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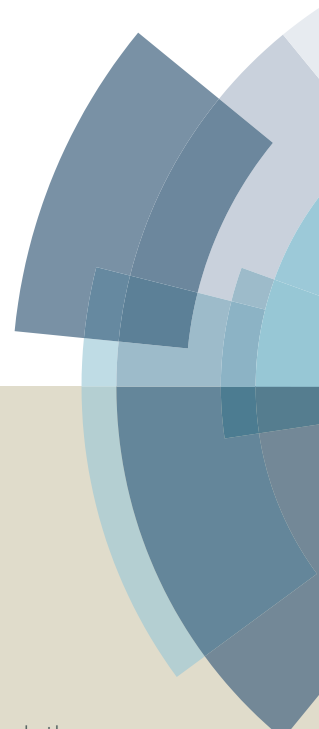
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Post-polymerisation Modification of Bio-derived Unsaturated Polyester Resins *via* Michael Additions of 1,3-dicarbonyls

T. J. Farmer, J. H. Clark,* D. J. Macquarrie, J. K. Ogunjobi and R. L. Castle

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Post-polymerisation modification of α,β -unsaturated polyesters (UPEs) is useful to deliver polymers with tuneable properties and applications different from their parent backbone. Bio-derivable itaconate unsaturated polyesters, with a range of co-monomers, were modified *via* a heterogeneously catalysed microwave-assisted Michael addition of pendants, acetylacetone (Hacac) and dimethyl malonate (DMM), to the polymer backbones with very short reaction times. Differential scanning calorimetry analysis showed an increase in the glass-transition temperatures of most of the saturated polyesters considered. Solubility and complexation studies demonstrated metal chelating abilities of the acetylacetone pendant can be retained, even following tethering to a polyester backbone. Additionally, it is demonstrated for the first time that Michael addition with Hacac and DMM can be used to reverse Ordelt saturation, an unwanted side-reaction in the synthesis of UPEs.

(Keywords: bio-based polymer, unsaturated polyester (UPE), itaconate polyester, Michael addition, Ordelt saturation)

Introduction

Increasing consumer demand for bio-based products, coupled with environmental challenges resulting from the use of petrochemical-derived feedstock and products, has led to widespread research in sourcing polymers from bio-based platform molecules.¹⁻³ Unsaturated polyester resins (UPEs) are one class of polymers with growing interest in their production from sustainable resources. UPEs are so desired because of their adjustable chemical and mechanical properties, dependent upon the choice of combining diacids, diols, crosslinking agent and additives used at production, as well as their corrosion resistance and low density.⁴⁻⁶ As such these versatile materials are suitable for robust and speciality applications with relatively low costs when compared with other polyesters.⁷ Maleic, muconic, fumaric, succinic, adipic and itaconic acids are examples of bio-based diacids (Figure 1); platform molecules from which bio-derived unsaturated copolyesters can readily be prepared.⁸⁻¹¹

Of the above mentioned platform molecules itaconic acid and its derivatives are receiving considerable attention in developing bio-derived polyester resins because of favoured fermentative production from carbohydrates.¹²⁻¹⁵

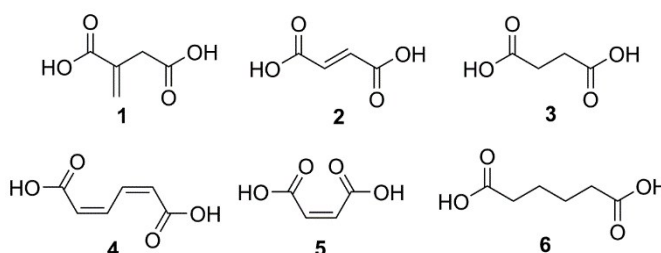


Fig. 1 Typical bio-derived diacids and used for unsaturated polyester synthesis. **1** – itaconic acid (IA); **2** = fumaric acid (FA); **3** = succinic acid (SA); **4** = cis,cis-muconic acid; **5** = maleic acid (via butane oxidation); **6** = adipic acid

While the dicarboxylic acid can easily be modified to form polyesters, the double bond leaves the possibility for additional functionalisation to control properties, for instance solubility, of resulting polyesters.¹⁶⁻¹⁸

Some unique and interesting polymers have been made by taking advantage of the itaconate double bond *via* radical polymerisation.^{19,20} Water-soluble linear polyesters, such as poly (itaconate sorbitol-co-succinate sorbitol), have been synthesised by direct polycondensation of diacids and diols with cross-linking at the double bond delivering interesting thermoset polymers.²¹ Itaconate-derived polyesters have also been made by tandem synthesis, in which the diacid was first converted to its cyclic anhydride with subsequent alternating co-polymerisation of this anhydride and an epoxide using salen-based chromium catalysts.²² One major challenge in preparing high molecular weight linear unsaturated polyesters from diacids and diols is the occurrence of Ordelt saturation.²³ Ordelt saturation involves the reaction of the hydroxyl group

Green Chemistry Centre of Excellence, Department of Chemistry, The University of York, Heslington, YO10 5DD, York, United Kingdom

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on the diol moiety with the carbon-carbon double bond on the unsaturated diacid and results in uncontrollably branched polymers.²⁴ Often, this branching means the polymers have undesirable properties, such as increased viscosity or reduced solubility, and hence minimising this saturation is preferable. For polymerisation involving unsaturated diacids or derivatives, isomerisation is another undesirable occurrence. This for example, has been reported for itaconate-, fumarate- and maleate-based unsaturated polyesters.^{23, 25} Enzymatic polymerisations of itaconic acids with various diols has been demonstrated as a means by which to avoid these undesirable side reactions, but the resulting polymers are often of low molecular weight and need careful selection of a suitable corresponding diol.^{15, 26}

In recent years post-polymerisation modification of high molecular weight UPEs, especially itaconate-based polyesters, with little or no *Ordel* saturation has attracted much interest.²¹ The synthesis of itaconate-derived polyesters using melt polymerisation and a dibutyltin dilaurate catalyst in which the double bond was functionalised *via* an *n*-propyl amine catalysed Michael addition affording a range of polymers with thio and amine pendants.²⁷ Likewise bio-derived polysulfones have been prepared *via* a thia-Michael addition to itaconate-based polyesters followed by oxidation of the resulting polysulfide.²⁸ Piperidine has also been used as pendants in Michael addition post-modification of high molecular weight unsaturated polyesters containing itaconates (in this instance formed *via* acyclic diene metathesis polymerisation) to deliver bio-derived polymers with tuneable and self-degradable properties.²⁹ Michael donors containing nitrogen can easily be added across already activated carbon carbon double bond of an enzymatically catalysed polycondensed itaconate-based polyester to form hydrogels.³⁰ Rather than Michael addition, crosslinking methods have been used to effect post-polymerisation of butylene succinate-co-itaconate based polyester with benzyl peroxide or dicumyl peroxide.^{31, 32} In many of the cases reported however, the modification progressed *via* a homogeneously catalysed Michael addition. There is therefore a pressing need to consider greener methodologies for carrying out the post polymerisation modification of UPEs through the use of recoverable and reusable heterogeneous catalysts. Additionally, greener methods of heating the modification reactions should be applied, such as the use of microwaves where dangerous exotherms can be mitigated by the ability of the microwave energy input to be instantly turned off. Where possible the use of solvents in the modification step should also be avoided, reducing the overall waste generated from such reactions.

While many pendants including thio, amine and piperidine derivatives, amongst others, have been considered in post-polymerisation modification (Figure 2), the use of diketones for this purpose has never been reported (Figure 3). Diketones, because of their structures, have a number of specific and interesting properties; they are versatile chelating agents and useful substrates for chemical syntheses including pharmaceuticals. As modifications, such as substitution to the methylene group on the β -diketone, do not ordinarily interfere

with the reactivity of the diketone compound,³³ the use of diketones as pendants in post-polymerisation modification should impart more useful functionality to the resulting polymers.

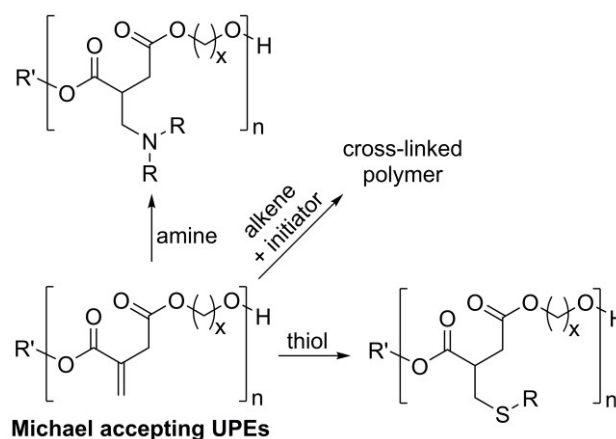


Fig. 2 Previously reported post-polymerisation modifications of bio-derived UPEs

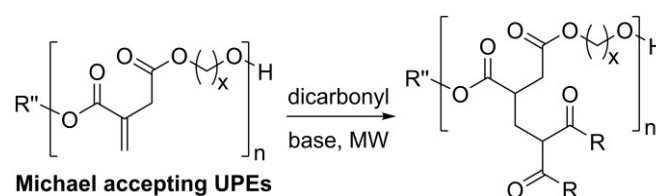


Fig. 3 Post-polymerisation modifications of bio-derived UPEs via the Michael addition of 1,3-dicarbonyls

We have earlier reported the greener synthesis of 1,3-dicarbonyl pendanted itaconate-based diesters *via* a Michael addition using alumina supported potassium fluoride ($\text{KF}/\text{Al}_2\text{O}_3$) heterogeneous catalysis, under solventless conditions and heated by microwaves over very short reaction times (less than 5 minutes). Initial attempts to form polyesters *via* the transesterification of the above dicarbonyl pendanted diester proved unsuccessful, it was assumed that the dicarbonyl species were interfering with catalytic cycle of the titanium alkoxide catalysts used. Herein we report the application of the green Michael addition methodology to unsaturated polyester resins from various bio-derived platform molecules.^{23, 34} As such we present a novel post-polymerisation functionalisation for a range of the bio-derived UPEs *via* a green heterogeneously catalysed Michael addition protocol, demonstrating the effective addition of dicarbonyl pendants to the electron deficient olefin of these polymers. This represents a new route to the post-polymerisation modification of UPEs, and also shows how the typical side reactions in the UPE synthesis (branching, cross-linking and isomerisation) are reversed during the Michael addition, resulting in a uniform constitution repeat unit.

Experimental Section

Synthesis of Unsaturated Polyesters

The unsaturated polyesters namely poly (propylene itaconate) (PPI), poly(butylene itaconate) (PBI), poly (butylene itaconate-co-butylene succinate) (PBIBS) and poly(butylene fumarate) (PBFu) were synthesized according to the previously published procedure.²³

Michael Addition to Unsaturated Polyester Backbones

1,3-dicarbonyl additions were performed in the CEM Labmate Discovery Microwave reactor (2.455 GHz (0.1222 m) magnetron), in standard 8 ml vessels using a fixed power method (25-300 W). Maximum pressure was set to 160 psi, with maximum observed between 60-150 psi depending on reagents, reaction time and power settings. Reaction temperature was measured using an inbuilt IR sensor, and reactions were continuously agitated using a magnetic stirrer bar (at fixed speed, low setting for CEM Discovery).

Acetylacetone Pendant on Unsaturated Polyesters

Unsaturated polyester (2.5 mmol with respect to constitutional repeat unit (CRU) of polymer) was dissolved in warmed (50 °C) acetylacetone (1.00 g, 10 mmol) in a standard 8 ml CEM microwave glass tube. To this 50 mg of 10 mmol g⁻¹ KF/Al₂O₃ catalyst was added and the reaction mixture was heated in the microwave for 5 minutes, 25 W fixed power. The resultant crude polymer product was dissolved in 20 ml acetone and filtered to remove the KF/Al₂O₃ catalyst, the acetone removed *in vacuo*. Excess acetylacetone was subsequently removed from the catalyst-free crude polymer sample by washing four times (*via* trituration) with 20 ml deionised water. The resulting wet polymers were re-dissolved in acetone, this removed *in vacuo*. The materials collected were highly viscous light brown to red liquids. ¹H-NMR confirmed C=C conversions of >95%. Analysis of PBI-acac; ¹H-NMR (400 MHz, CDCl₃, δ_H, ppm) 1.70 (4H, br m, RCO₂CH₂CH₂CH₂CH₂OR), 2.1-2.2 (1.6H, m, CHCH₂CH(CO₂CH₃)₂ and CHCH₂C(CO₂CH₃)₂H), 2.17 (2.8H, s, C(COCH₃)₂H), 2.20 (1.6H, s, CH(COCH₃)₂), 2.22 (1.6H, s, CH(COCH₃)₂), 2.4-2.5 (1H, m, CHCHHCO₂R, keto and enol), 2.6-2.8 (2H, m, CHCHHCO₂R and CHCHHCO₂R, keto and enol), 2.95 (0.4, m, likely CHCHHC(CO₂CH₃)₂H), 3.75 (~0.5H, m, RCO₂CH₃ and RCO₂CH₂CH₂CH₂CH₂OH, end-groups), 3.73 (0.6H, br, CH₂CH(COCH₃)₂), 4.09 (4H, br m, RCO₂CH₂CH₂CH₂CH₂OR), ~17 (0.4H, s, C(COCH₃)₂H); ¹³C-NMR (100 MHz, CDCl₃, δ_C, ppm) 23.0 (CHCH₂C(COCH₃)₂H), 24.9 (two equal peaks, RCO₂CH₂CH₂CH₂CH₂OR), 28.8 (~0.6C, CHCH₂CH(COCH₃)₂), 29.2 (~0.4C, CHCH₂C(COCH₃)₂H), 28.8 (~0.6C, CHCH₂CH(COCH₃)₂), 29.4 (~0.6C, CHCH₂CH(COCH₃)₂), 35.3 (CHCH₂CO₂R, enol), 36.1 (CHCH₂CO₂R, keto), 39.1 (CHCH₂CO₂R, keto), 41.7 (CHCH₂CO₂R, enol), 51.9 (~0.13C, two equal peaks, CO₂CH₃, end-group), 61.9 (~0.15C, RCO₂CH₂CH₂CH₂CH₂OH, end-group), 64.1 (2 equal peaks, RCO₂CH₂CH₂CH₂CH₂OR), 65.9 (CHCH₂CH(COCH₃)₂), 106.8 (CHCH₂C(COCH₃)₂H), 171.0 (CO₂R), 171.4 (CO₂R), 173.5

(CO₂R), 174.1 (CO₂R), 191.7 (CHCH₂C(COCH₃)₂H), 202.8 (CHCH₂CH(COCH₃)₂), 203.0 (CHCH₂CH(COCH₃)₂), IR (ν, cm⁻¹), 3518 (weak, broad, O-H), 2955 (C-H), 2924 (C-H), 1725 (C=O, ester) + shoulder (~1700, C=O, ketone), 1605 (complex enol bend).³⁵ NMR spectra for the other pendant polyesters are contained within the supplementary information.

Partial addition of Acetylacetone Pendant

Partial addition of Hacac to PBI was controlled by adjusting the microwave reactor power and run time. The extent of Hacac addition was determined using ¹H NMR, comparing the integral of the peaks for the CH₂CH₂OR of the diol section with CHs of the various C=C sections. Ratios of itaconate : mesaconate : citraconate were also determined by ¹H NMR, comparing the integrals of the peaks for the various C=C moieties.

UV-Vis spectrometry

UV-vis solutions (~2 mmol dm⁻³ in ethanol) of Fe chelators were analysed using a JASCO V-550 spectrophotometer in standard 1 cm path-length cells. Synthesis of 2-(2-acetyl-3-oxo-butyl)-dimethyl succinate (**10**) is available in prior literature.³⁴

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS was carried out on digested samples of polymer before and after Hacac addition to determine the content of Ti and K. The sample was digested in the Milestone ETHOS UP SK-15 microwave following the methodology to dissolve polyesters described by Milestone: ~0.060 g sample, 10 mL HNO₃ (trace SELECT, 69%) was added in a microwave vial and heated under a pre-set program (temperature programme was: over 40 minutes the initial room temperature was ramped up to 200 °C and held for a further 15 minutes). Digested samples were diluted up to 100 mL with ultrapure water. ICP-MS analysis was performed using an Agilent 7700x fitted with standard Ni sample and skimmer cones coupled to a mass spectrometer. The sample introduction line was rinsed for 60 seconds between samples with 0.5% HNO₃, followed by 40 seconds of stabilisation.

Dimethylmalonate Pendant on Unsaturated Polyesters

Unsaturated polyester (10 mmol) was dissolved in warmed (50 °C) dimethylmalonate (5.29 g, 40 mmol). To this 150 mg of 10 mmol g⁻¹ KF/Al₂O₃ catalyst was added and the reaction mixture was heated in the microwave for 15 minutes, 150 W. Crude reaction mixture was dissolved in acetone and catalyst removed by filtration. After *in vacuo* removal of the acetone the polymers were washed four times with 10 ml methanol. Residual methanol was removed *in vacuo* yielding highly viscous yellow to light brown materials. Analysis of PBI-DMM; ¹H-NMR (400 MHz, CDCl₃, δ_H, ppm), 1.71 (4H, br m, RCO₂CH₂CH₂CH₂CH₂OR), 2.13 (1H, m, CHCHHCH(CO₂CH₃)₂), 2.18 (1H, m, CHCHHCH(CO₂CH₃)₂), 2.51 (1H, dd, ³J = 16.7 and 5.1 Hz, CHCHHCO₂R), 2.71 (1H, dd, ³J = 16.7 and 8.6 Hz,

CHCHHCO₂R), 2.81 (1H, m, CHCH₂CO₂R), 3.47 (1H, dd, ³J = 8.8 and 6.0 Hz, CH₂CH(CO₂CH₃)₂), 3.70 (3H, s, RCO₂CH₃), 3.71 (3H, s, RCO₂CH₃), 4.10 (4H, br m, RCO₂CH₂CH₂CH₂CH₂OR); ¹³C-NMR (100 MHz, CDCl₃, δ_C, ppm) 25.0 (2C, 2 equal peaks, RCO₂CH₂CH₂CH₂CH₂OR), 30.3 (CH₂CH(CO₂CH₃)₂), 36.0 (CHCH₂CO₂R), 39.0 (CHCH₂CO₂R), 49.3 (CH₂CH(CO₂CH₃)₂), 52.7 (2C, 2 equal peaks, CH₂CH(CO₂CH₃)₂), 64.3 (2C, 2 equal peaks, RCO₂CH₂CH₂CH₂CH₂OR), 169.0 (CH₂CH(CO₂CH₃)₂), 171.1 (CO₂R), 173.5 (CO₂R); IR (ν, cm⁻¹), 2957 (C-H), 1726 (C=O, ester), 1437 (H-C-H, methyl ester).

Results and Discussion

Unsaturated Polyesters

The unsaturated polyesters (UPEs) used in this study have previously been synthesised and reported by Farmer et al.²³ The four UPEs are poly(propylene itaconate) (PPI), poly(butylene itaconate) (PBI), poly(butylene fumarate) (PBFu) and poly(butylene itaconate-co-butylene succinate) (PBIBS) and the structures are shown in Figure 4.

The synthesis of PBIBS was carried out *via* an intermediary *bis*-(4-hydroxyl butyl) itaconate to ensure complete incorporation of the itaconate moiety into the polymer. NMR spectroscopy was used to confirm the structures. M_N, M_w and Pd_i (Table 1, top) were determined by triple detection GPC, in duplicate, against a polystyrene standard (see SI for chromatograms of each polymer analysed). Two interesting observations should be noted from the syntheses of the UPEs. Firstly, PPI and PBI were found to exhibit a degree, ~8%, of isomerisation of the itaconate moiety to mesaconate, Figure 5, which the other two polymers did not show. This isomerisation can be seen as additional ¹H NMR signals at 2.2 and 6.7 ppm.

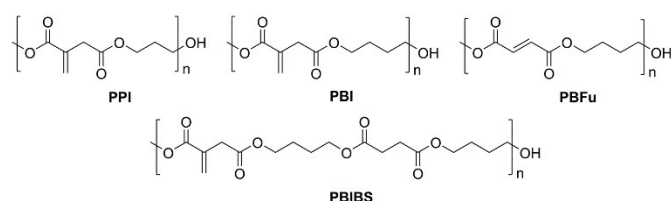


Fig. 4 Structures for poly(propylene itaconate) (PPI), poly(butylene itaconate) (PBI), poly(butylene fumarate) (PBFu) and poly(butylene itaconate-co-butylene succinate) (PBIBS).

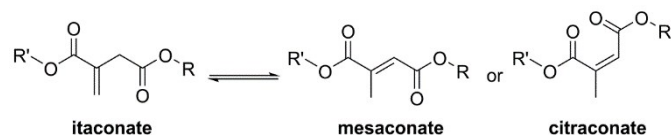


Fig. 5 Isomerisation to dimethyl mesaconate or dimethyl citraconate

Secondly, the M_w and Pd_i of the polymers containing itaconates were unexpectedly high, Table 1, and by GPC the molecular weight distributions were observed as bimodal with a low concentration, high M_w species present, Figure 6. This

high M_w species was confirmed to be branched and cross linked polymer formed *via* the Ordeli saturation, Figure 7. NMR calculations suggested ~4% diol in the polymer was involved in branching and this was less extensive in the fumarate polymer PBFu due to the lack of the more reactive geminal C=C bonds. This observation agrees with that stated by Ramakrishnan and Chandra, where microgel formation was attributed to the high Pd_i for these polymers.²⁷

Table 1 Data from GPC, DSC and TGA analysis of polyesters prior to and following the microwave activated, KF/Al₂O₃ catalysed, Michael addition of Hacac. §

	PBI-acac	[®] PPI-acac	PBIBS-acac	PBFu-acac	
Before Hacac addition	M _n	500 ± 100	N/A*	600 ± 100	2,400 ± 200
	M _w	11,000 ± 300	N/A*	70,000 ± 1,000	4,300 ± 100
	Pd _i	24 ± 1.1	N/A*	92 ± 14	1.8 ± 0.1
	T _g (°C)	-41.7	-51.5	-41.3	None Detected
T _d (°C)	396	406	399	381	
After Hacac addition	% Recovery	73	37	67	34
	M _n	4,400 ± 200	750,000 ± 65,000	8,600 ± 200	4,800 ± 100
	M _w	12,000 ± 500	1.2 × 10 ⁶ ± 60,000	84,000 ± 2,000	8,800 ± 200
	Pd _i	2.6 ± 0.1	1.7 ± 0.05	9.7 ± 0.5	1.8 ± 0.05
	T _g (°C)	-25.1 ± 0.6	-23.6 ± 0.5	-36.5 ± 0.1	-15.5 ± 0.1
	T _d (°C)	339	369	366	289 and 390

§ GPC data shown includes both the low concentration/high mass and high concentration/low mass components (THF eluent, except PBFu: CHCl₃ eluent). [®] = PPI-cross-linked/hyper-branched was used for the Hacac addition to PPI; * = GPC measurement not possible due to cross-linking/hyper branching of material causing the sample to be insoluble in THF.

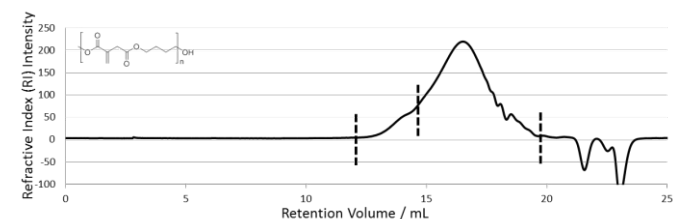


Fig. 6 GPC chromatogram for PBI UPE backbone (THF eluent, refractive index detector).

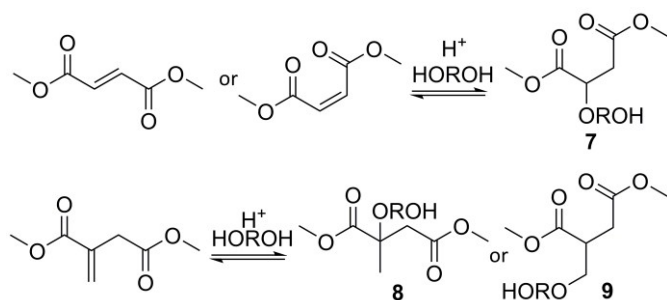


Fig. 7 The Ordelet reaction, C=C bond saturation by a diol, of; dimethyl fumarate or dimethyl maleate to compound 7 and dimethyl itaconate to compounds 8 and 9 via α - and β -addition respectively.

Acetylacetone Addition

Acetylacetone (Hacac) was added to PBI, PPI, PBIBS and PBFu *via* Michael addition under microwave irradiation (5 minutes, 25 W) using a heterogeneous KF/alumina (10 mmol g⁻¹) catalyst. The highest product recovery, 73%, obtained for the PBI-acac polymer. A four-molar excess of Hacac, relative to C=C in the polymer chain, was required to avoid issues with excessive viscosity during the reaction. Other than excess Hacac no solvent was required for the addition under microwave irradiation. Analysis by NMR spectroscopy confirmed successful incorporation of the diketone, with >95% loss of C=C (Figure 8) for all UPEs except PBIBs where residual mesaconate was detected (~30%, see supplementary information). Closer inspection of the ¹³C NMR spectra clearly shows the keto-enol tautomerism anticipated for the successful addition of Hacac to the polyester backbone. Keto-enol tautomerism also resulted in greater complexity in the ¹H NMR spectra and resulted in two signals for each of the protons in positions e, h, l and j (Figure 9). Contact of the polymeric samples to KF/Al₂O₃ presented the potential for K⁺ to become the counter-ion of the -acac pendant. ICP-MS was used to determine potassium content of the PBI polymer both before and after Hacac addition. The unreacted PBI UPE contained 0.018%wt K, this increasing to 0.053%wt after addition of the dicarbonyl pendant. However, with the loading of catalyst used (50 mg) the potential total K in the polymer sample, in the unlikely case that all was abstracted from the catalyst, would lead to a 1.75%wt K content. Therefore, the 0.053%wt observed represents only negligible contamination of the catalyst in the final polymer following Hacac addition to the UPE. This confirms that the chosen work-up procedure was effective in removing residual catalyst and that little K⁺ remained as a counterion to the -acac pendant. Residual titanium concentration in the polymers were also assessed by ICP-MS. Unreacted PBI UPE was found to contain 0.16%wt Ti, this being slightly higher than the anticipated 0.11%wt expected due to the loading of catalyst, Ti(IV), used in the polytransesterification to prepare PBI. Following Hacac addition and subsequent work-up Ti content reduced significantly to 0.03%wt. This indicates that the chosen work-up procedure (triteration with de-ionised water) was also effective in significantly reducing residual titanium catalyst from the sample.

GPC analysis showed no evidence of backbone scission on addition of Hacac (Table 1). These results suggested that Michael addition reversed the branching, caused by the Ordelet C=C saturation that had previously formed the low concentration/high molecular weight chains in the unsaturated polyester. As a result, polydispersity (Pd_i) improved significantly, typically showing a 10-fold reduction. However significant branching remained in the PPI-acac sample (see supplementary information Figure S6), demonstrated by high M_n and M_w values along with poor yields due to cross-linked sample loss from filtration. These increases in M_n observed after saturation may have been a result of the work-up to remove smaller chains previously present in the crude unsaturated polyester backbones. No change in Pd_i was seen for PBFu as there had been no branching from its C=C prior to Hacac addition. The change in T_g for the PBIBS backbone was less than observed for others and the reason for this is discussed in detail in relation to the dimethyl malonate (DMM) addition shown later. The T_g of PBFu-acac was higher than for the other polymer backbones as the close proximity of bulky pendant acac groups to the polyester backbone of PBFu would further limit free-rotation of the chain. In all cases addition of Hacac lowered the T_d, all decompositions being mono-modal, with the exception of PBFu-acac where T_g was observed to increase following Hacac addition.

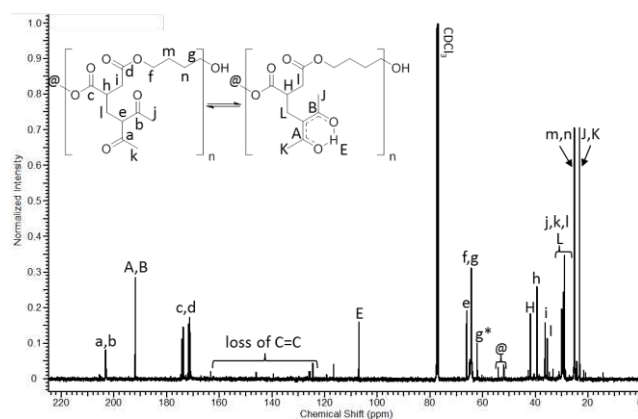


Fig. 8 ¹³C NMR spectrum of PBI-acac in CDCl₃. Lowercase assignment for diketone carbons in keto- form, uppercase signals for diketone carbons in enol- form. ~150 mg cm⁻³

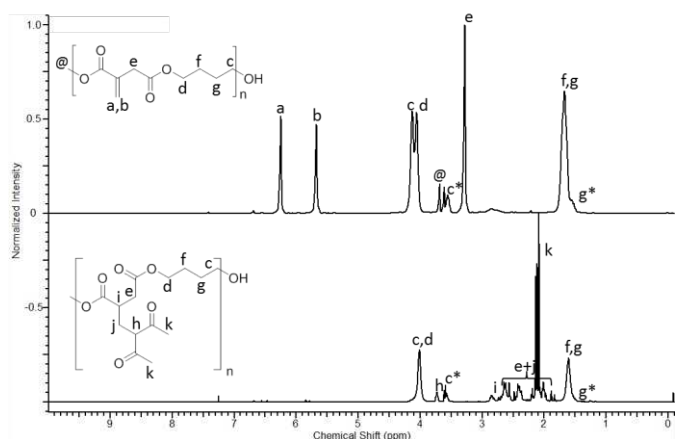


Fig. 9 ^1H NMR spectrum of PBI (top) and PBI-acac (bottom) in CDCl_3 . 150 mg cm^{-3}

Partial addition of Hacac was also investigated as a means to control the level of diketone pendant addition to the final polymer, and if required leaving some unsaturation available for further modification. It was found that the extent of Hacac addition to the PBI polyester backbone could be controlled by altering the conditions of the microwave activated reaction (Table 2).

Table 2 Control over extent of Hacac addition (%acac) to PBI by controlling microwave reaction conditions. 2.5 mmol PBI, 10 mmol Hacac, 50 mg 10 mmol g^{-1} KF/Al $_2$ O $_3$ catalyst; % acac determined by C=C loss from ^1H NMR (see SI, Figure S1)

Polymer	Time (mins)	MW Power (W)	% Recovery	%acac	Ita:Mes:Cit of residual C=C
PBI-acac-100b	5	25	73	100	N/A
PBI-acac-78c	1	200	43	78	1 : 1.71 : 0.30
PBI-acac-68c	1	100	76	68	1 : 0.34 : 0.07
PBI-acac-52c	1	50	70	52	1 : 0.14 : 0.02
PBI	-	-	-	0	1 : 0.03 : 0.01

a=%acac as determined by NMR analysis, and % acac pendant relative to C=C

b=PBI-acac is where >99% of C=C is converted to diketone pendant

c=number corresponds to %acac pendant

Lowering the reaction run time to 1 minute avoided high temperatures, while reductions in power (200 to 50 W) gave control over the extent of Hacac addition. Reduction in the amount of Hacac charged into the reaction vessel was an unsuitable method for controlling the extent of the reaction because of viscosities being too high for effective agitation and catalyst dispersion. The percentage of Hacac added as a pendant (%acac) was determined by the conversion of C=C calculated from the ^1H NMR spectra. The levels of mesaconate and citraconate relative to itaconate increased in line with %acac as mesaconate and citraconate moieties (shown in Figure 5) are less reactive to Michael addition and therefore dominate at higher conversions of C=C. Complexity of the NMR spectra due to keto-enol tautomerism made detection of any additional $-\text{CH}_3$ signal around 2.0-2.3 ppm for the pendanted mesaconate moiety (i.e. Hacac addition to mesaconate)

impossible. However, as Hacac addition increased from 52% to 78% there was no obvious unassigned corresponding additional peak in this region of the spectra (see Figure S1), This would indicate that the low reactivity of the mesaconate means that for addition to Hacac to occur these units must first isomerise back to itaconates, thus resulting in a more consistent constitutional repeat unit. We are currently investigating this dependence of isomerisation on pendant addition with other Michael donors. When studying thermal analysis for the partial addition samples it was observed that as %acac increased the temperature of decomposition decreased (Figure 10), although T_d remained above 250 $^\circ\text{C}$, and therefore all polymers remain stable under conditions of storage and use. As %acac increased, so did the T_g , following a linear trend (Figure 11) due logically to an increase in bulky side-chain content and therefore a reduction in ease of free-rotation. The acetylacetonate pendants also possessed the potential for intermolecular hydrogen bonding via the enol form (Figure 12), further increasing the rise in T_g . Interestingly PBI-acac-100 (PBI-acac) demonstrated a lower T_g than the PBI-acac-78, likely due to the 100% addition significantly reducing branching caused by Ordelt saturation (as indicated by the lower P_d from GPC data – Table 3) and thus increasing the ease of backbone rotation. This reduction in branching is further evidenced by PBI-acac giving a mono-modal GPC trace (see supplementary information, Fig. S2); showing loss of the microgel component of the reaction and indicating that Ordelt saturation is to some extent reversible via Michael addition of pendants.

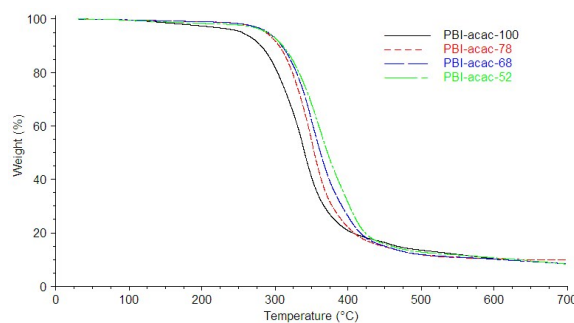


Fig. 10 Effects of altering the % Hacac added to the PBI backbone on the decomposition profile. 25 ml min^{-1} N_2 flow, 10 $^\circ\text{C min}^{-1}$ fixed heating ramp

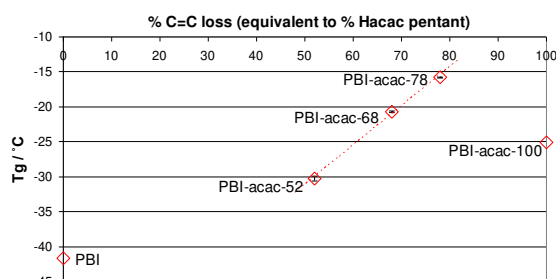


Fig. 11 Effects of altering the % Hacac added to the PBI backbone on the glass transition temperature (T_g) as measured by DSC. Heat/cool/heat cycle (-90 to 60 $^\circ\text{C}$ temperature range), 10 $^\circ\text{C min}^{-1}$ heating/cooling rate

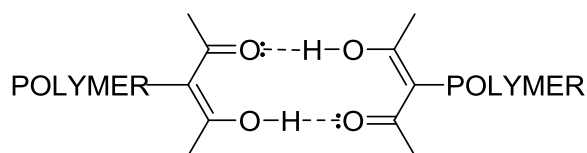


Fig. 12 Potential for chain-chain hydrogen

Table 3 Effects of extent of Hacac addition on molecular weight (M_n and M_w) and polydispersity index (Pd_i) as measured by GPC where 100, 78, 68 and 52 are number corresponding to %acac pendant. THF eluent

Polymer	M_n	M_w	Pd_i
PBI-acac-100	4,400 ± 200	12,000 ± 500	2.6 ± 0.1
PBI-acac-78c	4,700 ± 250	26,000 ± 1,000	5.4 ± 0.2
PBI-acac-68c	17,600 ± 50	90,000 ± 10,000	5.1 ± 0.6
PBI-acac-52c	5,700 ± 50	57,000 ± 3,500	10.0 ± 0.5
PBI	450 ± 25	11,000 ± 250	24.0 ± 1.1

Complexation Studies

Diketones are well known for their chelating power and as such have found diverse applications in adsorption studies and recovery of metals.⁴⁰⁻⁴³ Polymeric chelants have attracted global attention in recent times and are made by appending chelant group to the polymer backbone.⁴⁴ Because they are typically in solid form, polymeric chelants readily interact with metal ions in liquid form without undergoing significant structural degradation. Such chelants in addition to being reused also possess high porosity and resistance to swelling or shattering.⁴⁵ We investigated the complexation capacity of the resulting ethanol soluble polymer, bearing a diketone pendant, with ferric (Fe^{III}) ions. We compared these to acetylacetone and a non-polymeric diketone, 2-(2-acetyl-3-oxo-butyl)-dimethyl succinate (**10**). Analysis of Fe /diketone solutions by UV-Vis spectroscopy demonstrated that metal chelating abilities of Hacac can be retained, even following tethering to a polyester backbone. Owing to the poor solubility of PBI-acac in water, analysis was performed from ethanol stock solutions. $FeCl_3$ was used as the source of $Fe(III)$ ions, and mixed with 4 molar equivalents of diketones to obtain the spectra in Figure 13. A clear difference in colour from the three diketones studied (Figure 14) demonstrated effective chelation with Fe ions in ethanol solution. The absorbance spectra showed that all the complexes have a λ_{max} above 450 nm and the shift in λ_{max} clearly shows that each diketone is complexing in a slightly different manner (differing energy). The raised baseline for PBI-acac indicated turbidity in the sample as a result of incomplete solubility of the polymeric material. This initial screen of metal complexation demonstrates potential applications for these polymers as bio-based polymeric

chelants (for metal recovery). As only Fe metal was considered for complexation study, it would be interesting to see how the saturated polyester complexes with other metals and how polymer chain length and functionality on the polymer backbone affect chelation.

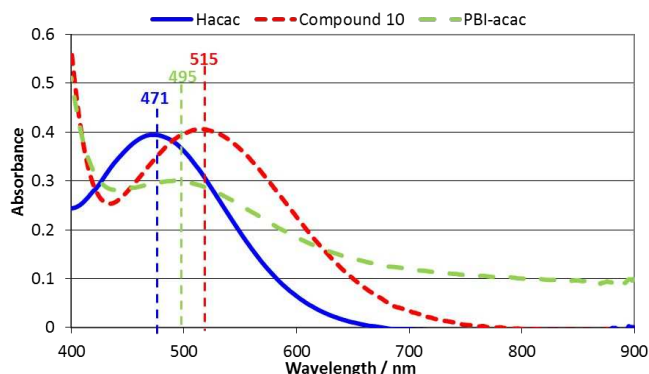


Fig. 13 400-900 nm UV-Vis absorbance spectra for $Fe(III)$ complexes with Hacac, compound **10** and PBI-acac in ethanol. Concentration of diketone = 2 mmol dm^{-3} , λ_{max} above 450 nm highlighted for each complex



Fig. 14 Colours of ethanol solutions on mixing Hacac (left), compound **10** (middle) and PBI-Hacac (right) with $FeCl_3$. Concentration of diketone = 2 mmol dm^{-3}

Dimethyl Malonate Addition

Our previous studies showed that DMM can be used as a replacement for Hacac in our Michael addition to dimethyl itaconate (DMI).³⁴ As such we wished to investigate if the same applies to the polymeric itaconate sample. Dimethyl malonate (DMM) was added to PBI and PBIBS using the same reaction method and work-up as for Hacac, the only difference being that a longer reaction time was required for total conversion.

Analysis by NMR spectroscopy was simpler for these polymeric products than those with Hacac pendants as no keto-enol tautomerism was observed for the DMM pendant (Figure 15). Michael addition was again found to reduce branching of the polyester, improving Pd_i (Table 4), and no depolymerisation *via* ester cleavage chain scission was evident following addition of DMM. The M_n for all three backbones studied increased on addition, likely as a result of both additional volume gained from the pendants (affecting GPC separation) or the additional work-up removing the majority of the smaller chains from the original synthesis of the UPEs.

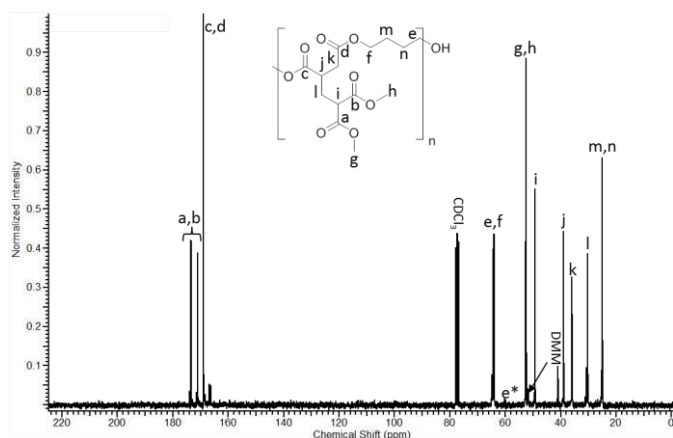


Fig. 15 ^{13}C NMR spectra of PBI-DMM in CDCl_3 , $\sim 100 \text{ mg ml}^{-1}$

Table 4 Data from GPC, DSC and TGA analysis of polyesters prior to (top) and following (bottom) the microwave activated, $\text{KF}/\text{Al}_2\text{O}_3$ catalysed, Michael addition of DMM. THF eluent used for GPC

	PBI-DMM	PBIBS-DMM
Before DMM addition	M_n	500 ± 100
	M_w	$11,000 \pm 300$
	P_d	24 ± 1.1
	T_g ($^\circ\text{C}$)	-41.7
	T_d ($^\circ\text{C}$)	396
After DMM addition	% Recovery	58
	M_n	$4,700 \pm 100$
	M_w	$40,000 \pm 1000$
	P_d	8.5 ± 0.1
	T_g ($^\circ\text{C}$)	-24.5
	T_d ($^\circ\text{C}$)	380

Addition of DMM to PBI was accompanied by an increase in T_g , as for Hacac, and was again attributed to steric bulk of the diketone side-chains reducing ease of backbone rotation. However, a reduction in T_g was observed when DMM was added to the itaconate/succinate co-polymer (PBIBS). Perhaps this is due to the difference in branching between PBI and PBIBS. If PBI had more branching (as it has more $\text{C}=\text{C}$ double bonds along its backbone) then the chains would have been held apart further in the UPE, this giving a larger free volume and a lower T_g . The total addition of acac to PBI removes this branching and therefore reduces the free volume thus raising the T_g . In the case of PBIBS there was less branching in the UPE as there was less $\text{C}=\text{C}$ to crosslink through, as such the free volume was less and the T_g higher. Following addition of Hacac to PBIBS the chains were now forced apart by the pendants, creating free volume and causing the T_g to increase.

Conclusions

Michael addition of dicarbonyl pendants (Hacac and DMM) to α,β -unsaturated polyesters was successfully demonstrated

for the first time as a viable means of delivering bio-based metal chelating polymers, and offering unique way to modify any Michael accepting polymers via post-polymerisation modification. The methodology used for the Michael addition is green and highly efficient, being solventless, heterogeneously catalysed (KF on alumina), fast (typically 5 minutes) and heated using low power microwaves (average of 25 W). The UPEs starting materials used within this study can be produced from bio-derived diacids and diols, their synthesis via a melt and thus inherently resulting in low waste (i.e. no solvent required), the largest contributor to waste being the methanol distillate. During Michael additions, itaconate residues in the polyester backbones underwent $\text{C}=\text{C}$ isomerisation to the less reactive mesaconate and citraconate isomers but such isomerisation (to maleate) was not observed with fumarate backbones. However, little Michael addition was observed onto the mesaconate and citraconate units, and instead the reversibility of the isomerisation meant that additions to itaconate was found to dominate. Known unwanted side-reactions from the synthesis of the UPEs, branching and cross-linking due to Ordelt $\text{C}=\text{C}$ saturation, were found to be reduced during the post-polymerisation protocol for all the pendants studied, showing that P_d for these materials can be improved. Additionally, we were able to effectively control the level of acetylacetone addition through control of reaction time. ICP-MS analysis confirmed that negligible contamination of catalyst in the acac-pendant polymer was evident. Following the post-polymerisation addition of acetylacetone the polymers were found to be effective $\text{Fe}(\text{III})$ chelators, and as such have potential as polymeric chelants for metal recovery or for the purification of heavy metal contaminated water. Our previously presented method for the rapid heterogeneously catalysed Michael addition of dicarbonyls to itaconates and fumarates diesters was found to be equally as suitable for polyester samples containing itaconate and fumarate moieties, allowing a broader choice of bio-derived unsaturated diacids to be utilised for this protocol.

Acknowledgement

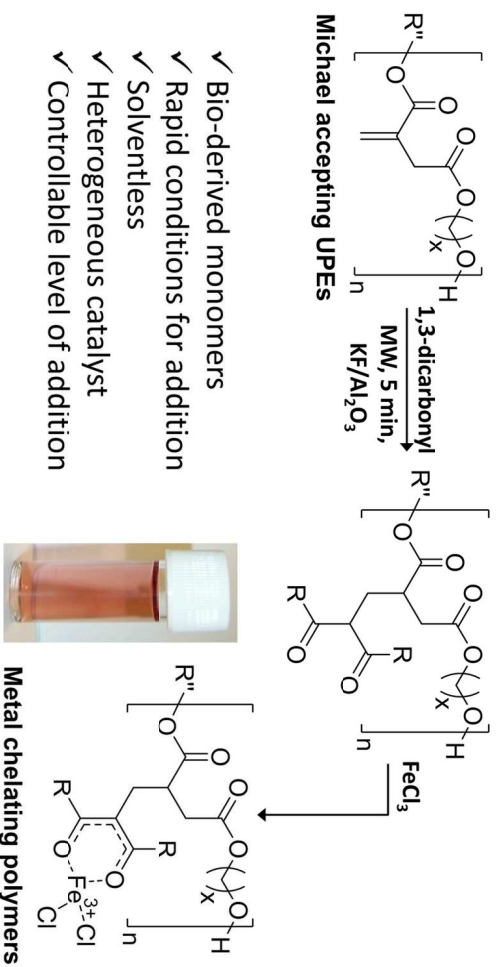
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A rapid (5 min), solventless and heterogeneously catalysed methodology is demonstrated for the first time for the Michael addition of 1,3-dicarbonyls to biomass derived unsaturated polyesters.



- ✓ Bio-derived monomers
- ✓ Rapid conditions for addition
- ✓ Solventless
- ✓ Heterogeneous catalyst
- ✓ Controllable level of addition

139x77mm (300 x 300 DPI)