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Properties of Novel Polyesters Made from Renewable 1,4-Pentanediol

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Novel polyester polyols were prepared in high yields from bio-based 1,4-pentanediol catalyzed by non-toxic phosphoric acid without using a solvent. These oligomers are terminated with hydroxyl groups and have low residual acid content, making them suitable for use in adhesives by polyurethane formation. The thermal behavior of the polyols was studied by differential scanning calorimetry, and tensile testing was performed on the derived polyurethanes. The results were compared with those of polyurethanes obtained with fossil-based 1,4-butanediol polyester polyols. Surprisingly, it was found that a crystalline polyester was obtained when aliphatic long-chain diacids ($>C_{12}$) were used as the diacid building block. The low melting point of the C_{12} diacid-based material allows the development of biobased shape-memory polymers with very low switching temperatures ($< 0\,°C$), an effect that has not yet been reported for a material based on a simple binary polyester. This might find application as thermosensitive adhesives in the packaging of temperature-sensitive goods such as pharmaceuticals. Furthermore, these results indicate that, although 1,4-pentanediol cannot be regarded as a direct substitute for 1,4-butanediol, its novel structure expands the toolbox of the adhesives, coatings, or sealants formulators.

Introduction

Petrochemicals are still the main raw material for plastics. However, oil reserves are limited, and their continued use leads to increased CO_2 emissions, resulting in climate change. Thus, it is clear that we need to switch to the use of biobased building blocks for the production of polymers. It is predicted that the global market for bioplastics will grow by approximately 20 % until 2022.[1] Polyesters are an attractive target market for this switch because they are industrially produced by well-established polycondensation reactions, which allow the use of the existing reactor infrastructure when renewable diols and diacids are used. This has resulted in the development of numerous (partially) biobased polyesters, which in addition show novel promising properties for several applications,[2] in particular for adhesives.[3]

Polyesters are materials that are produced on an overall scale of over one million tons per annum because they are used in everyday consumer goods (e.g., clothes, bottles), as soft segment in thermoplastic polyurethanes (TPUs) (e.g., medical devices), and in industrially used coatings and adhesives (mostly in the automotive industry). Whereas polyesters used in spinning and molding processes have molecular weights (M_n) of several 10 kg mol^{-1}, the materials used in TPUs and adhesives have a M_n that is typically substantially lower than 10 kg mol^{-1} to ensure processability, which requires lower viscosity and reasonable reaction times with crosslinking- and chain-extension agents.[4]

These oligo esters are basically building blocks the structural variation of which allows finetuning of the properties of the final products. The oligomer chains are usually OH-terminated and hence referred to as polyester polyols. In addition, the preparation of monomers, necessary for the production of polyester polyols, can be performed more atom-efficiently from biobased platform chemicals because they already contain oxygen atoms.[5] For instance, succinic acid obtained by fermentation can be selectively hydrogenated to 1,4-butanediol (1,4-BDO), a common building block in polyester polyols for polyurethanes. One common application of 1,4-BDO is as monomer in the synthesis of polyester polyols, which are then further utilized in polyurethanes or adhesives. The isocyanate component that is needed can also be obtained from renewables, for instance from renewable fatty acids as recently demonstrated by Mecking and co-workers.[6]

Furthermore, isocyanate-free crosslinking- and chain-extension protocols have been developed by using either the combination of cyclic carbonates with diamines[7] or a thiol–ene re-

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action between mercaptans and alkene containing oligomers, for example, based on limonene.[8] Other important platform chemicals for biobased polymers are levulinic acid (LA)[9] and its esters, which are accessible by treatment of lignocellulose with dilute acid at approximately 200 °C.[10] As shown in Scheme 1, hydrogenation of LA can either yield γ-valerolactone
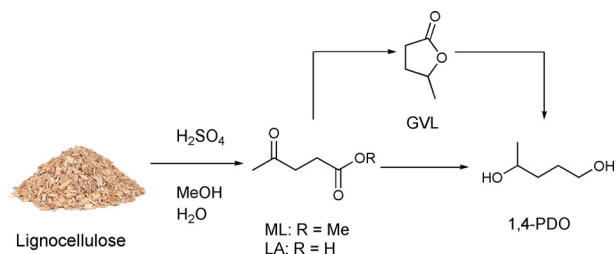
Scheme 1. Route from lignocellulose to 1,4-PDO.

(GVL) or 1,4-pentanediol (1,4-PDO) depending on the conditions.[11] Although GVL cannot be polymerized—with the exception of its copolymerization with very reactive lactones[12]—it is commonly used as a green solvent[13] because of its low reactivity and relatively high polarity compared with other esters. The diol 1,4-PDO, in contrast, can be regarded as a useful building block for polyester synthesis.[14] Consequently, various heterogeneous[11,15] and homogeneous[16] catalysts have been used for the hydrogenation of levulinates or GVL to 1,4-PDO.

However, to the best of our knowledge, there is no literature concerning the properties and applicability of 1,4-PDO polyesters apart from a study of the thermal behavior of 2,5-furan-dicarboxylic acid, succinic acid, and adipic acid polyesters.[17] However, this work does not provide insights into the mechanical performance of these compounds. This is rather surprising in view of the relevance of 1,4-PDO as biobased building block. In addition, the extra methyl group in 1,4-PDO is expected to impart unusual properties that cannot be found in conventional polyesters based on 1,4-BDO, such as lower viscosity and lower crystallinity. This effect has to some extent been observed in polyesters derived from the biobased diol 2,5-hexanediol.[17,18] Unfortunately, the two secondary alcohol groups makes this diol less reactive than 1,4-PDO in standard polycondensation procedures. This led us to develop a scalable protocol for the synthesis of biobased 1,4-PDO polyester polyols terminated with hydroxyl groups. For economic and ecological reasons, the oligomerizations were performed without the use of solvent. In addition, we decided against the usage of the traditional metal catalysts (e.g., alkoxides/carboxylates of Ti, Sb, or Sn) because in a viable technological process the catalyst is usually not removed from the oligomer, which could lead to unwanted side effects in products derived from the oligomer. Examples for disadvantageous side effects are toxicity of leaching metal residues (Sb/Sn)[19] and formation of yellow impurities (Sn).[20] In the synthesis of polyester polyols the molecular weight is usually controlled through the stoichiometry of the reactants. Because transesterification reactions are also promoted by metal catalysts, it makes them more suitable to

synthesize high-molecular-weight polyesters, whereas control of the molecular weight in the synthesis of lower-molecular-weight oligomers is more challenging.

In this paper we describe the preparation of polyester polyols from 1,4-PDO catalyzed by acid and compare their properties with the traditional 1,4-BDO-based analogues in films obtained by chain extension with 4,4′methylenediphenylisocyanate.

Results and Discussion

For mechanical characterization of polymers by tensile testing, amounts in the order of 100 g of polyesters and therefore of 1,4-PDO are necessary. However, 1,4-PDO is not commercially available in large quantities, so we decided to prepare the diol by hydrogenation of GVL.

Although there are existing heterogeneous catalysts that give good selectivities in this transformation, they often require high loadings and are not commercially available. Although this is of course no limitation when setting up a continuous process on reasonable scale, it is inconvenient for producing quantities for polymer development in batch mode. Thus, we decided to use a homogeneous ruthenium catalyst developed earlier in our group, which can be synthesized by a straightforward two-step protocol in high yield.[16c] The complex is air-stable and has already achieved one of the highest turnover numbers (TONs) reported so far in the solvent-free hydrogenation of GVL to 1,4-PDO (see Scheme 2). Fortunately,
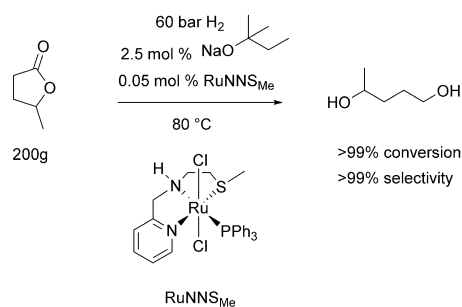
Scheme 2. Hydrogenation of GVL to 1,4-PDO.

we were able to scale this procedure up to a 200 g scale. Using only 0.05 mol % of catalyst, GVL was fully converted after 16 h at 80 °C and 60 bar H_2 with >99% selectivity to 1,4-PDO. With sufficient quantities of 1,4-PDO in hand we embarked on the solvent-free synthesis on an average scale of 100 g of different polyester polyol oligomers with a target hydroxyl number (OH-N) of 30 $mg_{KOH}g^{-1}$, corresponding to an average molecular weight of $M_n = 3450$ g mol^{-1}. This molecular weight is in the right range for application in adhesives.[4] In general, the molecular weight represents a compromise between viscosity, mechanical properties, reaction time (production cost of the polyester), and other performance parameters. The diacids used were succinic acid (C_4), sebacic acid (C_{10}), and azelaic acid (C_9), which are currently produced from renewable raw materi-

als,[21] as well as adipic acid (C_6) and dodecanedioic acid (C_{12}), for which processes from renewable feedstocks have been developed,[22] and tetradecanedioic acid (C_{14}), which is available from fermentation of glucose.[23] The polycondensation was conducted in a sequential approach consisting of a precondensation step at ambient pressure, followed by further condensation in vacuum in the presence of phosphoric acid as catalyst (Figure 1). Initially, 220 °C was used as reaction temperature, which is commonly used for polyester synthesis. However, at this temperature and under the acidic conditions most of the 1,4-PDO was converted to 2-methyl-teytrahydrofuran (2-MeTHF). Secondary reactions occurring during polyester synthesis are well documented.[24]
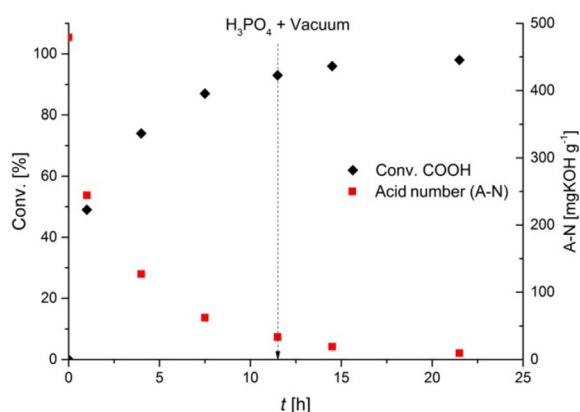

Figure 1. Acid number and derived conversion in the polycondensation reaction of succinic acid and 1,4-PDO; the dashed arrow marks the time and conversion of addition of 0.3 mol% H_3PO_4 and switching from ambient pressure to vacuum (0.1–0.8 mbar).

Typically, they occur at elevated temperatures and can change the stoichiometry of the reaction and cause a limitation of the molecular mass. Common side reactions are ether formation, ring-closure of the diol (e.g., 1,4-PDO to 2-MeTHF),

alkene formation, and formation of cyclic structures. These side reactions are an important issue that needs to be addressed when scaling up these polycondensations. At a reaction temperature of 180 °C, using only 0.3 mol% of H_3PO_4 as catalyst, the polyester polyols were obtained in 98–99.5% isolated yields; only trace amount of the side products 2-MeTHF, 5-hydroxypentan-2-one, GVL, and 1,4-PDO were found in the aqueous distillate, and small amounts of cyclic oligomers in the low-molecular-weight fraction could be observed (see S5, S6 in the Supporting Information). However, molecular weights close to the target could be reached. ^{1}H NMR spectra of these products verified the absence of impairing alkene groups, which could be formed from the dehydration of the secondary alcohol chain ends. As expected, the majority of chain ends consisted of secondary alcohols (secondary/primary: 67:33). Figure 1 shows the conversion of carboxylic acid groups versus time for the exemplary case of succinic acid. For comparative reasons polyesters with 1,4-BDO were prepared in a similar way. Table 1 gives an overview of the prepared polyesters and their molecular weight as well as the residual acid content expressed as acid number (A-N) [$mg_{KOH} g^{-1}$]. The thermal properties of the polyesters were thoroughly investigated by differential scanning calorimetry (DSC, see Figure 2). This showed that the polyesters obtained from 1,4-PDO and one of the C_4–C_{10} diacids were amorphous as expected, in contrast to their 1,4-BDO analogues.

Amorphous chain segments and side groups are usually important in polyurethane formulations to increase flexibility and strain recovery as well as viscosity. Furthermore, it was recently shown by Hillmyer and co-workers that amorphous chain segments in polyester-based elastomers can increase the hydrolyzability and thus the enzymatic degradability, which may reduce bioaccumulation.[25] We assume the amorphous character is caused by the random orientation of the extra methyl groups in the atactic polymer, which prevents crystallization (see the Supporting Information for the individual DSC traces). This may be further increased by the high degree of regio-ir-

Table 1. Poperties of the polyesters prepared with 1,4-BDO and 1,4-PDO.[a]
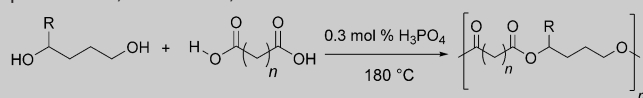
Entry	n	R	OH-N[b] [$mg\,g^{-1}$]	A-N[b] [$mg\,g^{-1}$]	M_n(calcd)[c] [$kg\,mol^{-1}$]	M_n(OH)[b] [$kg\,mol^{-1}$]	M_n(GPC)[d] [$kg\,mol^{-1}$]	$Đ$[d]	X(COOH)[b] [%]	T_g[e] [°C]	T_m[e] [°C]
1	2	Me	30	10	3.7	3.7	3.6	2.4	98	−32	n.d.
2	2	H	30	2	3.7	3.7	1.7	2.4	99.5	n.d.	113
3	4	Me	30	3	3.7	3.7	4.2	2.4	99.0	−52	n.d.
4	4	H	42	1	3.7	2.7	3.8	2.2	99.2	n.d.	53
5	7	Me	39	4	3.7	2.9	3.8	2.5	99.0	−63	n.d.
6	7	H	46	4	3.7	2.4	4.0	2.2	99.0	n.d.	44
7	8	Me	26	4	3.7	4.3	4.8	3.0	99.5	−63	n.d.
8	8	H	33	1	3.7	3.4	5.5	2.4	99.8	n.d.	61
9	10	Me	29	2	3.7	3.9	4.6	2.8	99.7	n.d.	−15/9
10	10	H	33	2	3.7	3.4	5.0	2.7	99.7	n.d.	70
11	12	Me	12	3	–	9.4	5.3	4.4	99.7	n.d.	9

[a] Polycondensation procedure: 480 mmol 1,4-PDO, diacid (0.85–0.89 equiv.), H_3PO_4 (0.3 mol%, 0.85 w/w in H_2O). [b] Determined by titration with KOH_{aq} (0.5 mol L^{-1}); OH-N analogous to DIN 53240-1. [c] Targeted molecular weight. [d] Measured by GPC. [e] Measured by DSC; n.d. = not possible to determine.
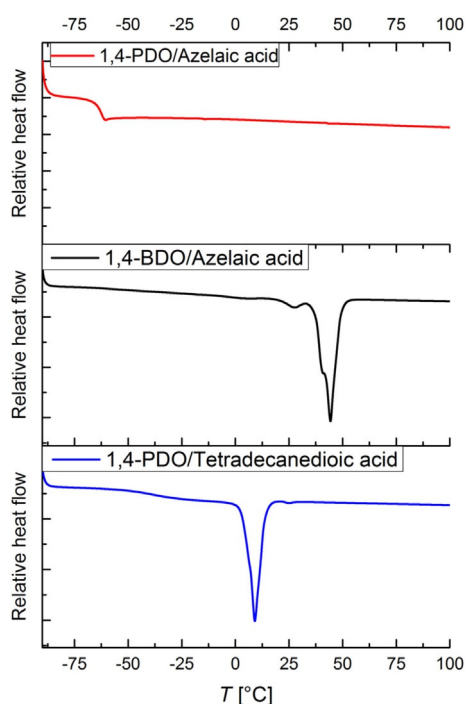
Figure 2. Influence of the diacid building block on the thermal behavior: comparison of the heating curves of 1,4-PDO/azelaic acid, 1,4-BDO/azelaic acid, and 1,4-PDO/tetradecanoic acid polyester polyols. Exothermic heat flow increases along the y axis.

regularity caused by the possible head–head, tail–tail, and tail–head orientation of the diol with respect to the dicarboxylic acid. This is generally observed in polyesters obtained from a racemic monomer mixture. Examples of this are the polycondensation product of racemic lactic acid,[26] polymers obtained from substituted lactones,[25] and the combination of methyl succinate with branched diols.[27]

Furthermore, it was observed that the glass transition temperature T_g ranged from -32 to $-64\,°C$ and decreased with the increasing number of carbons in the dicarboxylic acid block. An analogous trend was observed with the melting points of the crystalline 1,4-BDO polyester polyols (Table 1), which were solid below -15 and $8\,°C$ respectively. The reason for this behavior might be that the crystallization tendency of long aliphatic chains ($> C_{10}$) with an even carbon number now dominates over the disorder caused by the methyl groups. In addition, a higher degree of flexibility of the longer chains prompts crystallization. A similar effect has been observed for the polyesters of isosorbide with aliphatic diacids.[28]

Interestingly, the polyester polyol derived from 1,4-PDO and dodecanedioic acid showed a second melting point at $8\,°C$, which might indicate that it consists of two different crystal phases. All polyesters were prepared in the same molecular-weight range with low acid numbers that are suitable for curing experiments with diisocyanates (Table 1). In these chain-extension experiments, the polyesters were end-capped with 4,4'diphenylmethane diisocyanate (4,4'-MDI) at $80\,°C$ and casted in polytetrafluoroethylene (PTFE) molds, after which they were transferred to climate chambers with controlled temperature and air humidity ($23\,°C$, $50\,\%$ relative humidity).

The isocyanate-terminated polymers react with moisture, forming urea linkages resulting in the typical polyurethane networks (PUR).[29] Next, samples were punched out and subjected to tensile testing. The films obtained from the linear 1,4-BDO polyesters were brittle and fibrous materials as demonstrated by their stress–strain curves, which is attributed to their high degree of crystallinity. However, the films obtained from the branched 1,4-PDO behaved more like elastomers with tensile strengths and elongations increasing with the length of the carbon chain in the diacid.

Table 2 and Figure 3 summarize these results. The thermal transitions observed by DSC analysis of the PUR changed only very slightly (max. 8–9 °C) compared with the polyesters, and in PURs based on the amorphous polyols no crystallization phenomena were observed. The exception to this is the film

Table 2. Thermal properties and tensile testing of the corresponding 4,4'-MDI films.

Entry	n	R	Film	ε_{break} [%][a]	F_{break} [N mm^{-2}][a]	T_g[b] [°C]	T_m[b] [°C]
1	2	Me	A	55	0.2	–	–
2	2	H	B	n.d.[c]	25.1	n.d.	105
3	4	Me	C	136	1.1	−52	n.d.
4	4	H	D	681	31.5	n.d.	53
5	7	Me	E	892	4	−63	n.d.
6	7	H	F	720	30.1	n.d.	40
7	8	Me	G	936	3.1	−53	n.d.
8	8	H	H	33	1	n.d.	70
9	10	Me	I	1010	7.8	n.d.	−22
10	10	H	J	33	2	n.d.	72

[a] DIN 53504-SF3A-bones from 4,4'-MDI chain extended films; ε_{break}: elongation at break; F_{break}: stress at break; [b] measured by DSC of the films; [c] could not be determined owing to the brittleness of the film.

obtained from the 1,4-PDO/C$_{12}$ diacid-derived polyol (Table 2, entry 9). Instead of two peaks, a single peak was observed at $-22\,°C$ that could be attributed to the melting of the crystalline chain segments. This observation suggests the possibility to switch the shape of the PUR by changing the temperature. This shape-memory effect is usually observed in polymers that are crosslinked but still contain chains or domains that can undergo either phase transitions (melting or crystallization)[30] or reversible photochemical dimerization reactions between chains.[31]

Here we have the unusual situation that the phase transition would be feasible at low temperatures. Consequently, this material would be of use as a low-temperature shape-memory polymer. This prediction was borne out in praxis when film I (Table 2, entry 9) was fixated in a spiral shape, cooled to $-30\,°C$, and subsequently allowed to warm to room temperature. It was indeed observed that the morphology of the film changed over time and temperature. The timeline of this change is shown in Figure 4, and a full video can be found in the Supporting Information. Because the currently known low-temperature shape-memory polymers have switching points between 30 and 75 °C and are tailored for the use in medical
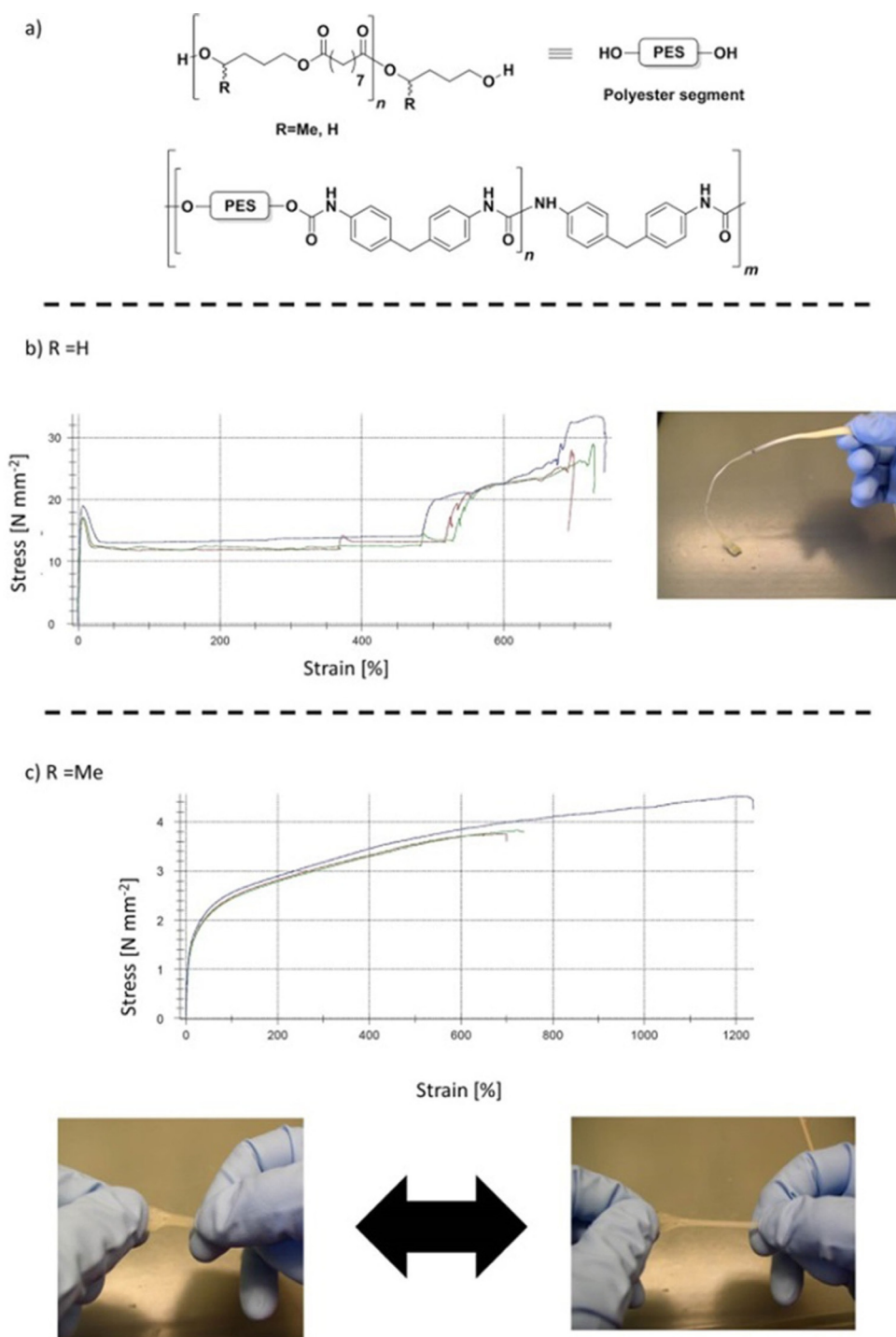
Figure 3. Differences between films obtained from the polyester polyols consisting of the C₉ diacid and 1,4-BDO respective 1,4-PDO. a) General structure of the polyurethanes; b) stress–strain curve of film E (Table 2, entry 5) and visual representation of the ductile behavior; c) stress–strain curve of film F (Table 2, entry 6) and visual demonstration of the elastic behavior of the specimen.

applications,[32] this finding opens the way to novel smart materials that may be used in low-temperature applications. One possibility would be its application as adhesive for smart labels for packaging of temperature-sensitive drugs. Exposure to undesired high temperatures would induce the loss or an irreversible change of the label or a QR-Code.

Conclusions

We have shown that we can prepare fully renewable polyesters based on 1,4-pentanediol (1,4-PDO), obtained from bio-based γ-valerolactone in excellent yields by homogeneous hydrogenation, and a series of diacids that can already be obtained from renewable resources or for which renewable
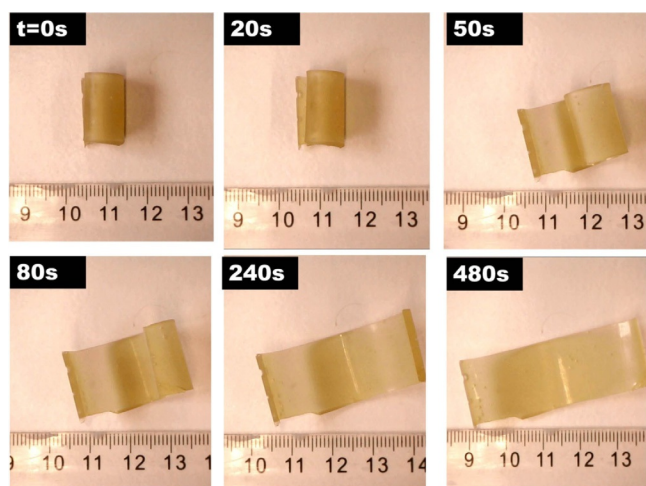
Figure 4. Deconvolution of a sample (film I) to its original form at room temperature. Prior, the specimen was formed to a coil and cooled in a freezer to $-30\,°C$ before transfer to ambient conditions.

routes have been developed. Yields are very high, and only traces of side products are formed. For the application in adhesives, diisocyanates need to be used, which are currently not made from renewable resources, although credible routes from renewables have been developed.[33]

Differential scanning calorimetry (DSC) experiments as well as the tensile testing of polyurethane films of the 1,4-PDO polyester polyols made with 4,4-MDI clearly demonstrate that 1,4-PDO cannot be regarded as a substitute for 1,4-butanediol (1,4-BDO). Instead, it can be used to obtain elastomeric/rubbery materials in contrast to the crystalline polyesters obtained with BDO.

The interesting feature of the polyester polyols based on 1,4-PDO and long-chain diacids is the combination of their crystallinity and melting point below room temperature. This phenomenon can be used to design shape-memory polymers with switching points far below and near room temperature. Beyond this aspect, these polyester polyols can be expected to have several use scenarios in the CASE (coatings, adhesives, sealants, and elastomers) market because they possess relatively low viscosity and are liquid at ambient conditions. These findings demonstrate that 1,4-PDO is a valuable biorenewable compound that can broaden the toolbox for polyurethane adhesives and coatings. Its use not only allows increasing the bio content but also results in promising performance features.

Experimental Section

Polycondensation of 1,4-PDO and various diacids

To obtain the necessary ratio of diol to diacid the following version of Carothers equation was used:

$$M_n = (M_A + M_B - 2M_{H_2O})\left(1 + \frac{n_B}{n_A}\right)/1 + \frac{n_B}{n_A} - 2X_A\frac{n_B}{n_A}$$

The indices A and B represent the diacid and the diol, X is the conversion, M the molecular weights of the components, M_n the

number average weight of the polymer, and n the number of moles. M_n is further connected with the hydroxyl number (OH-N) via the following equation:

$$\text{OH-N} = \frac{zM_{KOH}10^3}{M_n}$$

in which z is the number of hydroxy groups per polyol molecule. The OH-N corresponds to the amount of KOH needed to neutralize the amount of acid equivalent to the esterification of terminal OH groups with acetic acid anhydride. The OH-N in this work was determined by titration in an analogous procedure to DIN 53240-1. For determining the conversion of carboxylic acid groups, polyester (100–300 mg) was dissolved in a THF–ethanol mixture (30 mL, 3.1, v/v) followed by addition of a grain of phenolphthalein and subsequent titration with aqueous KOH (0.5 mol L^{-1}) by using a microliter syringe.

General polycondensation procedure

The ratio of diol and diacid for the desired target OH-Number was calculated by using the above-mentioned equations. Typically, an OH-N of 30 mg g^{-1} was targeted. The reaction setup consisted of a two-neck flask equipped with a magnetic stirrer, a Vigreux column, and a distillation setup. The calculated amounts of components were weighed into the flask, and the whole setup was subjected to three vacuum/argon cycles and left under an argon atmosphere at ambient pressure. After that, the reaction mixture was heated to 150 °C. When all solid components were dissolved/molten, the stirrer was started, and the mixture was subsequently heated to 180 °C. When conversion of 80–85 % of the acid groups was reached (14–20 h), H$_3$PO$_4$ was added (0.3 mol %, 0.85 w/w in H$_2$O). After that, vacuum was applied (0.2–1 mbar). When the conversion of the carboxylic acid groups had slowed down, (e.g., $X > 98$ %, 40–48 h) corresponding to an acid value below 5 (if possible), the reaction mixture was placed under an argon atmosphere and allowed to cool. Typically, no further purification of the obtained polyester was necessary.

Poly(2-methyl-butylene-succinate)

1,4-Pentanediol (50 g, 480 mmol) and succinic acid (50.78 g, 430 mmol) were reacted, giving poly(2-methyl-butylene-succinate) as clear, viscous, slightly yellowish liquid. $X(\text{COOH}) = 98$ %; OH-N: 30 mg g^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.87$ (h, $J = 6.2$ Hz, 1 H), 4.02 (t, $J = 5.9$ Hz, 2 H), 2.58–2.50 (m, 4 H), 1.65–1.47 (m, 4 H), 1.16 ppm (d, $J = 6.3$ Hz, 3 H); ^{13}C NMR (101 MHz, CDCl$_3$): $\delta = 172.31$, 171.87, 70.82, 64.39, 32.27, 29.39, 29.07, 24.61, 19.93 ppm; GPC: $M_n = 3600$ g mol^{-1}, Đ = 2.4.

Poly(2-methyl-butylene-adipate)

1,4-Pentanediol (50 g, 480 mmol) and adipic acid (61.40 g, 420 mmol) were reacted, giving poly(2-methyl-butylene-adipate) as clear, viscous, slightly yellowish liquid. $X(\text{COOH}) = 99$ %; OH-N: 32 mg g^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.86$ (h, $J = 6.2$ Hz, 1 H), 4.06–3.95 (m, 2 H), 3.76 (q, $J = 6.2$ Hz, 0.09 H, CHOH), 3.58 (t, $J = 6.2$ Hz, 0.04 H, CH_2OH), 2.35–2.19 (m, 4 H), 1.66–1.43 (m, 9 H), 1.15 ppm (d, $J = 6.4$ Hz, 3 H); ^{13}C NMR (101 MHz, CDCl$_3$): $\delta = 173.30$, 172.89, 77.36, 70.32, 64.05, 34.19, 33.84, 32.35, 24.71, 24.44, 24.36, 19.99 ppm; GPC: $M_n = 5800$ g mol^{-1}, Đ = 2.4.

Poly(2-methyl-butylene-azelate)

1,4-Pentanediol (50 g, 480 mmol) and azelaic acid (77.46 g, 411 mmol) were reacted, giving poly(2-methyl-butylene-azelate) as clear, viscous liquid. $X(COOH) = 99.5\%$; OH-N: 39 mg g^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.91$ (q, $J = 6.0$ Hz, 1H), 4.06 (dt, $J = 11.8$, 6.5 Hz, 2H), 3.81 (q, $J = 6.2$ Hz, 0.09H), 3.63 (t, $J = 5.7$ Hz, 0.05H), 2.26 (q, $J = 7.8$ Hz, 4H), 1.59 (ddd, $J = 12.3$, 8.2, 5.4 Hz, 7H), 1.30 (s, 5H), 1.20 ppm (d, $J = 5.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): $\delta = $ 173.79, 173.72, 173.43, 173.32, 70.12, 63.92, 34.55, 34.19, 32.36, 28.93, 28.92, 28.89, 28.85, 24.92, 24.84, 24.71, 19.99 ppm; GPC: $M_n = 4200$ g mol^{-1}, $Đ = 2.4$.

Poly(2-methyl-butylene-sebacate)

1,4-Pentanediol (50 g, 480 mmol) and sebacic acid (82.7 g, 409 mmol) were reacted, giving poly(2-methyl-butylene-sebacata) as clear, viscous liquid. $X(COOH) = 99.5\%$; OH-N: 26 mg g^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.91$ (p, $J = 6.0$ Hz, 1H), 4.06 (dt, $J = 11.8$, 6.5 Hz, 2H), 3.81 (q, $J = 6.2$ Hz, 0.09H), 3.63 (t, $J = 5.7$ Hz, 0.05H), 2.26 (q, $J = 7.8$ Hz, 4H), 1.59 (ddd, $J = 12.3$, 8.2, 5.4 Hz, 7H), 1.20 ppm (d, $J = 5.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): $\delta = $ 173.79, 173.72, 173.43, 173.32, 70.12, 63.92, 34.55, 34.19, 32.36, 28.93, 28.92, 28.89, 28.85, 24.92, 24.84, 24.71, 19.99 ppm; GPC: $M_n = 5700$ g mol^{-1}, $Đ = 3.0$.

Poly(2-methyl-butylene-dodecanedioate)

1,4-Pentanediol (50 g, 480 mmol) and dodecanedioic acid (92.91 g, 404 mmol) were reacted, giving poly(2-methyl-butylene-dodecandioate) as clear, viscous liquid. $X(COOH) = 99.7\%$; OH-N: 29 mg g^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.91$ (h, $J = 6.0$ Hz, 1H), 4.06 (dt, $J = 11.8$, 6.5 Hz, 2H), 3.81 (q, $J = 6.2$ Hz, 0.09H), 3.63 (t, $J = 5.7$ Hz, 0.05H), 2.26 (q, $J = 7.8$ Hz, 4H), 1.59 (ddd, $J = 12.3$, 8.2, 5.4 Hz, 7H), 1.30 (s, 5H), 1.20 ppm (d, $J = 5.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): $\delta = 173.79$, 173.72, 173.43, 173.32, 70.12, 63.92, 34.55, 34.19, 32.36, 28.93, 28.92, 28.89, 28.85, 24.92, 24.84, 24.71, 19.99 ppm; GPC: $M_n = 4600$ g mol^{-1}, $Đ = 2.8$.

Poly(2-methyl-butylene-tetradecanedioate)

1,4-Pentanediol (46.4 g, 446 mmol) and tetradecanedioic acid (100 g, 387 mmol) were reacted, giving poly(2-methyl-butylene-tetradecanedioate) as clear, viscous liquid $X(COOH) = 99.7\%$, OH-N: 18 m g^{-1}, ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.91$ (h, $J = 6.0$ Hz, 1H), 4.06 (t, $J = 11.8$, 6.5 Hz, 2H), 3.81 (m, $J = 6.2$ Hz, 0.09H), 3.6 (t, $J = 5.7$ Hz, 0.05H), 2.3 (q, $J = 7.8$ Hz, 4H), 1.5–1.8 (m, 8H), 1.30 (m, 16H), 1.20 ppm (d, $J = 5.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): $\delta = 174.2$, 173.8, 70.5, 64.3, 35.9, 35.0, 34.7, 34.7, 32.8, 30.0, 29.8, 29.8, 29.7, 29.5, 29.5, 25.4, 25.1, 24.0, 20.4 ppm; GPC: $M_n = 5300$ g mol^{-1}, $Đ = 4.4$.

Chain-extension reactions with 4,4′-MDI

Polyester (25 g) was heated to 80 °C and kept at this temperature under vacuum (< 0.001 mbar) for 1.5 h. After this, 4,4′-MDI (2.2 equiv. with regard to polyester) was added, and the mixture was stirred for 1 h. Subsequently, films with 1 mm thickness were casted and stored at ambient conditions for one week.

Acknowledgements

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