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New bio-based monomers: tuneable polyester properties using branched diols from biomass†

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A family of monomers, including 2,5-hexandiol, 2,7-octandiol, 2,5-furandicarboxylic acid (FDCA), terephthalic acid (TA), and branched-chain adipic and pimelic acid derivatives, all find a common derivation in the biomass-derived platform molecule 5-(chloromethyl) furfural (CMF). The diol monomers, previously little known to polymer chemistry, have been combined with FDCA and TA derivatives to produce a range of novel polyesters. It is shown that the use of secondary diols leads to polymers with higher glass transition temperatures (T_g) than those prepared from their primary diol equivalents. Two methods of polymerisation were investigated, the first employing activation of the aromatic diacids via the corresponding diacid chlorides and the second using a transesterification procedure. Longer chain diols were found to be more reactive than the shorter chain alternatives, generally giving rise to higher molecular weight polymers, an effect shown to be most pronounced when using the transesterification route. Finally, novel diesters with high degrees of branching in their hydrocarbon chains are introduced as potential monomers for possible low surface energy materials applications.

Introduction

Current industrial processing methods enable mega-scale production of diverse classes of polymeric materials with a wide range of properties. The plastics industry in the UK alone had a turnover of £23.5 billion in 2015, producing 1.7 MT

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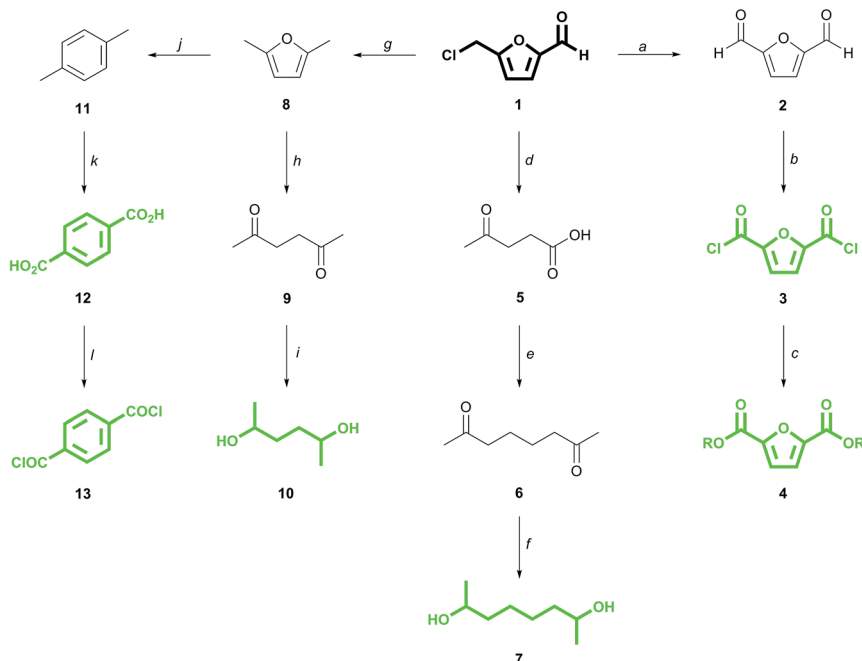
of plastics and employing some 170 000 staff distributed across 5200 manufacturers.¹ However, the production of industrial polymers maintains a disquieting reliance on non-renewable fossil resources, raising concerns regarding the long-term sustainability of this key sector of the chemical industry. Markets in this area have tended to be somewhat conservative, focusing their development around the use of conventional and readily available monomers, such as light olefins, acrylates, styrene, butadiene, ethylene glycol and terephthalic acid, which together account for the great majority of the plastics market. Many of these monomers and their corresponding polymers were first prepared and characterised in the infancy of the petrochemical revolution in the early 20th century.

The last decade however has witnessed the introduction of a wave of new monomers derived from biomass, the unconventional structures of which broaden the range of accessible polymer properties while also supplying a renewable alternative to the use of petroleum as an industrial feedstock.² There are already a number of well-established bio-based plastics on the market, such as polylactic acid and polybutylene succinate, but several other systems have been described, and the diversity of chemical functionality in bio-based platform molecules leaves many more to be explored. In 2015, Becer and Isikgor published a comprehensive review of current lignocellulose-derived materials which captured the depth of the functional space available for polymer chemists to explore within this platform.³ Lignocellulose is heavily oxygenated compared to petroleum-based feeds, and this allows oxygen to be imported from biomass-derived platform molecules through to the monomer and carried finally into the polymer.⁴ Herein, we report in detail on the synthesis of novel polyesters from monomers having a common precursor in the form of biomass-derived 5-(chloromethyl)furfural (CMF) **1**. We further introduce two new bio-based diesters that showcase the versatility of the CMF derivative levulinic acid **5** as a source of novel monomers.⁵

CMF **1** is an up and coming platform molecule that is functionally analogous to the well-known fructose derivative 5-(hydroxymethyl)furfural (HMF) but, unlike HMF, can be produced in high yield directly from raw biomass.⁶ We have previously demonstrated that CMF can be converted into 2,5-furandicarboxylic acid (FDCA) esters **4** *via* the diacid chloride **3** (Scheme 1).⁷ FDCA is currently being commercialized as a renewable substitute for terephthalic acid (TA) **12**, which is produced globally from petroleum on an enormous scale, and which itself can be derived renewably from CMF by direct reduction to 2,5-dimethylfuran **8**,⁸ followed by cycloaddition with ethylene to *para*-xylene **11** and ultimate oxidation to **12**.^{9,10} Derivatives of FDCA and TA serve as the diacids used in this study.

We have also recently described how the CMF derivative levulinic acid **5** can be coupled electrochemically to give 2,7-octanedione **6**, the hydrogenation of which produces the monomer 2,7-octanediol **7**.¹¹ 2,5-Hexanediol **10** is likewise derived from its corresponding dione **9**, which is the hydration product of 2,5-dimethylfuran **8**, itself a reduction product of CMF.¹² While secondary diol **7** is virtually unknown to polymer chemistry,¹³ diol **10** has seen limited use in materials applications, often in amorphous polymers of low molecular weight.^{7a,14} These α -branched diols, along with commercial 2,3-butanediol **14** (ref. 15) and dianhydro- β -glucitol (isosorbide) **15**,¹⁶ are paired with the above mentioned diacids to produce the novel, renewable polyesters which are the focus of this work.





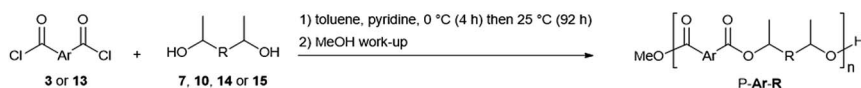
Scheme 1 Conversion of 5-(chloromethyl)furfural (**1**) to monomers (in green). (a) DMSO, 150 °C, 18 hours, 81% yield;^{7b} (b) *t*-BuOCl, 24 hours;^{7a} (c) EtOH, 50 °C, 6 hours; 76% yield over 2 steps from **2**;^{7a} (d) H₂O, 190 °C, 20 min, 91% yield;^{6b} (e) e⁻, KOH/MeOH, Pt–Pt, undivided cell, 65% yield;¹¹ (f) 12 atm H₂, Pd/C, aq. KOH, 80 °C, 94% yield;¹¹ (g) BuOH, cat. H⁺, then H₂, Pd/C, 80% yield;⁸ (h) H₂O, 250 °C, 30 min, quantitative yield;^{12b} (i) H₂O, H₂, 3 MPa, Pt/C, 120 °C, 2 hours, 80% yield;^{12c} (j) ethylene (62 bar), P-BEA or Zr-BEA, 250 °C, 24 h, 97% or 89% yield, respectively;⁹ (k) O₂, cat, >90% yield;^{10a} (l) SOCl₂, DMF, quantitative.^{10b}

Results and discussion

Polyesters *via* diacid chlorides

Secondary diols possess intrinsically lower reactivity than α,ω -diols, and the high boiling points of diols like **7** hamper the common strategy of using them in excess to drive the polymerization reaction forward. Both of these issues can, however, be circumvented by the use of reactive diacid chlorides (Scheme 2).^{16b}

The method involves the use of a 1 : 1 stoichiometric ratio of diol to diacid chloride in a suitable solvent and with an excess of pyridine to neutralise the HCl condensate. Such conditions have, for example, been successfully employed for



Scheme 2 General solution-phase polymerisation procedure *via* diacid chlorides and diols. **3**: Ar = furan; **13**: Ar = benzene; **7**: R = (CH₂)₄; **10**: R = (CH₂)₂; **14**: diol = 2,3-butanediol; **15**: diol = isosorbide.



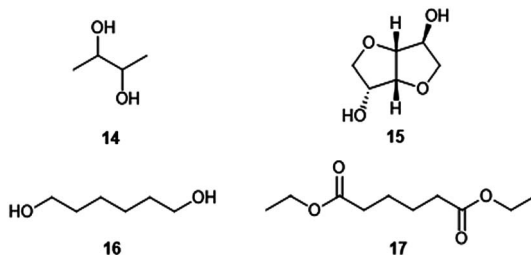


Fig. 1 Additional monomers studied.

the preparation of polyesters containing the secondary bicyclic diol isosorbide **15** (Fig. 1).¹⁷ The results of the polymerization reactions between FDCC **3** or terephthaloyl chloride **13** and CMF-derived diols **7** and **10** or the alternative bio-based diols **14** (Fig. 1) and **15** are shown in Table 1.

All diacid chloride polymerisations gave reasonable yields of 50–90%, although a long reaction time of 92 hours was required. When the duration was reduced in one case to 24 hours for the reaction between **3** and **7**, the isolated yield of polymer decreased from 61% to 27%, with a concomitant reduction in the polymer chain length. A likely cause for the non-quantitative yields observed was the loss of polymer during methanol washes/trituration. These were necessary to remove the pyridinium chloride by-product (PyCl) from the samples, and attempts to reduce the number of washes resulted in residual PyCl, evident in the TGA (degradation around 140–200 °C, see Fig. S1†).

Table 1 Solution-phase polymerisation of diacid chlorides with diols^a

Polymer	Ar	R ^b	% yield ^c	M _n ^d (g mol ⁻¹)	M _w ^d (g mol ⁻¹)	D ^d	TD ₁₀ ^e (°C)	TD ₅₀ ^e (°C)	T _g ^f (°C)
P-13-14	Benzene	—	84%	3100	4100	1.3	339	365	101 (127) ^h
P-13-10	Benzene	(CH ₂) ₂	75%	4600	6900	1.5	326	343	65
P-13-7	Benzene	(CH ₂) ₄	63%	8500	12 000	1.4	312	331	63
P-13-15	Benzene	Iso	79%	2100	2700	1.3	391	420	169 (155–197) ⁱ
P-3-14	Furan	—	56%	8700	13 000	1.5	325	344	84 (87) ^j
P-3-10	Furan	(CH ₂) ₂	69%	8300	11 000	1.3	285	300	56
P-3-7	Furan	(CH ₂) ₄	61%	6100	8900	1.5	291	304	40
P-3-7 ^g	Furan	(CH ₂) ₄	29%	4500	5400	1.2	293	302	31
P-3-15	Furan	Iso	60%	Sample insoluble in GPC solvent			371	401	159 (173) ^k

^a 2.6 mmol of diacid chloride (**3** or **13**), 2.6 mmol of diol (**7**, **10**, **14** or **15**), 1.7 mL of pyridine, 3 mL of toluene, 6 hours at 0 °C then 86 hours at 25 °C, 2 × 15 mL MeOH wash. ^b R = — corresponds to 2,3-butanediol (**14**), R = Iso corresponds to isosorbide (**15**). ^c Mass of isolated polymer after methanol wash as a % of anticipated total mass assuming 100% conversion. ^d Determined by GPC. ^e Determined by TGA, see ESI Fig. S5.† ^f Determined by modulated DSC, see ESI Fig. S6.† ^g Shortened reaction time (24 hours). ^h Literature value of 127 °C for T_g of poly(2,3-butylene terephthalate).^{20b} ⁱ Literature value over the range of 155 °C to 197 °C for T_g of poly(isosorbide terephthalate).¹⁹ ^j Literature value of 87 °C for T_g of poly(2,3-butylene furanoate).²¹ ^k Literature value of 173 °C for T_g of poly(isosorbide furanoate).^{17b}



As the number of CH₂ groups in the diols increases, there is typically a corresponding increase in M_n and M_w , indicating that the longest diol **7** ($R = (CH_2)_4$) is the most reactive and least hindered by steric effects. This highlights the potential value of this bio-based monomer as it allows for comparatively high chain lengths for a secondary diol, markedly out-performing C₄ diol **14**. Low dispersity ($\bar{D}$) values were observed in the GPC analyses of all these novel polymers, indicating little evidence of issues such as chain branching (which can arise from aldehyde impurities leading to branched acetals) or gelation-induced bi-modal mass distributions.

Modulated differential scanning calorimetry (DSC) was used to investigate the thermal transitions of the polyesters. For both the terephthalate and furan series there is a noticeable drop in T_g between the polyesters of the C₄ diol **14** and the C₆ diol **10** (Fig. 2). However, from **10** to the C₈ diol **7** there was little change, although this effect is skewed somewhat by differences in degrees of polymerisation, which increase the T_g . The effect of higher polymer chain length increasing the T_g can be clearly seen when comparing the standard 92 hour reaction in P-3-7 with its 24 hour counterpart, where the latter has a lower M_n and M_w and as a result a T_g of 31 °C *versus* 40 °C for the former. The link between increasing polymer chain length and a subsequent increase in T_g is well-established and associated with larger chains resulting in greater restrictions on the long-range coordinated molecular motions associated with progression through the glass transition.¹⁸

Looking to the literature, Boyd *et al.* compared adipate polyesters of linear 1,6-hexanediol **16** (Fig. 1) with its branched isomer **10** and showed that the former produced highly crystalline polymers (~60%) while polyesters of the latter were entirely amorphous.^{14b} It is common for polymers to contain both crystalline and amorphous regions, but this can be in widely varying distributions between the two.

Crystalline regions result in distinct melting points, while amorphous regions result, instead, in a secondary phase transition (T_g) between a hard, glassy state and a rubbery state. Boyd attributed the entirely amorphous nature of polyesters of **10** to its stereo-irregularity. As all diols in this work (with the exception of isosorbide **15**) were used as mixtures of diastereomers, we too observed predominately amorphous behaviour in our polymers, with DSC traces showing

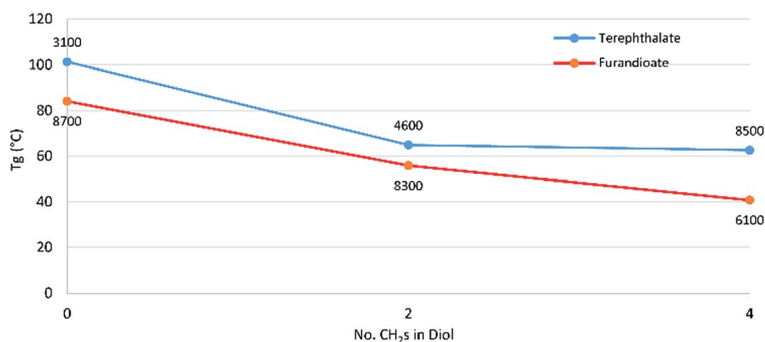


Fig. 2 Effect of increasing secondary diol length on the glass transition temperature for polyesters of **3** and **13**. Labels of each data point are the M_n of the sample as determined by GPC.



distinct T_g s but little evidence of melts. The study by Boyd also indicates how a simple regioisomeric variation in a monomer can drastically alter the T_g of the resultant polymer. Table S1 (ESI†) shows previously reported T_g data for a range of other polyesters produced using both primary and secondary diols. Evident from this comparison is the strong influence secondary diols have on raising the T_g values. Terephthalate and furandioate polyesters of **14**, for example, display T_g s of 84–127 °C, while the equivalent isomeric polyesters made from 1,4-butanediol have T_g s of 26–41 °C, with the terephthalates marginally higher than the furandioates. As the diols progress from C₄ to C₆ to C₈, the T_g values steadily decrease, but in all cases the secondary diols give higher T_g s than their primary diol isomers (Fig. 3). The decrease in T_g in the primary diol series is larger between butanediol and hexanediol than between hexanediol and octanediol for both the terephthalate and furandioate polyesters. This is consistent with our observations in the secondary diol series (Fig. 2), and would suggest that the high T_g associated with polyesters of **14** is both a function of the number of intervening CH₂ groups (A in Fig. 3) and the presence of the CH₃ branches (B in Fig. 3). Thus, the use of linear diols results in increased crystallinity but a reduced T_g for their amorphous regions, while stereoirregular secondary diols show reduced crystallinity but an increased T_g for the amorphous regions of their polyesters.

As anticipated from previously reported data, polyesters of **3** and **13** with isosorbide **15** possessed high T_g values (169 and 160 °C, respectively). The rigidity of the bicyclic structure of this diol is widely observed to increase glass transition temperatures and improve thermochemical properties as the molecular motions associated with the T_g are hindered.¹⁶

The measured T_g of 169 °C for poly(isosorbide terephthalate) (P-13-15) was within the range of literature values (155–197 °C).²⁰ The high T_g value obtained by Ballauf (197 °C) employed a solution-phase polymerisation method similar to our own, but using tetrachloroethane instead of toluene as the solvent. We attribute our lower T_g value to a low polymer chain length for this particular polyester (M_n of 2100 g mol⁻¹). Our value for the T_g of poly(isosorbide furandioate) (P-3-15) was also somewhat lower than a prior literature value (159 vs. 173 °C). This again is likely due to a lower chain length, although we were unable to analyse this particular sample by GPC as it was only sparingly soluble in the eluent (THF).^{16b}

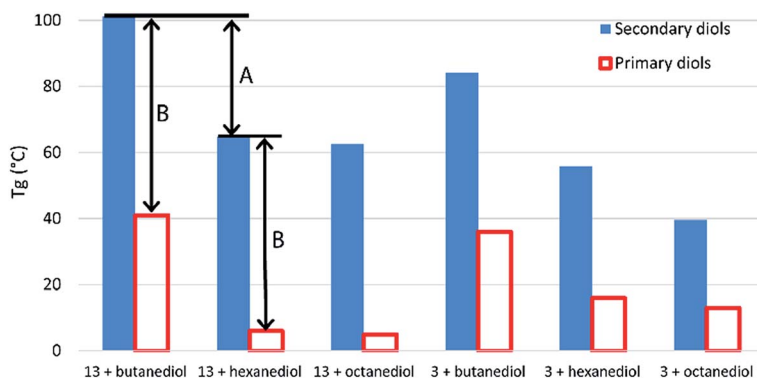


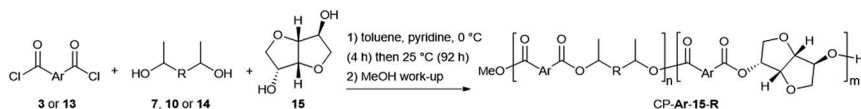
Fig. 3 Comparison of glass transition temperatures for polyesters of **3** and **13** with primary and secondary diol isomers. Data for literature values can be found in Table S1 (ESI†).¹⁹



Thermogravimetric analysis (TGA) under an inert N₂ atmosphere also indicates a general trend of decreasing thermal stability as the length of the secondary diols increases (Table 1). All TGA traces for these polyesters were monomodal, although very minor (<5%) additional mass losses were occasionally observed between 100–180 °C. These additional losses may be attributed to small amounts of residual toluene (solvent), pyridine or end-groups, the two former were also detected in the ¹H-NMR spectra (ESI, Fig. S4†). As was the case for the *T_g* trend, this decrease in stability was significantly more pronounced between **14** and **10** than **10** and **7**. However, all of the polymer samples had a TD₁₀ (a measure of thermal stability indicating the temperature of 10% mass loss) of >280 °C, indicating that all would remain suitable for common applications such as coatings and packaging. The polyesters of isosorbide **15** were found to have the highest thermal stabilities (TD₁₀ > 370 °C for P-**13-15** and P-**3-15**), again demonstrating how this monomer can be used to enhance the properties of plastics. As such, we subsequently investigated the impact of co-polymerisation of **15** with diols **7**, **10**, and **14** to determine whether the thermal stability and *T_g* values could be tailored for this series of bio-based polyesters.

Isosorbide co-polymers

Isosorbide co-polyesters of the above polymers were prepared using a 2 : 1 : 1 ratio of aromatic diacid chloride : isosorbide : aliphatic diol (Scheme 3). ¹H-NMR spectroscopy was used to confirm the successful incorporation of **15** (% iso, see Fig. S2†), with all polyesters showing a % iso in the range of 47–56% (Table 2). The furandioate co-polyesters exhibited marginally higher % iso values than the equivalent terephthalates, although all were acceptably close to the 50% target. GPC analysis showed all *ca.* 50 : 50 co-polymers to have similar chain lengths, with all *M_n*s in the 3300–4900 g mol^{−1} range (Table 2). This range sits within the values observed for the polyesters in Table 1 without isosorbide, while P-**13-5** (% iso = 100%) gave a low *M_n* of 2100 g mol^{−1}. Thus, we prepared a co-polymer of **3** starting with a 25 : 75 ratio of **15** to **7**, resulting in a copolymer with a % iso of 27% and an improved *M_n* of 6800 g mol^{−1}, consistent with expectations. For the terephthalate co-polyesters, a trend again was observed that the longer diols gave rise to higher chain length polymers. This mirrors the observation for the simple polyesters of **13**, although the differences in mass in the co-polymer series were less prominent (4000, 4500, 4900 g mol^{−1}). The addition of **15** into the co-polyester structure resulted in increased thermal stability (TD₁₀ and TD₅₀) for all the polymers studied. This can be seen by comparing the values in Tables 1 and 2 where, for example, P-**3-14** has a TD₁₀ of 325 °C *versus* 336 °C for the corresponding isosorbide copolymer CP-**3-15-14**. Of additional note is that the co-



Scheme 3 Co-polymerisation of isosorbide **15** and secondary diols with diacid chlorides **13** or **3**. Ar = furan; **13**: Ar = benzene; **7**: R = (CH₂)₄; **10**: R = (CH₂)₂; **14**: diol = 2,3-butanediol; **15**: diol = isosorbide.



Table 2 Co-polymers of isosorbide **15** and secondary diols with **13** or **3**^a

Polymer	Ar	R ^b	% yield ^c	% iso ^d	M _n ^e (g mol ⁻¹)	M _w ^e (g mol ⁻¹)	D ^e	TD ₁₀ ^f (°C)	TD ₅₀ ^f (°C)	T _g ^g (°C)
CP-13-15-14	Benzene	—	86%	53%	4000	6600	1.6	350	399	138
CP-13-15-10	Benzene	(CH ₂) ₂	86%	47%	4500	7300	1.6	324	393	66
CP-13-15-7	Benzene	(CH ₂) ₄	72%	48%	4900	8200	1.7	323	393	43
CP-3-15-14	Furan	—	84%	54%	4400	7800	1.8	336	382	137
CP-3-15-10	Furan	(CH ₂) ₂	76%	56%	3300	4400	1.4	303	382	116
CP-3-15-7	Furan	(CH ₂) ₄	90%	55%	4400	6700	1.5	302	381	79
CP-3-15-7 ^h	Furan	(CH ₂) ₄	92%	27%	6800	9700	1.4	294	308	63

^a 2.6 mmol of diacid chloride (**3** or **13**), 1.3 mmol of isosorbide (**15**), 1.3 mmol of co-diol (**7**, **10** or **14**), 1.7 mL of pyridine, 3 mL of toluene, 6 hours at 0 °C then 86 hours at 25 °C, 2 × 15 mL MeOH wash. ^b When R = — this corresponds to 2,3-butanediol (**14**). ^c Mass of isolated polymer after methanol wash as a % of anticipated total mass assuming 100% conversion.

^d As determined by the ¹H NMR spectrum of the collected polymer, see ESI Fig. S4.†

^e Determined by GPC. ^f Determined by TGA, see ESI Fig. S5.† ^g Determined by modulated DSC, see ESI Fig. S6.† ^h 25 : 75 **15** : **7** load ratio (molar).

polymers of **15** typically give two-staged degradations in TGA traces, while the equivalent polyesters from Table 1 were single-staged (Fig. 4 for polymers of **3** and Fig. S3† for polymers of **13**). This suggests differing temperatures of degradation for the different regions of the copolymer. The TGA trace of the *ca.* 25 : 75 **15** : **7** polyester CP-3-15-7 clearly shows that it is the isosorbide region that possesses the higher stability, as the % mass loss for the first degradation (moiety in the polymer resulting from **7**) increases as the fraction of isosorbide monomer is reduced.

Finally, incorporation of **15** into the polyester also resulted in high values of *T_g*, with the notable exception of the terephthalate copolymers CP-13-15-7 and CP-13-15-10, which were lower than expected. While the simple terephthalate polyesters

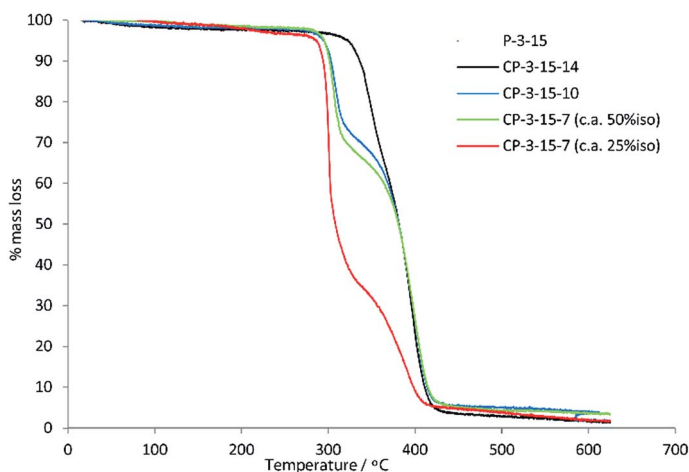


Fig. 4 Comparison of the TGA traces for co-polymers of isosorbide **15** and secondary diols (**14**, **10** and **7**) with **3**.



had shown higher T_g s than the equivalent furandioates using secondary diols (Fig. 3), for the isosorbide co-polymers the opposite was true, as can be seen in Fig. 5. The interpretation of this phenomenon is challenging, but may involve the combination of isosorbide and furandioate leading to more efficient chain packing, or the restriction of interchain mobility by noncovalent interactions. When the fraction of **15** in CP-3-15-7 reduced to 25% iso the T_g drops, although the value of 63 °C is still about 20 °C higher than the polyester without **15** (P-3-7). What remains evident from the experimental data is that **15** can effectively modify the properties of these polyesters, and that the secondary diols introduced in this study continue to demonstrate favourable effects on their resultant polymeric materials.

Polyesters *via* diester transesterification

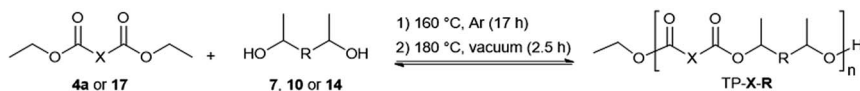
The above solution-phase diacid chloride polymerisation suffers from drawbacks that could limit its suitability for large-scale synthesis. Activation of the aromatic diacids to the corresponding acid chlorides (**3** and **13**) and the subsequent use in reactions generates salt waste, which reduces efficiency, negatively influences polymer yield, and offsets some of the benefits gained by using bio-based starting materials. This method also required the use of a solvent, and while earlier applications of the protocol employed toxic tetrachloroethane,¹⁷ we were able to use toluene. To further reduce the environmental impact and potential toxicity issues, we investigated whether our branched diols could be used in more industrially relevant transesterifications with 2,5-furandicarboxylic acid diethyl ester (FDEE, **4a**, Scheme 4).

Titanium isopropoxide was chosen as the catalyst as this was found to perform adequately without the toxicity associated with common alternatives such as tin(II) bis(2-ethylhexanoate). Similar to the furandioate polyesters produced using **3**, the molecular weights of the polyesters synthesised *via* **4a** transesterification were found to increase across the series significantly (entries 1–3, Table 3). The



Fig. 5 Effect on the T_g of co-polymers of isosorbide **15** and co-diols (**7**, **10** or **14**) with **3** (furandioate) and **13** (terephthalate). *25 : 75 **15** : **7** molar load ratio.





Scheme 4 General polymerisation *via* transesterification of diols and diesters. **4a**: X = furan; **17**: X = (CH₂)₄; **7**: R = (CH₂)₄; **10**: R = (CH₂)₂; **14**: diol = 2,3-butanediol.

branched hexanediol **7** gave the highest M_n and M_w of the series (TP-**4a-7**, entry 3), comparable to the molecular weights achieved using the acid chloride route (P-3-7). Evidently, our initial misgivings regarding the potential drawbacks of the low volatility of diols **7** and **10** were overcautious. In fact, the most volatile diol **14** was found to give the lowest molecular weight polymer, achieving an M_n of only 830 g mol⁻¹ (TP-**4a-14**), in agreement with previous studies where **14** was found to typically produce amorphous, low molecular mass polyesters.^{16a,21} This observation is best illustrated in Fig. 6 where polymer TP-**4a-7** gives a broad monomodal distribution and, despite not having a Gaussian type peak shape (suggesting a slightly higher population of lower molecular mass chains within the sample), the overall molecular masses and polydispersity are good. In contrast, TP-**4a-14** shows a series of low molecular weight oligomer peaks, corresponding to a step-wise increase in the number of repeating units. In keeping with the trend, TP-**4a-10** sits in between the two, with the majority of the material consisting of chain lengths between 5000–10 000 g mol⁻¹, yet including a quantity of lower molecular weight oligomers.

The low degree of polymerisation seen when using **14** may be attributed to a greater steric hindrance of the alcohol groups by methyl groups in both α and β positions. Steric hindrance appears to have a greater impact when using diester monomers in comparison with highly reactive acid chlorides, which may be partially due to the larger ethyl ester group further restricting attack on the carbonyl. The T_g values appear to follow a similar trend to the polyesters synthesised *via* diacid chlorides, where the C₆ (**10**) and C₈ (**7**) diols gave polymers with

Table 3 Diester and diol transesterification polymerisations^a

Entry	Polymer	X	R		% yield ^d	M _n ^e (g mol ⁻¹)	M _w ^e (g mol ⁻¹)	D ^e	T _g ^f (°C)
1 ^b	TP-4a-14	Furan	—	—	82	830	1200	1.4	40
2 ^b	TP-4a-10	Furan	—	(CH ₂) ₂	90	3300	5500	1.7	32
3 ^b	TP-4a-7	Furan	—	(CH ₂) ₄	97	6400	9900	1.6	34
4	TP-17-14	—	(CH ₂) ₄	—	65	2300	3700	1.6	−43
5	TP-17-10	—	(CH ₂) ₄	(CH ₂) ₂	72	8900	15 000	1.7	−36
6	TP-17-7	—	(CH ₂) ₄	(CH ₂) ₄	77	18 000	38 000	2.1	−44
7 ^c	TCP-4a-17-10	Furan	(CH ₂) ₄	(CH ₂) ₂	87	11 000	16 000	1.5	2
8 ^c	TCP-4a-17-7	Furan	(CH ₂) ₄	(CH ₂) ₄	73	9900	19 000	2.0	−8

^a 20 mmol of diester (**4a** or **17**), 25 mmol of diol (**7**, **10** or **14**), 3 mol% catalyst relative to diester, 160 °C for 17 hours followed by removal of unreacted species under vacuum – see experimental for full conditions. ^b 1% wt Irganox radical scavenger added. ^c 10 mmol of each diester with 25 mmol of diol and 3 mol% catalyst relative to **4a**. ^d Isolated.

^e Determined by GPC. ^f Determined by modulated DSC, see ESI Fig. S6.†



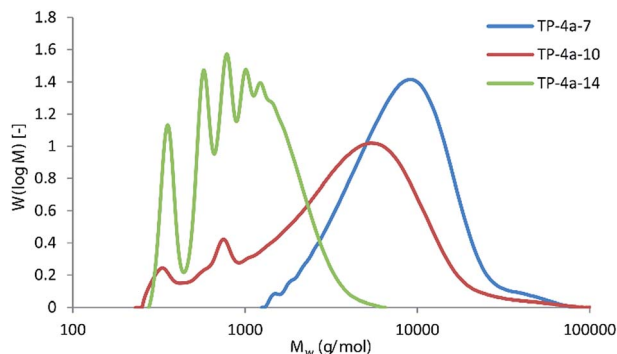


Fig. 6 Comparison of M_w distributions for polymers TP-4a-7, TP-4a-10 and TP-4a-14, as determined by GPC.

lower T_g s, presumably due to increased chain flexibility. Again, the T_g data is skewed somewhat due to the lower molecular weights obtained when using **14**, giving a T_g of 40 °C in entry 1 rather than 87 °C as reported in the literature.²² Promisingly, yields obtained using the transesterification procedure are high, as the washing steps required to remove the salts formed with the acid chloride route are no longer necessary.

Transesterification polymerisations were performed on a larger scale (20 mmol of limiting reagent) compared to the diacid chloride (2.6 mmol), which may have also contributed towards increased yields. With similar molecular weights achieved using either diester **4a** or diacid chloride **3** with diol **7**, transesterification would appear to be the method of choice for the furandioate polyester of diol **7**. However, the lower M_n s observed for TP-4a-10 and TP-4a-14 (3300 and 830 g mol⁻¹, respectively) suggest that the diacid chloride method may give better results when using diols **10** or **14**.

To expand the scope of the transesterification route with diols **7**, **10**, and **14**, a series of aliphatic polyesters were also synthesized using diethyl adipate **17** (entries 4–6, X = (CH₂)₄, Table 3). The molecular weights had a similar trend to those previously discussed, with **14** giving significantly lower M_n and M_w values than **10** and **7**. As previously observed, lower degrees of polymerisation had an impact on the T_g of TP-17-14 (−43 °C as opposed to −23 °C reported in the literature^{15a}). All the polyesters in the adipate series had higher M_n s compared to their furandioate equivalents, with the octanediol adipate polyester (TP-17-7) achieving an M_n of >18 000 g mol⁻¹. The T_g s across the adipate polyester series were much lower than the corresponding furandioates, reaching values in the range of −44 to −36 °C, compared to the latter, with T_g s of 32 to 40 °C. This observation was anticipated, as the greater rigidity within the chains offered by the furan moiety would logically lead to higher T_g s. Yet again, the higher degree of polymerisation seen when using **7** resulted in its T_g being only marginally below that of TP-17-10. With such an impact on the T_g , it is clear that the ability of **7** to produce polyesters of higher chain lengths relative to **10** and **14** highlights a significant benefit in using this bio-based monomer.

In an attempt to incorporate rigidity and yet achieve increased molecular weights, two adipate–furandioate co-polymers were synthesized using diols **7** and **10** (entries 7 and 8, Table 3). The M_n s of polymers TCP-4a-17-7 and TCP-4a-17-7



were superior to the simple furanodiesters, at 9900 and 11 000 g mol⁻¹, respectively. As expected, the introduction of rigidity into the polymer by the incorporation of the furandioate caused the T_g s of both polymers to lie between their homo-polymer equivalents.

Steric effects also appear to play an important role between **14** and **17**, leading to lower M_n s and yields in the formation polymer TP-17-14. In general, the furandioate monomer gave lower M_n values than the adipate, and this may be attributed to the lower degree of electrophilicity of the carbonyl carbon in the furan. This effect can be circumvented to some extent by employing the above diacid chloride methodology, where higher chain lengths for polyesters of diol **14** were achieved. In contrast, diols **7** and **10** performed well with either of the diester monomers when using the transesterification method, illustrating how high molecular weights and favourable polymer properties can be achieved using secondary diols.

Branched diesters from levulinic acid

Whereas CMF **1** can serve directly as a source of the aromatic diacid derivatives **3**, **4a**, and **13** used in this work, its versatility as a platform for renewable monomers is greatly expanded through its hydration product levulinic acid **5**, which further provided branched diols **7** and **10**, and which we now present as a means to access novel aliphatic diester monomers with branching in the hydrocarbon chain.

We have previously described the reduction of the angelica lactone dimer **19** to provide a mixture of branched C₇–C₁₀ hydrocarbons that constitutes cellulosic gasoline.²³ Angelica lactone **18** is accessed from levulinic acid **5** in high yield, as shown in Scheme 5. In place of total deoxygenation of **19**, we have found that gentle hydrogenation in methanol solution in the presence of La(OTf)₃ leads cleanly to dimethyl 3-ethyl-4-methylpimelate **20**, a molecule unknown to polymer chemistry. A separate approach that further takes advantage of the remarkable versatility in the reactivity of **5** is the base-induced dimerization of ethyl levulinate **21** to cyclopentadienyl diester **22**. Hydrogenation of **22** gives the annulated adipic ester **23**. Remarkably, compound **22** was first described in 1903 (ref. 24) and was revisited by other workers in 1950, who misassigned the structure.²⁵ The yield of the condensation reaction was however low (<10%), due mainly to low conversion, and we are currently working to upgrade this method to a standard of preparative usefulness.

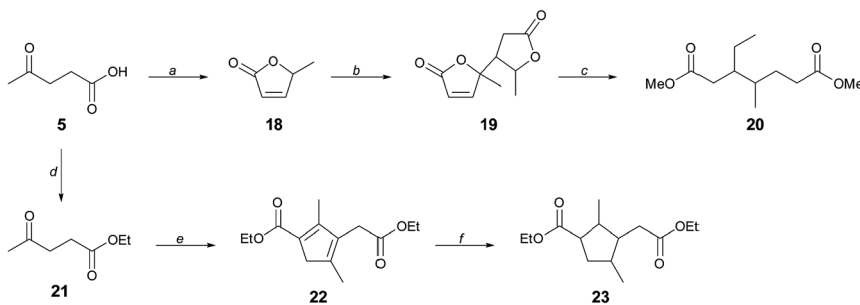
Monomers with substantial branching in the hydrocarbon chain are precursors to polymers with weak interfacial forces, resulting in what are referred to as “low surface energy materials” (LSEMs), which possess nominal surface tensions. LSEMs possess a range of useful applications, including as emulsification/suspension agents, lubricants, detergents, antifog coatings, and hydrophobic textiles and fibers.²⁶ Towards this end, we look forward to preparing polymers of these diacid derivatives, possibly in combination with branched diols **7** and **10**.

Experimental

Materials and methods

Terephthaloyl chloride, 2,3-butanediol, 2,5-hexanediol, isosorbide, diethyl adipate, ethyl levulinate, methanol, anhydrous toluene, anhydrous pyridine,





Scheme 5 Synthesis of branched chain diesters **20** and **23** from levulinic acid. (a) K10 montmorillonite, 165 °C, 50 Torr, 92% yield; (b) K₂CO₃, 70 °C, 94% yield; (c) 20 bar H₂, Pd/C, La(OTf)₃, MeOH, 220 °C, 60% yield; (d) EtOH, H⁺ cat, reflux; (e) NaOEt, CaO, EtOH; 70 h, then H₂SO₄, reflux 24 h; (f) H₂, Pd/C.

titanium isopropoxide, ReadyCal polystyrene standards, tetradecane standard and Irganox radical scavenger were purchased from Sigma-Aldrich and used as received. 10% Pd/C and La(OTf)₃ were purchased from Strem Chemicals. 2,5-Furandicarboxyl chloride **3** and 2,7-octanediol **7** were prepared using previously reported methods.^{7,11} Diols were dried over molecular sieves prior to use in the polymerisations. Angelica lactone dimer **19** was prepared based on a literature procedure.²³

Gel permeation chromatography to determine polymer molecular weight was carried out using a set (Polymer Standard Service (PSS) SDV Combination High) of three analytical columns (300 × 8 mm, particle diameter 5 µm) of 1000, 105 and 106 Å pore sizes, plus guard column, supplied by PSS GmbH installed in a PSS SECurity GPC system. Elution was with stabilised tetrahydrofuran at 1 mL min⁻¹ with a column temperature of 23 °C and detection by refractive index. 20 µL of a 1 mg mL⁻¹ sample in THF was injected for each measurement and eluted for 40 min. Calibration was carried out in the molecular weight range 400–2 × 10⁶ Da using ReadyCal polystyrene standards and with a toluene reference.

Modulated differential scanning calorimetry (DSC) experiments were carried out on a TA Instruments Q2000 DSC under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ over a temperature range of –60 to 200 °C and using a sample mass of approximately 10 mg. The *T_g* values were reported from second heating scans.

Thermogravimetric analysis (TGA) was performed on a PL Thermal Sciences STA 625 thermal analyser. ~10 mg of accurately weighed sample in an aluminium sample cup was placed into the furnace with a N₂ flow of 100 mL min⁻¹ and heated from room temperature to 625 °C at a heating rate of 10 °C min⁻¹. From the TGA profiles the temperatures at 10% and 50% mass loss (TD₁₀ and TD₅₀ respectively) were subsequently determined.

Gas chromatography-mass spectrometry (GC-MS) was performed on an Agilent Technology 6890N equipped with a Varian Factor Four capillary column (VF-5ms, 30 m length, 0.25 mm inner diameter, 0.25 µm film). The injection temperature and the split ratio were 250 °C and 60 : 1, respectively. The oven temperature was held at 60 °C for 2 min, increased to 250 °C (10 °C min⁻¹), and finally increased to



300 °C (20 °C min⁻¹). The initial column pressure was 4.5 psi. The column flow was 0.7 mL min⁻¹. Mass spectrometry was performed using electron impact (EI) ionization. A pure sample of dimethyl 3-ethyl-4-methylpimelate **20** was used to calculate the response factor against the tetradecane internal standard.

For the synthesis of the polyesters, ¹H NMR spectra were recorded using a Jeol 400 spectrometer at an operating frequency of 400 MHz. For the synthesis of **20**, **22**, and **23**, ¹H NMR spectra were recorded using a VNMRs 600 spectrometer at an operating frequency of 600 MHz. ¹³C NMR spectra were recorded on the same instrument at an operating frequency of 150 MHz. All NMR data was processed using MestReNova (version 10.0) desktop NMR data processing software.²⁷

General polymerization procedures

Polyesters via diacid chloride. Diacid chloride **3** or **13** (2.6 mmol) was dissolved in anhydrous toluene (1.5 mL) in a dried 25 mL one-neck round-bottom flask sealed with a rubber stopper. The flask was cooled in a water/ice bath and continually purged with argon. A solution of the selected diol **7**, **10**, **14** or **15** (2.6 mmol) and anhydrous pyridine (1.7 mL) in anhydrous toluene (1.5 mL) was also prepared. The diol mixture was added *via* syringe to the argon-purged diacid chloride solution with slow agitation by a magnetic stirrer bar. Upon mixing, the reaction became cloudy and slightly viscous, with the viscosity increasing over time. After 6 h the flask was removed from the water/ice bath and allowed to reach room temperature and left to stir slowly. After 48 h from the start of the reaction (42 h at room temperature), additional diacid chloride (5 mg) in anhydrous toluene (0.2 mL) was added. This same addition was repeated again after 76 h. After a total reaction time of 92 h (86 h at room temperature), the excess pyridine and toluene were mostly removed *in vacuo* and the solid tacky residue was triturated twice with dry methanol (15 mL). The amount of residual pyridine was reduced by redissolving the product in toluene (5 mL) and evaporation of the solvent *in vacuo*. The solid product was dried under high vacuum (<1 mbar) overnight prior to analysis.

Isosorbide co-polyesters via diacid chloride. Diacid chloride **3** or **13** (2.6 mmol) was dissolved in anhydrous toluene (1.5 mL) in a dried 25 mL one-neck round-bottom flask sealed with a rubber septum. The flask was cooled in a water/ice bath and continually purged with argon. A solution of the selected diol **7**, **10** or **14** (1.3 mmol), isosorbide **15** (1.3 mmol) and anhydrous pyridine (1.7 mL) in anhydrous toluene (1.5 mL) was also prepared. The diol mixture was added *via* syringe to the argon-purged diacid chloride solution with slow agitation by a magnetic stirrer bar. Upon mixing, the reaction became cloudy and slightly viscous, with the viscosity increasing over time. After 6 h the flask was removed from the water/ice bath and allowed to reach room temperature and left to stir slowly. After 48 h from the start of reaction (42 h at room temperature), additional diacid chloride (5 mg) in anhydrous toluene (0.2 mL) was added. This same addition was repeated again after 76 h. After a total reaction time of 92 h (86 h at room temperature), the excess pyridine and toluene were mostly removed *in vacuo* and the solid tacky residue was triturated twice with dry methanol (15 mL). The amount of residual pyridine was reduced by redissolving the product in toluene (5 mL) and evaporation of the solvent *in vacuo*. The solid product was dried under high vacuum (<1 mbar) overnight prior to analysis.



Polyesters *via* transesterification. A mixture of diester **4a** or **17** (20 mmol), diol **7**, **10**, or **14** (25 mmol) and titanium isopropoxide (3 mol% relative to the diester) was introduced into a dry, wide-neck round bottom flask with a magnetic stirrer bar mounted with a Dean–Stark condenser. The system was evacuated and backfilled with argon four times and then heated at 160 °C with a stirring rate of 300 rpm. After 17 h the temperature was steadily increased to 210 °C and the stirring rate reduced along with a gradual application of vacuum over 2.5 h until the pressure reached <0.5 mbar. Upon completion of the reaction, the system was backfilled with argon and the mixture was left to cool with stirring. The resulting polymer was analysed as collected. For entries 7 and 8 in Table 3, the adipate ester was added separately after 2 h initial reaction between **4a** and diol.

Conclusions

A range of bio-based monomers, both diacid derivatives and diols, can be accessed from the cellulose-derived platform molecule CMF. A systemic study into the effects of hydrocarbon chain branching in diol monomers yields some novel insights. In terms of reactivity, for polymers prepared using terephthaloyl chloride **13** or by transesterification of diethyl 2,5-furandicarboxylate **4a**, an increase in the number of intervening CH₂ groups between the branch points leads to higher molecular mass polymers. On the other hand, the combination of 2,5-furandicarbonylchloride **3** with branched diols gave products of similar masses irrespective of diol chain length. In all cases, dispersity values of the polymers were low and thermal stabilities were more than adequate for common materials applications. 2,7-Octanediol **7**, in particular, has shown strong potential for tailoring the properties of its resultant polyesters in terms of increasing the glass transition temperature relative to its isomeric non-branched equivalent. Diol **7** was also found to be best suited for use in more industrially relevant transesterification polymerisations, giving markedly higher degrees of polymerisation relative to the other diols studied. As such, **7** represents an excellent candidate for a new commercial diol, allowing for the tailoring of glass transition temperatures whilst also overcoming the low chain length of polyesters typically observed when using secondary diols. This study has demonstrated how a range of diols and diacids accessible from a single renewable platform molecule (CMF **1**) can be combined to produce novel polyesters with tuneable thermal properties for bio-based materials markets.

Access statement

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References

- 1 British Plastics Federation Annual Review, 2015, http://www.bpf.co.uk/about_the_bpf/BPF_Annual_Review.aspx, accessed 14th December 2016.
- 2 (a) I. Delidovich, P. J. C. Hausoul, L. Deng, R. Pfützenreuter, M. Rose and R. Palkovits, *Chem. Rev.*, 2016, **116**, 1540–1599; (b) A. Gandini and T. M. Lacerda, *Prog. Polym. Sci.*, 2015, **48**, 1–39; (c) Y. Zhang and E. Y.-X. Chen, *Top. Curr. Chem.*, 2014, **353**, 185–227.
- 3 F. H. Isikgor and C. R. Becer, *Polym. Chem.*, 2015, **6**, 4497–4559.
- 4 T. J. Farmer, M. Mascal, J. H. Clark, and F. E. I. Deswarte, *Platform Molecules in Introduction to Chemicals from Biomass*, John Wiley and Sons, Chichester, UK, 2nd edn, 2015, ch. 4, pp. 89–156.
- 5 (a) J. J. Bozell, L. Moens, D. C. Elliott, Y. Wang, G. G. Neuenschwander, S. W. Fitzpatrick, R. J. Bilski and J. L. Jarnefeld, *Resour., Conserv. Recycl.*, 2000, **28**, 227–239; (b) D. W. Rackemann and W. O. S. Doherty, *Biofuels, Bioprod. Biorefin.*, 2011, **5**, 198–214; (c) F. D. Pileidis and M. M. Titirici, *ChemSusChem*, 2016, **9**, 562–582.
- 6 (a) M. Mascal, *ChemSusChem*, 2015, **8**, 3391–3395; (b) M. Mascal and E. B. Nikitin, *Green Chem.*, 2010, **12**, 370–373; (c) M. Mascal and E. B. Nikitin, *Angew. Chem., Int. Ed.*, 2008, **47**, 7924–7926.
- 7 (a) S. Dutta, L. Wu and M. Mascal, *Green Chem.*, 2015, **17**, 3737–3739; (b) C. Laugel, B. Estrine, J. Le Bras, N. Hoffmann, S. Marinkovic and J. Muzart, *ChemCatChem*, 2014, **6**, 1195–1198.
- 8 S. Dutta and M. Mascal, *ChemSusChem*, 2014, **7**, 3028–3030.
- 9 (a) J. C. Hong, L. Ren, V. Vattipalli, Y.-H. Yeh, N. Gould, B. Xu, R. J. Gorte, R. Lobo, P. J. Dauenhauer, M. Tsapatsis and W. Fan, *ChemCatChem*, 2017, **9**, 398–402; (b) C.-C. Chang, H. J. Cho, J. Yu, R. J. Gorte, J. Gulbinski, P. Dauenhauer and W. Fan, *Green Chem.*, 2016, **18**, 1368–1376.
- 10 (a) P. Raghavendrachar and S. Ramachandran, *Ind. Eng. Chem. Res.*, 1992, **31**, 453–462; (b) M. G. Rüther, F. Frehill, J. E. O'Brien, A. I. Minett, W. J. Blau, J. G. Vos and M. Panhuis, *J. Phys. Chem. B*, 2004, **108**, 9665–9668.
- 11 L. Wu, M. Mascal, T. J. Farmer, S. Pérocheau Arnaud and M.-A. Wong Chang, *ChemSusChem*, 2017, **10**, 166–170.
- 12 (a) R. J. Sullivan, E. Latifi, B. K.-M. Chung, D. V. Soldatov and M. Schlaf, *ACS Catal.*, 2014, **4**, 4116–4128; (b) B. Kuhlmann, E. M. Arnett and M. Siskin, *J. Org. Chem.*, 1994, **59**, 3098–3101; (c) H. Zhou, J. Song, Q. Meng, Z. He, Z. Jiang, B. Zhou, H. Liua and B. Han, *Green Chem.*, 2016, **18**, 220–225.
- 13 B. A. C. van As, J. van Buijtenen, T. Mes, A. R. A. Palmans and E. W. Meijer, *Chem.–Eur. J.*, 2007, **13**, 8325–8332.
- 14 (a) J. J. O'Malley and W. J. Stauffer, *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12**, 865–874; (b) P. R. H. Boyd and P. A. Aylwin, *Polymer*, 1984, **25**, 330–339; (c) P. J. M. Serrano, E. Thüsst and R. J. Gaymans, *Polymer*, 1997, **38**, 3893–3902; (d) K. Bouma, M. Regelink and R. J. Gaymans, *J. Appl. Polym. Sci.*, 2001, **80**, 2676–2682.
- 15 (a) E. Gubbels, L. Jasinska-Walc and C. E. Koning, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 890–898; (b) E. Gubbels, J. P. Drijfhout, C. Posthuma-van Tent,



- L. Jasinska-Walc, B. A. J. Noordover and C. E. Koning, *Prog. Org. Coat.*, 2014, **77**, 277–284; (c) X. Hu, X. Shen, M. Huang, C. Liu, Y. Geng, R. Wang, R. Xu, H. Qiao and L. Zhang, *Polymer*, 2016, **84**, 343–354; (d) M. Köpke, C. Mihalcea, F. Liew, J. H. Tizard, M. S. Ali, J. J. Conolly, B. Al-Sinawi and S. D. Simpson, *Appl. Environ. Microbiol.*, 2011, **77**, 5467–5475; (e) X.-X. Wang, H.-Y. Hu, D.-H. Liu and Y.-Q. Song, *New Biotechnol.*, 2016, **33**, 16–22.
- 16 (a) T. Debuissy, E. Pollet and L. Averous, *Polymer*, 2016, **99**, 204–213; (b) F. Fenouillot, A. Rousseau, G. Colomines, R. Saint-Loup and J.-P. Pascault, *Prog. Polym. Sci.*, 2010, **35**, 578–622; (c) B. A. J. Noordover, V. G. van Staalduinen, R. Duchateau, C. E. Koning, R. T. M. van Benthem, M. Mak, A. Heise, A. E. Frissen and J. van Haveren, *Biomacromolecules*, 2006, **7**, 3406–3416; (d) M. Rose and R. Palkovits, *ChemSusChem*, 2012, **5**, 167–176.
- 17 (a) M. Gomes, A. Gandini, A. J. D. Silvestre and B. Reis, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 3759–3768; (b) R. Storbeck and M. Ballauff, *Polymer*, 1993, **34**, 5003–5006.
- 18 J. W. Nicholson, *The Chemistry of Polymers*, The Royal Society of Chemistry, Cambridge, edn 3, 2006.
- 19 (a) M. Pyda, E. Nowak-Pyda, J. Heeg, H. Huth, A. A. Minakov, M. L. Di Lorenzo, C. Schick and B. Wunderlich, *J. Polym. Sci., Part B: Polym. Phys.*, 2006, **44**, 1364–1377; (b) T. H. Ng and H. L. Williams, *Makromol. Chem.*, 1981, **182**, 3323–3330; (c) Y. Jiang, A. J. J. Woortman, G. O. R. Alberda van Ekenstein and K. Loos, *Polym. Chem.*, 2015, **6**, 5198–5211.
- 20 (a) J. Thiem and H. Lueders, *Polym. Bull.*, 1984, **11**, 365–369; (b) R. Storbeck and M. Ballauff, *J. Appl. Polym. Sci.*, 1996, **59**, 1199–1202.
- 21 (a) R. W. Watson, N. H. Grace and J. L. Barnwell, *Can. J. Res.*, 1950, **28b**, 652–659; (b) W. J. Jackson and J. J. Watkins, *US pat.*, 4,600,768, Eastman Kodak Company, 1986.
- 22 S. Thiagarajan, W. Vogelzang, R. J. I. Knoop, A. E. Frissen, J. van Haveren and D. S. van Es, *Green Chem.*, 2014, **16**, 1957–1966.
- 23 M. Mascal, S. Dutta and I. Gandarias, *Angew. Chem., Int. Ed.*, 2014, **53**, 1854–1857.
- 24 P. Duden and R. Freytag, *Ber. Dtsch. Chem. Ges.*, 1903, **36**, 944–952.
- 25 S. Shimizu, *Nippon Nogei Kagaku Kaishi*, 1950, **23**, 288–294.
- 26 (a) S. Alexander, J. Eastoe, A. M. Lord, F. Guittard and A. R. Barron, *ACS Appl. Mater. Interfaces*, 2016, **8**, 660–666; (b) S. Alexander, G. N. Smith, C. James, S. E. Rogers, F. Guittard, M. Sagisaka and J. Eastoe, *Langmuir*, 2014, **30**, 3413–3421.
- 27 *MestReNova (Mnova)*, version 10.0, Mestrelab Research, SL, Santiago de Compostela, Spain.

