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# Renewable Self-Blowing Non-isocyanate Polyurethane Foams from Lysine and Sorbitol

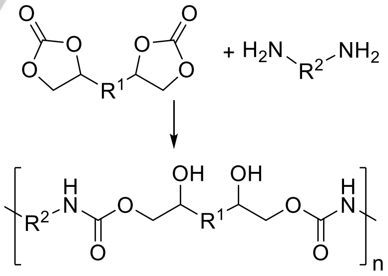
James H. Clark,[a] Thomas J. Farmer,[a] Ian D. V. Ingram,[a] Yann Lie[a] and Michael North*[a]

**Abstract:** Copolymerisation of a sorbitol-derived bis-carbonate with simple diamines, including cadaverine that was sustainably produced from lysine, under solvent free conditions was shown to produce rigid foams. Thermogravimetric analysis carried out in tandem with infrared spectroscopy of the released gases confirmed that the foaming agent was carbon dioxide produced during the polymerisation process itself. Such a bio-based foam, being made under mild conditions from stable, benign precursors, with no toxic isocyanates, has great potential application for both thermal insulation and packaging.

## Introduction

Polyurethanes are widely used polymers, both in coatings and varnishes, and as foams for insulation applications. Most commonly, these materials are made by combining a polyol, often a polyether, with a diisocyanate. Isocyanates are extremely toxic, with the most serious chemical accident in history, the Bhopal disaster, being the result of a release of methyl isocyanate.[1] Although less hazardous than methyl isocyanate due to their lower volatilities, the toluene diisocyanate or methyl diisocyanates used in the polyurethane industries are considered to be a concern, especially for workers at polyurethane plants.[2] Additionally, for foam applications, a gas must be generated in-situ, often by the injection of water which reacts with some of the isocyanate to yield carbon dioxide. Clearly, therefore, a more sustainable and safer route to polyurethanes is very desirable. To date, a significant amount of work has been done to achieve renewable (or partially renewable as they tend to be used in blends) polyol components,[3] and several of these have become commercially successful. Most notably, the Ford motor company have been using soybean oil derived foams in their car upholstery for more than a decade.[4] Researchers also recently evaluated the environmental impact of partially replacing propylene oxide in poly(propylene oxide) polyols with carbon dioxide to form poly(ether carbonate) copolymer polyols, Covestro's pioneering "dream process", concluding that the most significant impact was made by using less propylene oxide, rather than by any carbon dioxide incorporated into the material itself.[5]

Over recent years, as well as addressing polyol sustainability, research has focused on routes to polyurethanes which avoid isocyanates entirely.[6] The most significant chemistry to achieve this has been the copolymerisation of a bis-cyclic carbonate with a diamine to give polyhydroxyurethanes (Scheme 1).[7] Five membered cyclic carbonates are attractive monomers as they are usually non-toxic; indeed, propylene carbonate is considered safe enough to find widespread use in cosmetics.[8] In the most sustainable scenario, cyclic carbonates can be derived from biomass either by epoxidation of olefins and reaction of the resulting epoxide with carbon dioxide in the presence of a suitable catalyst,[9] or by transesterification of a bio-based diol with dimethyl carbonate,[10] which is widely considered to be a "green" reagent.[11] From a sustainability standpoint, the use of phosgene to convert diols to cyclic carbonates, whilst effective, is ruled out by toxicity and atom economy considerations.



**Scheme 1.** Synthesis of polyhydroxyurethanes from cyclic carbonates and diamines.

Sorbitol **1** is an attractive feedstock for sustainable polymers as it is readily available at low cost by reduction of glucose.[12] It is non-toxic, and is commercially produced for use as a sweetener and as a thickening agent in many food and cosmetic formulations. Partial dehydration of sorbitol leads to sorbitan **2**, esters of which are important non-ionic and non-toxic surfactants (known commercially as "Spans") used as emulsifiers in personal care formulations. Sorbitan possesses two diol moieties which suggests the possibility of preparing the corresponding sorbitan bis-carbonate **3** via transesterification with dimethyl carbonate. Indeed, Rokicki's group, reported that bis-carbonate **3** can be prepared directly from sorbitol **1** by reaction with dimethyl carbonate and catalytic base, without the need to first prepare the sorbitan intermediate (Scheme 2).[13] The same group subsequently reported the formation of low molecular weight oligomers by the solution phase polymerisation of bis-carbonate **3** and petrochemically derived diamines. The

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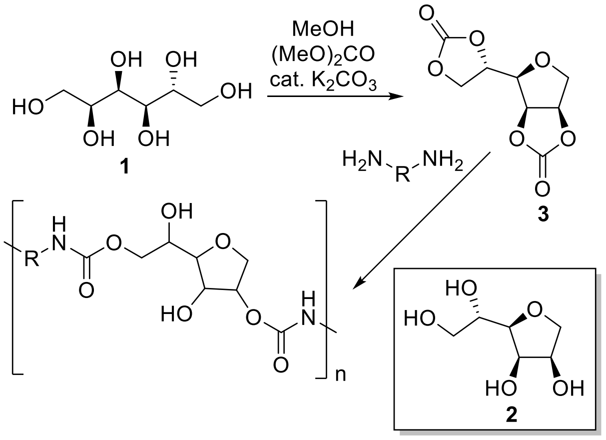
oligomers were then treated with a six-membered ring bis-carbonate to form poly(carbonate-urethanes). These polymerisations were however carried out in DMF, a solvent which is known to be reprotoxic and a substance of high concern under REACh regulations.[15]



**Scheme 2.** Synthesis of polyhydroxyurethanes from sorbitol derived bis-carbonate **3**.

In this paper we show that monomer **3** can also be polymerised under solvent-free melt polymerisation conditions and that this results in the unique formation of rigid foams without the need for any additional blowing agent. This route is complimentary to post-polymerisation foaming methods, such as those using rapid expansion of the polymer with supercritical carbon dioxide.[16] In addition we show that a wholly bio-based polyhydroxyurethane can be prepared by this methodology by utilising pentamethylene diamine (cadaverine) obtained by the decarboxylation of lysine.

## Results and Discussion

Sorbitan bis-carbonate was produced by the method reported by Rokicki[13] using methanol as solvent and was purified by first washing with warm acetone, and then recrystallisation from water to give fine white crystalline needles. When equimolar amounts of bis-carbonate **3** and hexamethylene diamine (HMDA) were ground together and then heated at 100 °C, a rigid foamy material was obtained and gas evolution was observed. The foaming reaction was observed by hot-stage microscopy to occur immediately upon heating the thoroughly mixed monomers (Figure 1). NMR spectroscopy indicated that the monomers had been consumed and that the polymer contained both sorbitan and HMDA derived units (see supporting information). Three urethane NH signals were clearly present at 7.0-7.5 ppm and the hexamethylene units could be identified at 2.9 and 1-1.5 ppm. Unfortunately, all of the sorbitan CHO signals appeared as a single multiplet between 3.4 and 4.1 ppm which prevented a detailed analysis of the stereo- and regiochemistry of the polymerisation. Never the less, the presence of three NH signals is suggestive that the ring-opening of bis-carbonate **3** is not completely regiospecific and the polymer is likely to contain more than one sorbitan derived monomer unit (four different ring-opened repeat units are possible from bis-carbonate **3** as shown in Figure 2). Precipitation of the polymer from DMSO solution into ethyl acetate successfully removed residual monomer, but the complexity of the resulting NMR spectra was still such that end-groups could not be identified, preventing an estimate of molecular weight being made by this method.

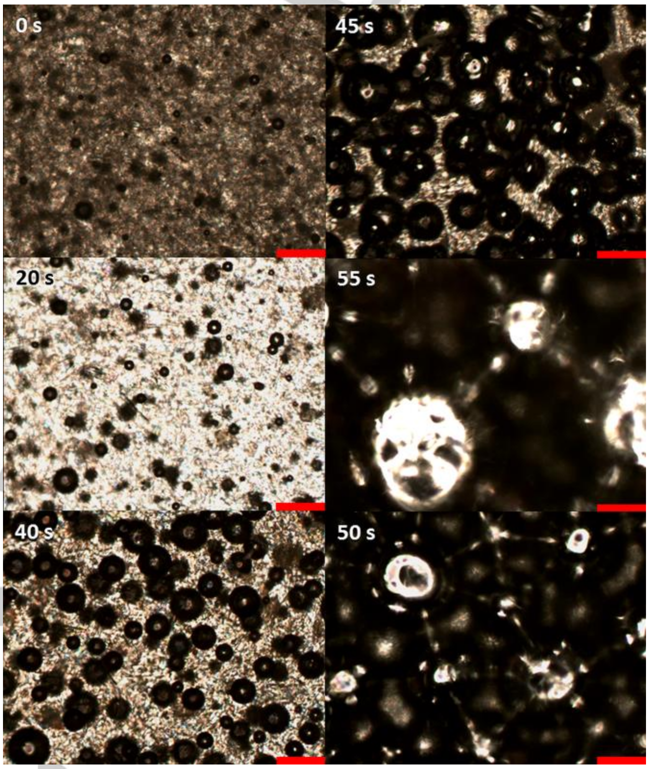


**Figure 1.** Hot stage microscope images showing the evolution of bubbles (black) in the reaction mixture during the first minute of heating. Red scale bars are 100 µm.

Thermal analysis (Figure 3) by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) revealed that the foamed material was relatively thermally stable, having a $T_{10\%}$ (the temperature at which 10% of the initial mass was lost) of 205 °C. The DSC trace showed an exothermic feature at 180 °C, possibly due to a crystallization, and a low-temperature feature at -6 °C similar to a glass transition. This might represent a glass transition in some low molecular weight oligomers within the polymeric material as the bulk polymer is a hard material at room temperature, making a genuine below-room-temperature $T_g$ implausible.

An initial hypothesis was that the foaming was the result of some of the bis-carbonate monomer undergoing decarboxylation under the reaction conditions. However, thermogravimetric analysis of compound **3** revealed it to be stable at 100 °C, and indicated that the foaming must instead be due to a side reaction during the polymerisation. To identify the gas responsible for the foam formation, thermogravimetric analysis of the polymerisation mixture in tandem with infra-red spectroscopy of the gases released was carried out. At temperatures relevant to the polymerisation, carbon dioxide release was observed (Figure 4), along with a small amount of sublimation of HMDA, which could also be seen condensed on the sides of the reaction vessel when the polymerisation was carried out on a preparative scale.

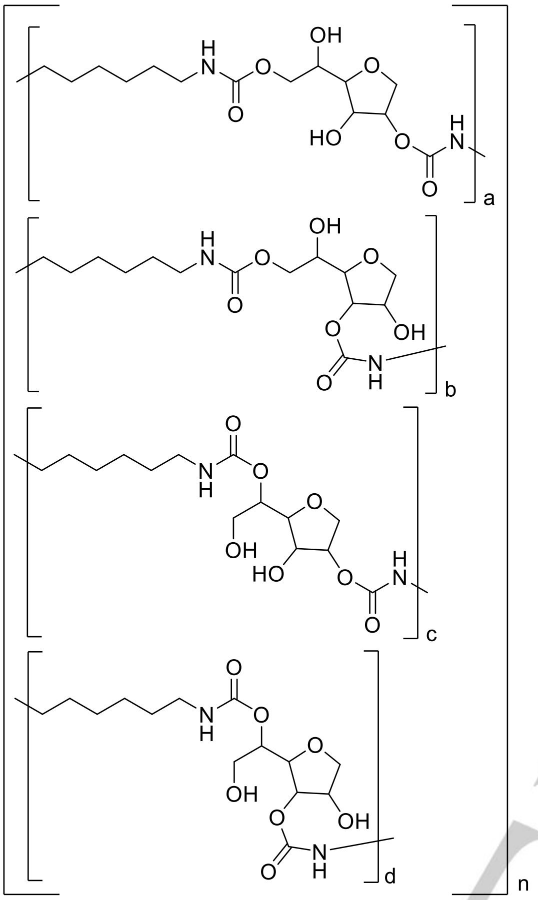


**Figure 2.** Structure of the polymer obtained from monomers **3** and HMDA showing the four possible repeat units obtained by ring-opening of monomer **3**.

Having confirmed that the foaming gas was carbon dioxide, its formation can be explained by a side reaction where the addition-elimination step of the amine reacting with bis-carbonate **3** is followed by cyclisation of the resulting primary hydroxyl group to give an isosorbide type structure with release of carbon dioxide (Scheme 3). Evidence to support this mechanism came from model reactions under the same reaction conditions between bis-carbonate **3** and one or two equivalents of n-dodecylamine, used as an analogue for the amino terminus of a growing polymer chain. Isosorbide derivative **4** was detected by mass spectrometry in these control experiments. In addition, analysis of the HMDA-Sorbitan bis-carbonate polymer by MALDI mass spectrometry showed several series of peaks spaced with the expected repeat unit corresponding to various combinations of end-groups including sorbitan diols, amines and carbonates. It is difficult to determine whether this side-reaction is end-capping or if the resulting alcohol acts as a nucleophile and becomes incorporated into the polymer chain. Infrared spectroscopy on the polymer showed carbonyl signals only for urethanes (1690 cm$^{-1}$) and a small amount of residual starting carbonate (1779 cm$^{-1}$) (Figure 5).

An attempt was made to quantify the amount of carbon dioxide released during polymerisation, and thus the extent of the end-capping side reaction, by thermogravimetric analysis under the reaction conditions. However, when the two monomers were ground together and held at 100 °C in the TGA apparatus under a flow of nitrogen, only a constant and very slight mass loss was observed, which was ongoing for at least 20 hours, making it apparent that the released carbon dioxide was trapped within the foam and was not readily released upon standing. Analysis of foams prepared in preparative reactions, by collapsing the foam structure using methanol to release trapped carbon dioxide and removing solvent thoroughly under vacuum, proved irreproducible. However, polymerisation under

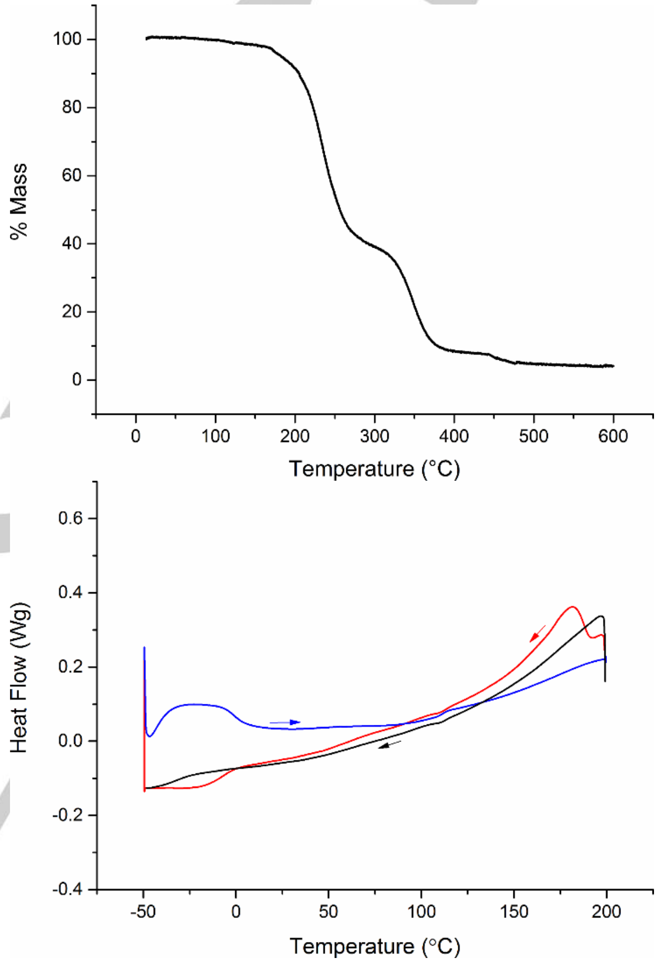
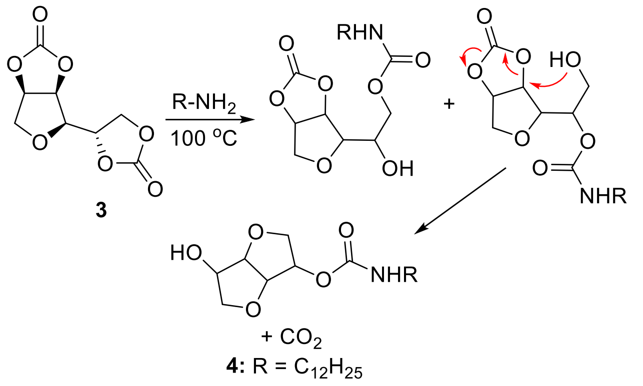


**Figure 3.** Thermogravimetric analysis (top) and differential scanning calorimetry (bottom) of polyhydroxyurethane derived from sorbitol bis-carbonate 3 and hexamethylene diamine.



**Scheme 3.** Generation of carbon dioxide during reaction of bis-carbonate **3** with amines.

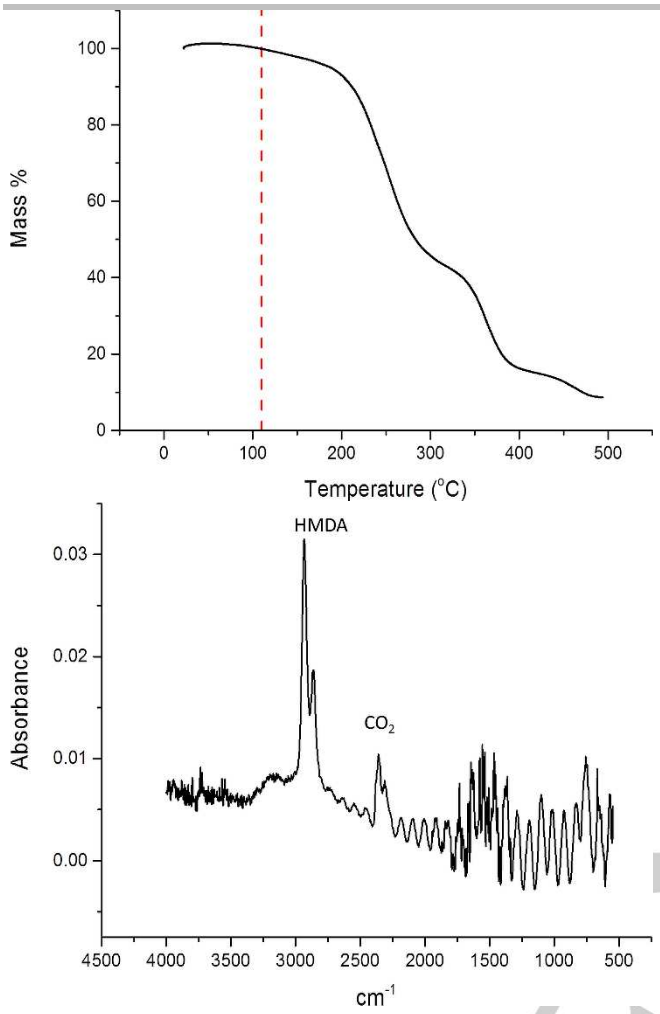


**Figure 4.** Thermogravimetric analysis of a 1:1 mixture of sorbitan bis-carbonate and HMDA (top) with the infra-red spectrum (bottom) corresponding to the spectrum of the gases released at the temperature marked with the dashed red line.

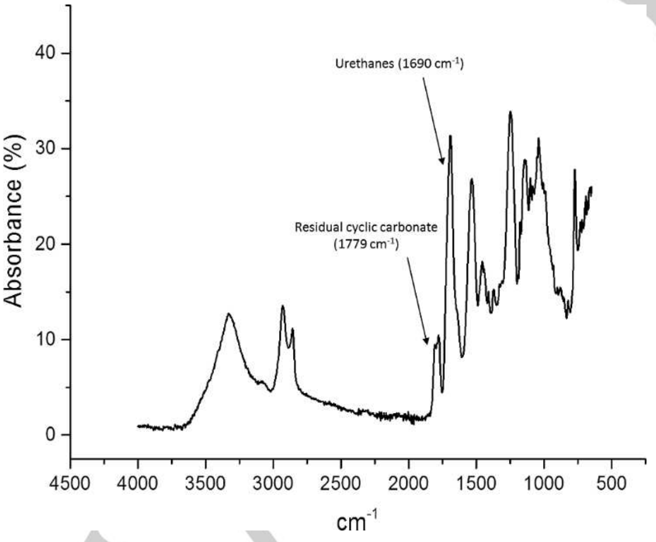


**Figure 5.** Infra-red spectrum (ATR-FTIR) of the polyhydroxyurethane produced from sorbitan bis-carbonate and HMDA indicating the carbonyl signals for both urethane linkages of the polymer backbone, and a small amount of residual cyclic carbonate.

vacuum to remove carbon dioxide as it was formed gave more consistent results, with 6.5-8% of the total mass (relative to the monomers) being lost after heating at 100 °C overnight. Whilst some of this mass can be ascribed to loss of HMDA (see TG-IR in Figure 4), this nevertheless provides an upper limit on the stoichiometry of the foaming reaction of approximately one carbon dioxide released for every two equivalents of bis-carbonate monomer **3** polymerised, under non-stirred conditions, which is consistent with the molecular weights of the oligomers observed in MALDI.

To better understand the polymerisation and to evaluate the influence of monomer mixing, polymerisations were carried out in a Brookfield viscometer and the viscosity of the polymerising mixture was monitored (Figure 6). It is worth noting that Figure 6 shows the apparent viscosity, as the presence of bubbles leads to a lower measured value. As might be expected, viscosity increases over time with increased degree of polymerisation, reaching a peak after roughly two hours. The apparent viscosity then decreased significantly, probably as a result of continued foaming beyond the point at which polymer growth had largely ceased, before stabilising at a value substantially below the maximum in a little under three hours. These samples appeared to contain bubbles which were persistent even under continual shearing.

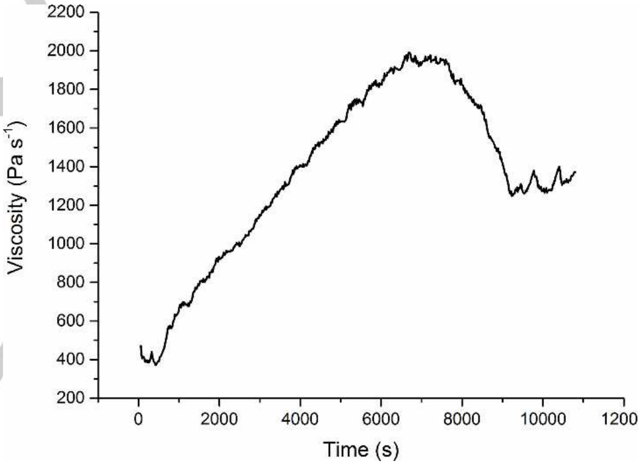


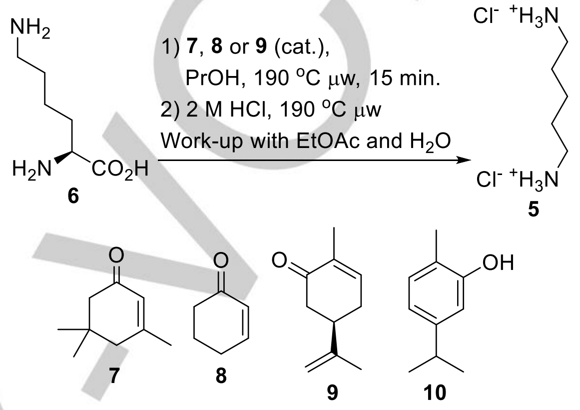
**Figure 6.** Plot of measured viscosity against time for the copolymerisation of sorbitan bis-carbonate **3** with HMDA at 100 °C at a shear rate of 0.8 s$^{-1}$.

Whilst HMDA is derivable from biomass via hydroxymethylfuran, it has been argued that the bio-based routes to it are neither economically nor environmentally superior to the conventional fossil-based route.[17] Therefore it was decided to investigate the use of cadaverine **5** which can be prepared by the decarboxylation of lysine (Scheme 4) in order to demonstrate this polyhydroxyurethane production with fully-biobased monomers. Lysine is already produced on a large scale at low cost by fermentation for use as an animal feed supplement,[18] and as a dietary supplement for humans. It is therefore a promising feedstock for diamines. Amino acids such as lysine can also be sourced from protein hydrolysate and the development of bio-refineries will generate large amounts of protein-rich residues that may not be suitable for use as foodstuffs due to the presence of other species.

The decarboxylation of L-lysine **6** to cadaverine **5** has been previously described by Omeis,[19] Hashimoto[20] and Jackson,[21] although all these methods suffer from limitations that reduce their acceptability as clean production pathways. In the 2009 patent by Omeis, isophorone **7** is utilised as an α,β-unsaturated carbonyl compound to induce the decarboxylation of a range of L-lysine derivatives.[19] Although this protocol has the advantage of being a continuous distillation process, it omits recovery of the isophorone and requires the use of high boiling point solvents such as isononanol and dibenzyltoluene. Additionally, although the patent claims the method is applicable to other amino acids, only the example of L-lysine presented. The method of Hashimoto uses 2-cyclohexen-1-one **8** as the α,β-unsaturated carbonyl compound, and was demonstrated for a range of amino acids, including L-lysine. Again however, there is no evidence of recovery of compound **8**, indeed no work-up is described, and cyclohexanol is used as the solvent over long reaction times (3 hours for L-lysine). A more recent method reported by Jackson *et al.* further developed the Hashimoto method by using microwave irradiation at 190 °C to reduce reaction times, whilst also finding that bio-derived (*R*)-carvone **9** was an effective decarboxylation inducer, having a similar reactivity to **8**.[21] Again, no recovery and reuse of the carvone was attempted, with the authors describing how the (*R*)-carvone was found to convert to inactive carvacrol **10** during the process.

Initially, the three previously described cyclic enones **7-9** were compared following a modified version of Jackson's microwave procedure for the production of cadaverine dihydrochloride **5** (Scheme 4 and Table 1). For the washing of the aqueous phase during the work-up, diethyl ether was substituted with safer ethyl acetate and a trituration with n-propanol was added to improve the purity of the isolated product **5**. Under these conditions, yields of compound **5** were similar with all three catalysts (31-37%, Table 1). However, both compounds **8** and **9** proved impossible to reuse for subsequent reactions. In the case of compound **9**, whilst some excess catalyst could be recovered, the material that had actually participated in the reaction was converted to carvacrol **10**. An 89% conversion of **9** into **10** under these conditions was observed by gas chromatrography (see supporting information). Compound **8** was also unrecoverable from the reaction mixture, forming an insoluble, waxy, byproduct which is believed to be the result of either an aza-Michael addition reaction with lysine or cadavarine, or polymerisation of the α,β-unsaturated carbonyl compound. These issues with the recovery of enones were also reported by Jackson.[21] By contrast, isophorone **7** is not susceptible to aromatization, due to the dimethyl substituents at the 5-position, and has reduced susceptibility to aza-Michael addition due to the methyl substituent at the 3-position. Isophorone **7** was found to be both recoverable, and reusable in this reaction, with the organic phase isolated during the work-up, when dried and concentrated, being able to induce a second reaction directly with only slightly reduced yield (27%). Therefore, of the enone systems tested, isophorone **7** is clearly the more sustainable choice in this case.

Initially, the preparation of a poly-hydroxyurethane from commercial cadaverine free base was investigated. Sorbitan bis-carbonate **3** was found to react with this cadaverine to give a rigid foam very similar to that obtained with HMDA. This foam showed the expected repeat unit by MALDI-MS with end groups similar to those observed for the HMDA variant. Thermal analysis (Figure 7) showed that the polymer also had similar stability to that prepared from HMDA, with a $T_{10\%}$ of 193 °C. Differential scanning calorimetry was also similar to the HMDA polymer, with a high temperature crystallisation event at 190 °C, and a small, low temperature $T_g$-like feature at -31 °C. As for the HMDA derived polymer, this foam was rigid at room temperature, making a true $T_g$ below room temperature unlikely. Also similarly to the HMDA polymer, infra-red spectroscopy showed carbonyl signals consistent with urethanes (1688 $cm^{-1}$) and a small amount of residual carbonate (1779 $cm^{-1}$) (Figure 8).



**Scheme 4.** Decarboxylation of L-lysine **6** to cadaverine dihydrochloride **5** using organocatalysts **7-9**.

**Table 1.** Isolated yields and description of organocatalyst recovery for the decarboxylation of of L-lysine **6** to cadaverine dichloride salt **5**.[a]

| | Isophorone<br>**7** | 2-Cyclohexene-1-one<br>**8** | (*R*)-Carvone<br>**9** |
|---|---|---|---|
| **Yield (%)** | 31 % | 32 % | 37 % |
| **Catalyst recovery** | Easy and straight-forward | Not possible – insoluble material formed | Possible to recover excess prior to imine-hydrolysis step, but any formed from the imine converts to carvacrol **10** |

[a] Reaction conditions: 5 mmol L-lysine, 3 mL n-propanol, 10 mmol carbonyl catalyst, 190 °C, 3 min ramp followed by 15 min hold time followed by addition of 10 mL 2 M HCl and heated until 190 °C reached (no hold time).

Cadaverine obtained by desalting cadaverine hydrochloride prepared from L-lysine, by reaction with excess sodium hydroxide and extraction with ethyl acetate gave a similar result to that obtained using commercial cadaverine free base. Encouraged by this, we also attempted to prepare a foam by directly reacting the cadaverine hydrochloride with sorbitan bis-carbonate **3** in the presence of stoichiometric base. This also produced a rigid foam of similar appearance; however, the salt content of this material made it very hygroscopic, resulting in formation of a deliquescent foam that collapsed upon standing in moist air over the course of a day.

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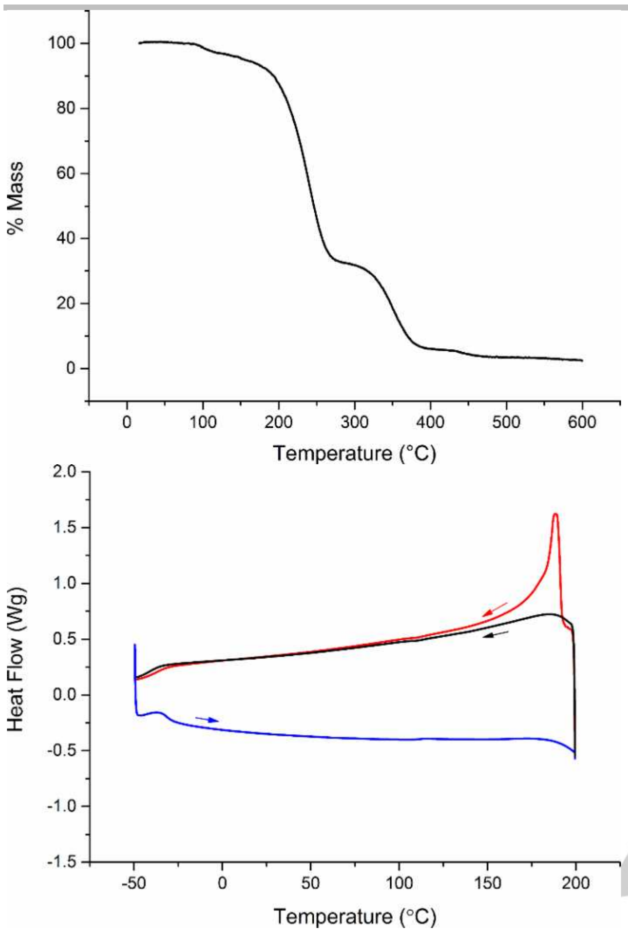

**Figure 7.** Thermogravimetric analysis (top) and differential scanning calorimetry (bottom) of PHU derived from cadaverine **5** and carbonate **3**.

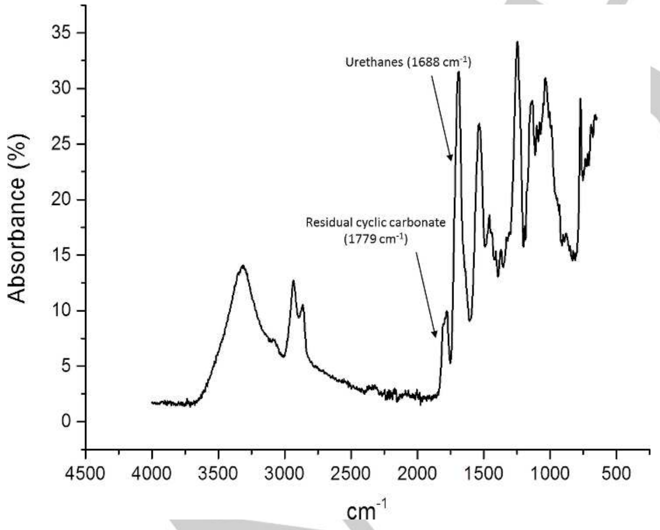

**Figure 8.** Infra-red spectrum (ATR-FTIR) of the polyhydroxyurethane produced from sorbitan bis-carbonate and cadaverine indicating the carbonyl signals for both urethane linkages of the polymer backbone, and a small amount of residual cyclic carbonate.

## Conclusions

We have shown that, when prepared under solvent-free conditions, isocyanate free polyhydroxyurethanes prepared from a diamine and sorbitan bis-carbonate spontaneously liberate carbon dioxide, forming a rigid foam. This self-foaming behaviour is not only a significant improvement in sustainability over preparation of foams by addition of a foaming agent, and especially over the hydrolysis of excess isocyanate as is used commercially to foam conventional polyurethanes, but is also very efficient, with the carbon dioxide produced largely remaining trapped within the bubbles rather than being released into the atmosphere. Both monomers required for the synthesis of these polyhydroxyurethane foams were prepared from bio-based starting materials. As the monomers used to prepare these materials are bio-based, inexpensive, and of low-toxicity, this type of material shows promise for insulation and packaging applications.

## Experimental Section

### Materials

D-sorbitol, dimethyl carbonate, hexamethylenediamine, lysine (>98%) and cadaverine were purchased from Sigma Aldrich and used as supplied. Sorbitan bis-carbonate was prepared according to the literature procedure,[14] recrystallised from water to give white needle crystals, and dried thoroughly under vacuum before use. Isophorone was vacuum distilled using a Kugelrohr short-path distillation apparatus and stored in a sealed vial at 4 °C prior to use.

### Instrumentation

Nuclear magnetic resonance spectroscopy was carried out using a JEOL 400 MHz instrument in deuterated dimethyl sulfoxide. MALDI mass spectrometry was performed on a Bruker solariX XR FTMS 9.4T instrument, with the plates loaded in methanol using dihydroxybenzoic acid (DHB) as the matrix. Viscometry was carried out using a Brookfield R/S plus rheometer fitted with a C50-1/3 cone. Thermogravimetric analysis (TGA) was carried out using a PL Thermal Sciences STA 625 instrument from ambient (22 °C) to 600 °C at a ramp rate of 10 degrees per minute in an open aluminium sample pan under $N_2$. TG-IR was carried out using a Netsch STA409 linked to a gas cell in a Bruker Equinox 55 Infra-red spectrometer by a heated gas line. Differential scanning calorimetry (DSC) was carried out using a TA Instruments MDSC Q2000 instrument in a closed aluminium sample pan under $N_2$.

### Typical polymerisation procedure

Hexamethylene diamine (0.102 g, 1.0 mmol) and sorbitan bis-carbonate **3** (0.216 g, 1.0 mmol) were placed into a small agate mortar and ground together thoroughly for several minutes until a completely homogeneous gummy mixture was formed. This mixture was transferred to a glass vial and heated for 20 hours at 100 °C, giving a rigid, colourless, foamy material.

### Preparation of cadaverine by decarboxylation of L-lysine

L-Lysine (0.73 g, 5.0 mmol) was mixed with of 1-propanol (3 mL) and of vacuum-distilled isophorone (1.5 mL, 10 mmol). A magnetic stirrer was then added and the vial was placed in a CEM discover microwave chamber. The temperature was set at 190 ºC and was reached within 3 min. The temperature was held for 15 minutes. After this first heating, HCl was added (10 mL of a 2 M solution, 4 eq.). The vial was returned to the microwave chamber and subjected to a second heating step until 190 ºC was reached, then immediately allowed to cool to room temperature. The reaction was then washed with EtOAc (1x25 mL), the water phase was then collected and the organic phase was washed with 2 M HCl (10 mL) and water (10 mL). The collected aqueous phases were washed with EtOAc (2x25 mL) and the solvent removed *in vacuo*. The resulting light brown oil was triturated with 1-propanol to give a solid which was isolated by filtration and dried under vacuum (72 mbar) at 80 ºC for 2 hours to afford the desired cadaverine dihydrochloride salt as white needle-like crystals (0.287g, 32%). $^1$H-NMR (400 MHz, [$D_2O$]): δ 3.01 (t, *J* = 7.6 Hz, 4H), 1.71 (quintet, *J* = 7.7 Hz, 4H), 1.46 (quintet, *J* = 7.9 Hz, 2H). $^{13}$C NMR (101 MHz; [$D_2O$]): δ 39.2, 26.3, 22.7. FT-IR ṽ (cm$^{-1}$): 2928, 2521, 1568, 1521, 1484, 1400, 1321, 1295, 1175, 1125, 1018, 999, 929, 825, 738. ESI-MS: $C_5H_{15}N_2$ 103.1230 found 103.1229

**Recycling of isophorone for the preparation of cadaverine by decarboxylation of L-lysine**

The isophorone recycling experiment was conducted at a 2 mmol scale using 600 uL of collected organic phases from a first reaction, dried over $MgSO_4$ and evaporated under reduced pressure. 40% of the isophorone was recovered and used in a second reaction without further purification under the same reaction conditions and work-up as described above (0.095g, 27%).

## Acknowledgements

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**Keywords:** Polyurethanes, foams, renewable materials, sorbitol, cyclic carbonates

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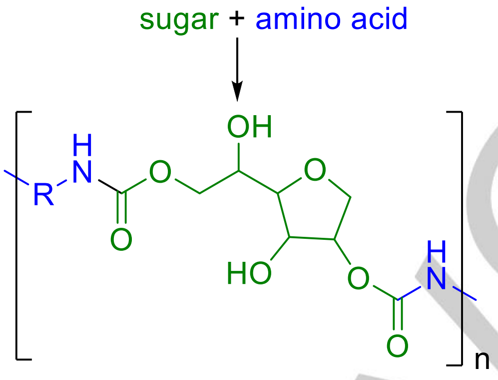
## Entry for the Table of Contents

## FULL PAPER

**Nothing artificial about this sweet foam.** A bis-carbonate derived from sorbitol, which is both non-toxic and bio-derived, and pentamethylene diamine produced by the decarboxylation of lysine, are polymerised to form a polyhydroxyurethane. The polymerisation releases carbon dioxide, resulting in a sustainable self-foaming material made entirely without the use of isocyanates or blowing agents.



*James H. Clark, Thomas J. Farmer, Ian D. V. Ingram, Yann Lie and Michael North**

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**Renewable Self-Blowing Non-isocyanate Polyurethane Foams from Lysine and Sorbitol**

**Key Topic:** Sustainable polyurethane foams