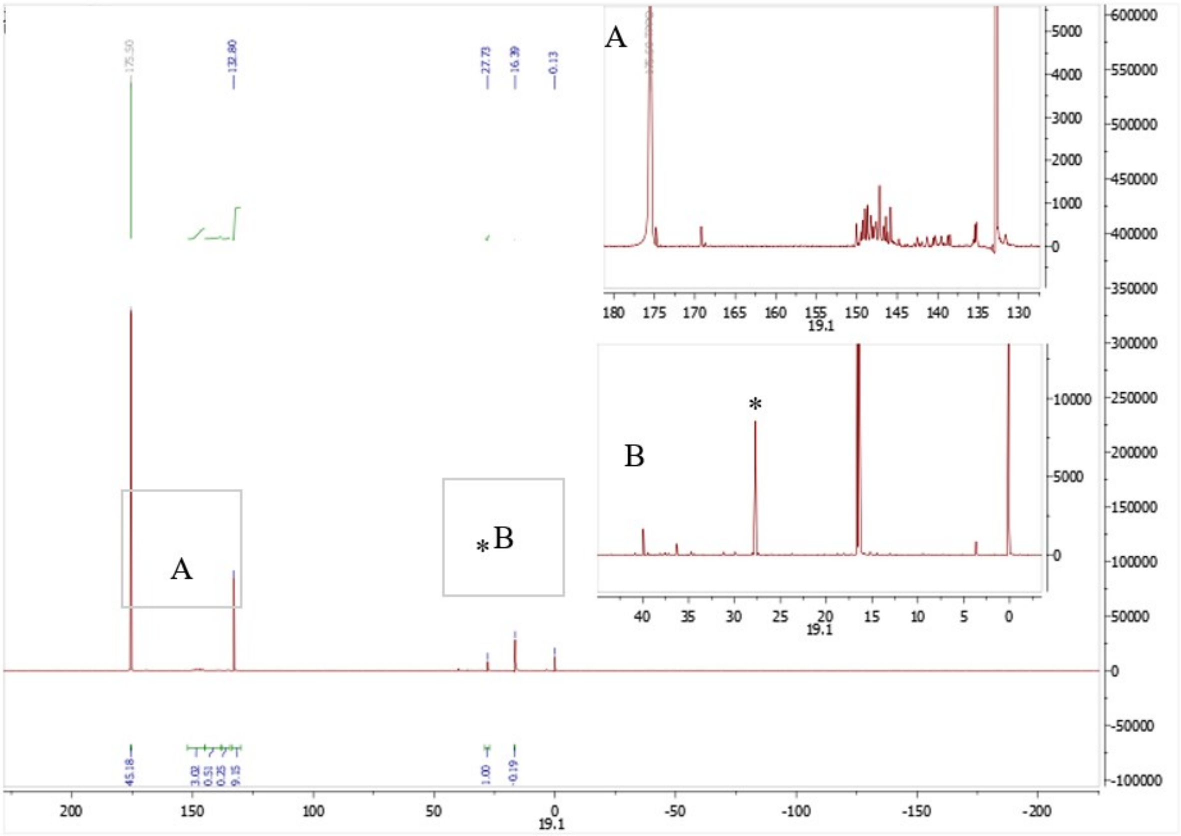
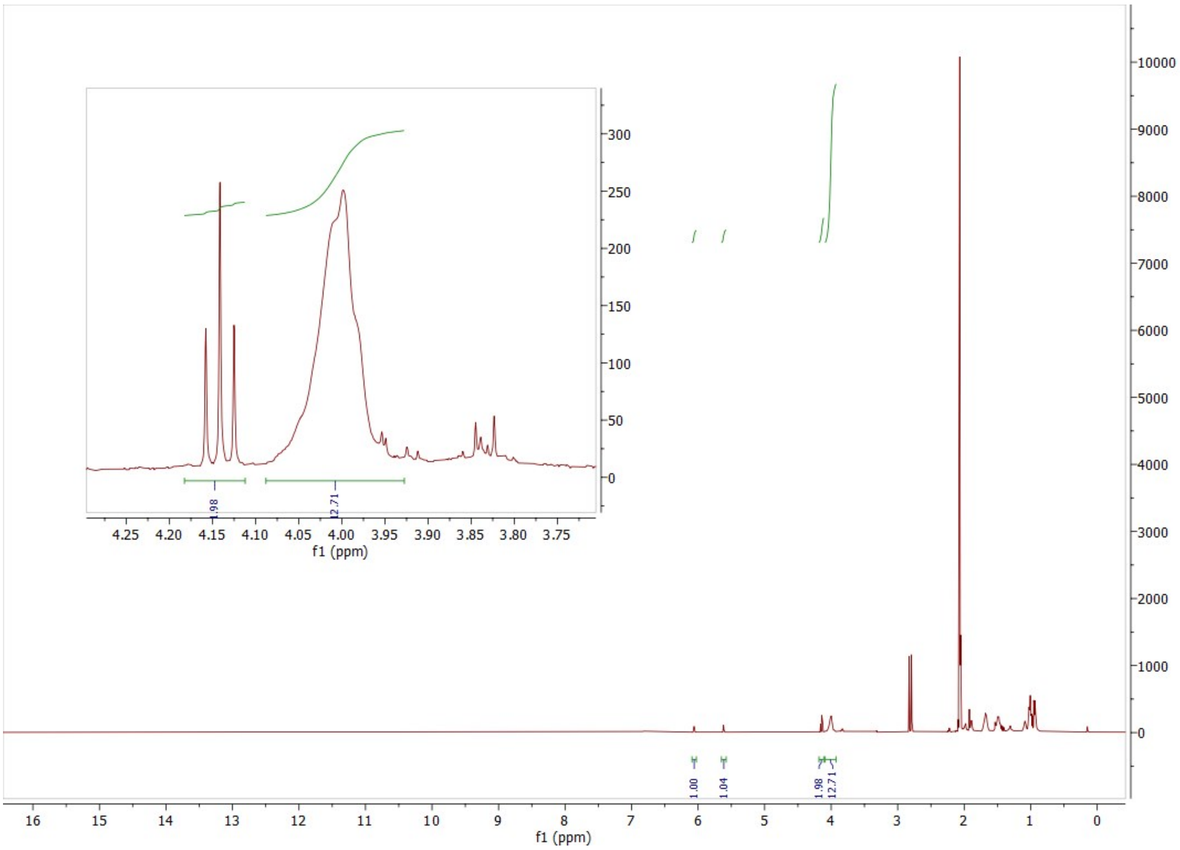


Table S1: Example pyrolysis liquid ^{31}PNMR OH assignments

Integral region (ppm)	Assignment
δ = 27.91	TPPO
δ =175.5	TMDP
δ =152-145	Aliphatic OH - TMDP adduct
δ =145-138	Aromatic OH - TMDP adduct
δ =138-134.6	Carboxylic acid OH - TMDP adduct
δ =133.7-130	Water dimer - TMDP adduct
δ =16.75	Water- TMDP adduct

Figure S2 ^{1}H-NMR conversion method

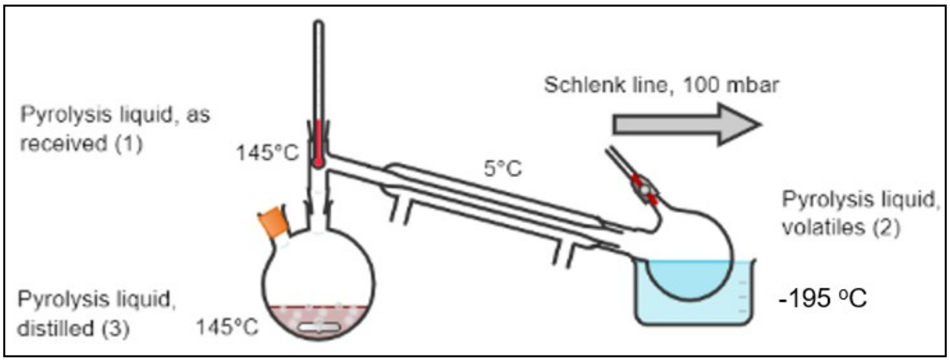
.



Conversion was calculated by proton peak change in chemical environment. Note that there are 4 CH proton equivalents in the broad peak at 4.00 and two in the triplet at 4.15.[1]

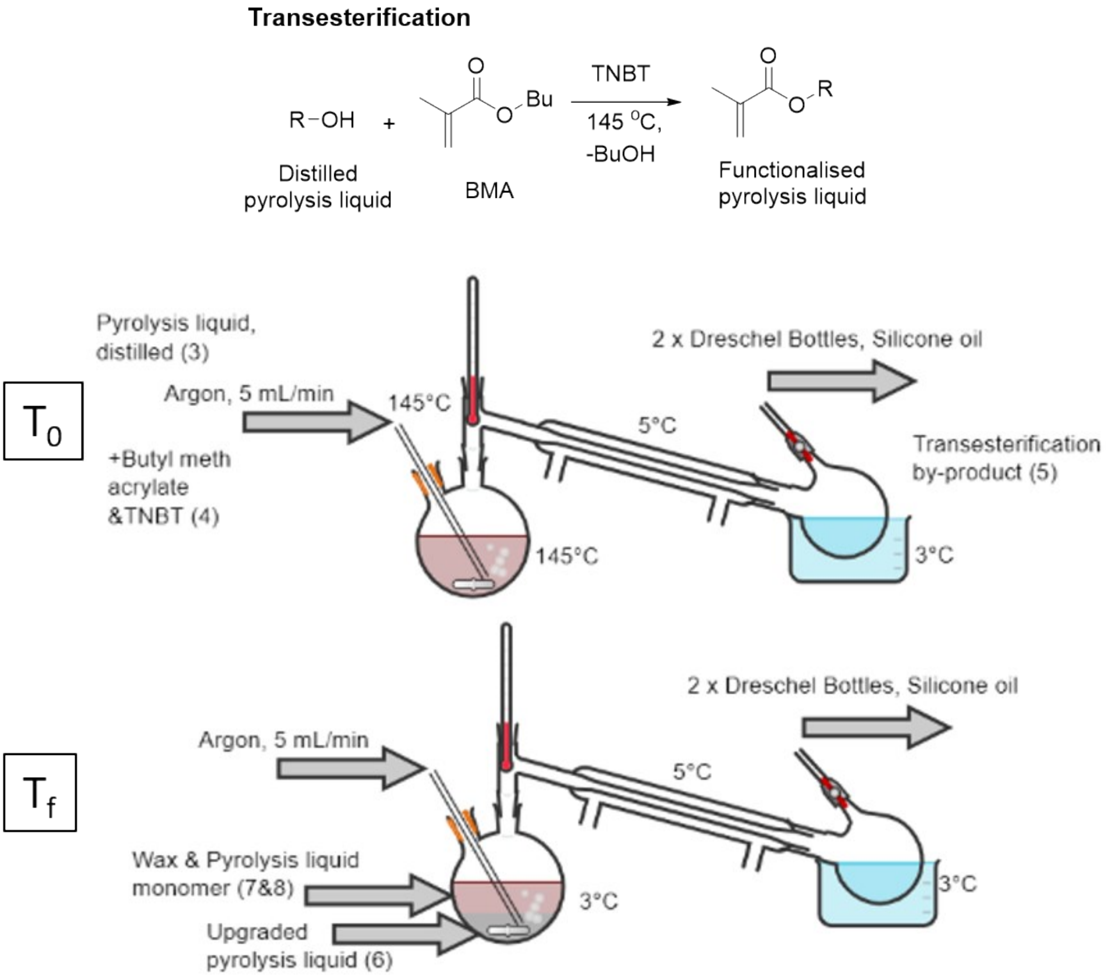
$$Conversion\ (\%) = \frac{[P]}{[M]+[P]} = \frac{(\frac{12.7}{4})}{\left(\frac{1.98}{2}\right) + (\frac{12.7}{4})} = \frac{3.175}{4.175} = 0.76$$

Figure S3 Experimental setup and method for pyrolysis liquid drying



Pyrolysis liquid as received was added to a round bottom flask (RBF) in a Drysyn heating mantle at 145 °C. This was attached to a vacuum distillation head and trap, which was cooled to -195 °C to condense all vapours. Pressure was reduced to 100 mbar over a period of 20 minutes via a Schlenk line vacuum pump. Temperature was monitored in the Drysyn and still head. Aliquots of this distilled pyrolysis liquid and the distillate were set aside for subsequent analysis. Water content was confirmed by KF analysis prior to transesterification, and the drying step was repeated if more than 0.5% water was detected. Concentration of OH in the distilled pyrolysis liquid, was determined by ^{31}P-NMR, before addition of BMA. Ratios of 0.6, 1.2 and 2.4 were used in this work.

Figure S4 Reaction mechanism, experimental setup at T_o and T_f and method for pyrolysis transesterification[2]



The experimental setup, consisted of a two-neck round bottom flask with Suba seal and vacuum distillation head, followed by dreschel bottles, to prevent gas backflow. Stirring and Argon sparge, 5mL minute^{-1} were begun 5 minutes prior to temperature increase. Temperature was measured in the oil bath, reaction vessel and still head. Addition of TNBT (0.6 mg, 0.0026 mmol) was treated as reaction start time (T_0). After reaction (T_f), the argon sparge and agitation were stopped and the mixture was then cooled to 3 °C for one hour, where T=145^{o}C, phase separation was observed. The upper, clear brown liquid monomer was separated, into a vial, from the lower, highly viscous opaque brown, upgraded pyrolysis liquid.

Figure S5: Reaction mechanism and experimental method for functionalised pyrolysis liquid polymerisation.

C) In this study, AIBN (0.2 wt%) was added to the transesterified pyrolysis liquid products (1.78g, 2mL) in a sealed vial. The sample was degassed via “freeze pump thaw” three times and backfilled with Argon. The temperature was subsequently raised to 85 °C in an oil bath and held for four hours with constant agitation. The reaction mixture was then allowed to cool to room temperature before the crude polymer was dissolved in approximately 5 mL acetone and precipitated into 600 mL of petroleum ether held at 0 °C. The precipitation solvent was separated from the polymer by decanting it from the light brown solid, which was the polymer product. The precipitation was repeated and the resulting polymer was then dried under vacuum at 50 °C for 7 days.

Table S2: Comparison of established methacrylate transesterification temperatures for [OH] from ^{31}P-NMR and observed time taken for sample to turn solid in minutes. *denotes no solid onset observed.

Temperature (°C)	Crosslink onset (minutes)	[OH] (mmol·g^{-1})		Degree of transesterification (%)
		t_0	t_{120}	
160	8	28.01	0	100
155	14	28.01	0.8	97.1
150	20	28.01	1.2	95.7
145	*	28.01	5.83	79.2

Figure S6: Typical pyrolysis liquid GC chromatogram

Figure S7: Typical upgraded pyrolysis liquid GC chromatogram, with annotated peaks

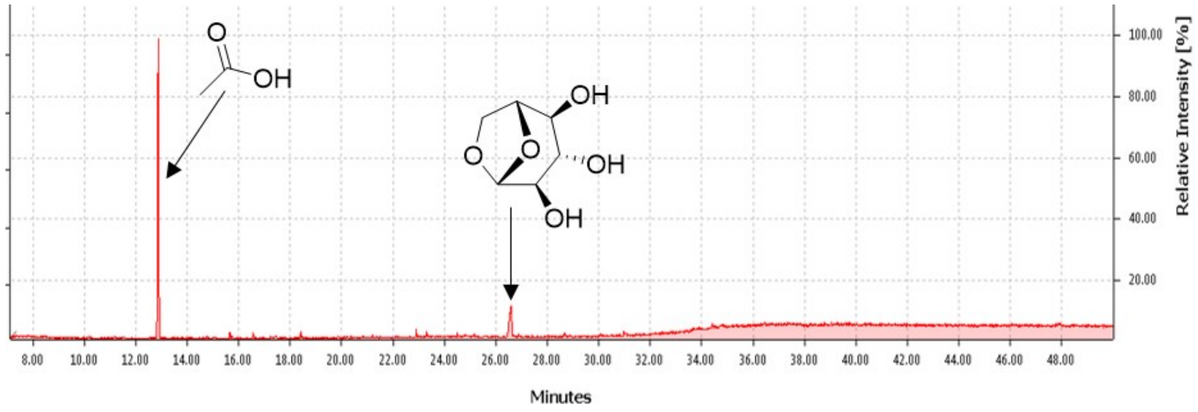


Figure S8: Time resolved size exclusion chromatography of pyrolysis liquid derived polymer polymerisation

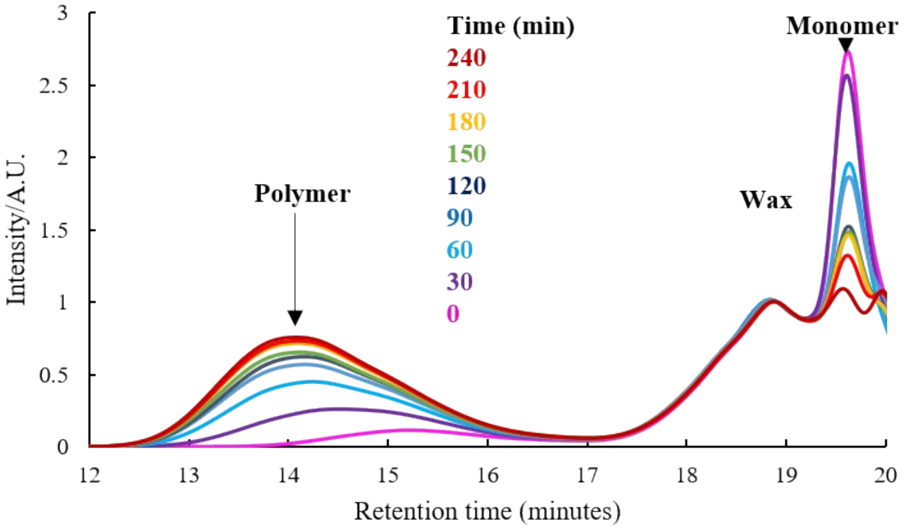


Figure S9 Outline of the wax content origin by SEC

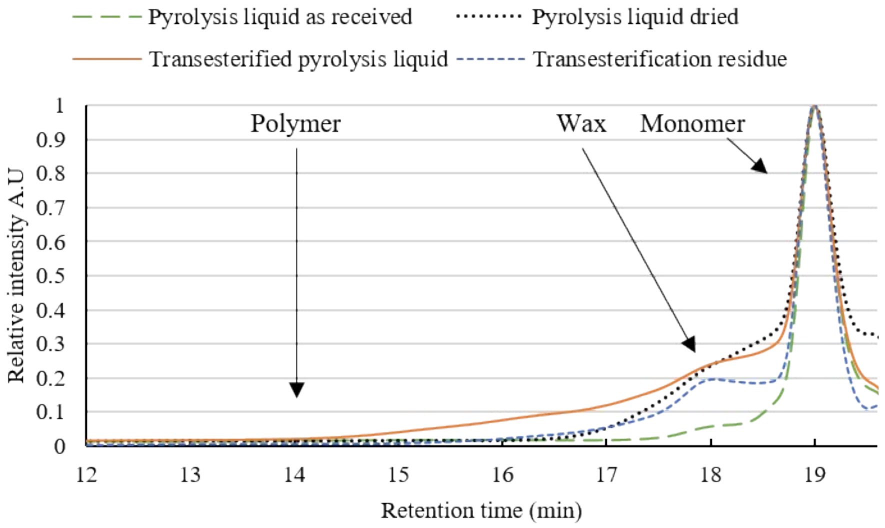


Table S3: Outline molar ratio calculations, the concentration of OH in PL is 13.7 mmol g^{-1} and molar mass BMA is 142.198 g mol^{-1}

BMA: pyrolysis liquid OH ratio	Mass of pyrolysis liquid added (g)	# moles OH	Mass of BMA added (g)	#moles BMA added	Mass BuOH distilled (g)	# moles BuOH distilled	# moles reacted from ^{31}PNMR	Molar ratio BMA/ Pyrolysis liquid monomer (by BuOH)	Molar ratio BMA/ Pyrolysis liquid monomer (by ^{31}PNMR)
0.6	19.53	0.27	22.83	0.16	4.68	0.063	0.230	2.54	0.70
1.2	18.6	0.25	43.48	0.31	7.15	0.096	0.213	3.17	1.44
2.4	20.29	0.28	94.87	0.67	9.08	0.123	0.238	5.45	2.80

Figure S10: TGA for pyrolysis polymer and p(BMA) heated from T = 30 – 500 °C in nitrogen.

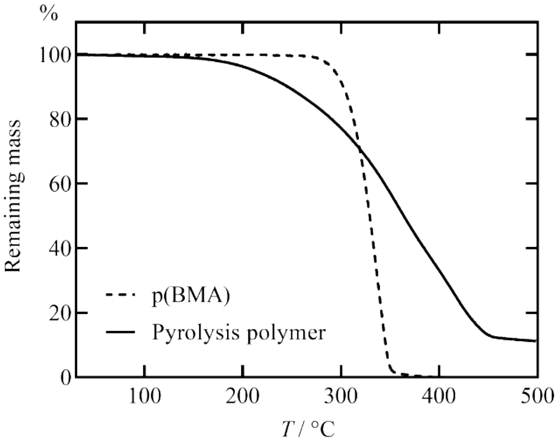


Figure S11: Photograph of pyrolysis polymer material

References

(1) Gramlich, W. M.; Theryo, G.; Hillmyer, M. A. Copolymerization of Isoprene and Hydroxyl Containing Monomers by Controlled Radical and Emulsion Methods. *Polym. Chem.* **2012**, *3*, 1510–1516.

(2) Dundas, A. A.; Hook, A. L.; Alexander, M. R.; Kingman, S. W.; Irvine, D. J. Methodology for the Synthesis of Methacrylate Monomers Using Designed Single Mode Microwave Applicators. *React. Chem. Eng.* **2019**, 4, 1472–1476.