[*n*]-Polyurethanes: Synthesis and Characterization**

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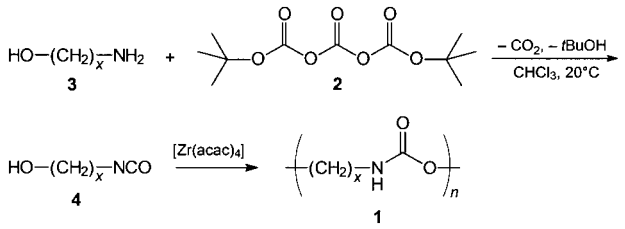
Polyurethanes are a versatile class of polymers that are used in a broad range of applications.[1] In most, if not all, cases of linear polyurethanes, the macromolecular structure is based on the reaction of dihydroxy compounds with diisocyanates, yielding A_2B_2 polymers or the [*m,n*]-polyurethanes. A comprehensive study of the parent aliphatic [*m,n*]-polyurethanes was reported by Otto Bayer in *Angewandte Chemie* in 1947.[2] These, at that time, novel structures were compared and proposed to compete with the two series of aliphatic polyamides, the [*n*]- and [*m,n*]-nylons. Whereas the disclosure of the [*n*]-nylons quickly followed Carothers' first description of the [*m,n*]-nylons, the general class of linear aliphatic [*n*]-polyurethanes is notably absent in the impressive list of linear macromolecules, despite its structural simplicity. Here, we report on a general and convenient route to aliphatic α,ω-isocyanato alcohols and their in situ polymerization into the corresponding [*n*]-polyurethanes **1** of respectable molecular weight.

Why is it that these aliphatic [*n*]-polyurethanes have not been prepared before despite their simple structure? Obviously, this is due to the unavailability of the appropriate monomers; both the α,ω-isocyanato alcohols and the cyclic carbamates were not known and there was hitherto no general route to these classes of substances. As a result the aliphatic series is limited to a few specific structures, which were prepared using ring-opening polymerization of trimethylene urethane,[3] while some oligomers were synthesized by a stepwise sequence.[4] The poly(1,4-phenylene urethane) was prepared by the Curtius rearrangement of hydroxy benzoyl azide, as was reported by Kinstle and Sepulveda, and by several others.[5] The much higher nucleophilicity of alcohols over phenols requires, however, a much milder conversion of the amino group of the easily accessible α,ω-amino alcohol into an α,ω-isocyanato alcohol, followed by a controlled polymerization. Unfortunately, most of the methods known to transform amines into isocyanates are not mild enough and furnish undefined products as the result of uncontrolled side reactions. Recently, we reported on using di-*tert*-butyltricarbonate **2** as a versatile and mild reagent for the synthesis of unusual mono- and multi-isocyanates within minutes at room temperature.[6] The high selectivity and reactivity of reagent **2** is used here to synthesize α,ω-isocyanato alcohols. The latter are easily polymerized in high yields to obtain [*n*]-polyurethanes **1**.

The general reaction sequence to prepare the series of [*n*]-polyurethanes **1** with $x = 4-12$ is given in Scheme 1. The starting α,ω-amino alcohols **3** are either commercially available or were prepared by standard procedures.[7] The synthesis of di-*tert*-butyltricarbonate **2** has been optimized and



Scheme 1. Synthesis of [*n*]-polyurethanes ($x = 4-12$).

described in detail.[8] This reagent is the key element for the selective formation of the intermediate α,ω-isocyanato alcohols **4**. Reaction of a small excess of **2** with **3** in chloroform at room temperature gives within 10 min the isocyanato alcohol monomer **4**. This reaction is accompanied by the formation of two equivalents of carbon dioxide and *tert*-butyl alcohol. The former escapes from the solution, while the latter stays in the reaction mixture. Under the condition employed here, *tert*-butyl alcohol is unreactive to the isocyanate, hence, it is harmless. The amino alcohol solution was added by injecting it under the surface of the di-*tert*-butyltricarbonate solution, in order to avoid turbidity of the reaction mixture, due to the formation of carbamic acid by reaction of escaping carbon dioxide and the amino alcohol. After decomposition of the unstable carbamic acid into the initial amino alcohol, the latter reacts with already formed isocyanate, resulting in urea derivatives. This side reaction distorts the perfect stoichiometry of the AB-type polymerization, and consequently, limits the molecular weight of the polymer.

The formation of the α,ω-isocyanato alcohols has been confirmed by IR and ^{1}H NMR spectroscopy. In the IR spectrum, a strong absorption of the N=C=O stretch at 2274 cm^{-1} is observed for solutions of **4** in chloroform. Figure 1b shows the ^{1}H NMR spectrum of 5-isocyanato-1-pentanol after reaction of 5-amino-1-pentanol (spectrum in Figure 1a) with di-*tert*-butyltricarbonate **2**. Figure 1b reveals the absence of any side products, and also proves the relative stability of **4** in solution, however, evaporation to dryness furnished undefined products.

The polymerization of **4** is performed in situ by addition of a catalytic amount of zirconium(IV) acetylacetonate or dibutyltin dilaurate. For the short isocyanato alcohols with $x = 2$ or 3, the polymerization procedure failed and resulted in the formation of cyclic urethanes, with five- and six-membered rings, respectively. For the longer isocyanato alcohols, the precipitation of polymer **4** was observed after a few hours. The polymer was isolated by filtration in a yield of about 60%. Since the polymerization was performed in solution, a relatively large amount of soluble, cyclic oligomers was formed. Electrospray mass spectra of the filtrate showed the presence of cyclic dimers up to cyclic hexamers. The polymers

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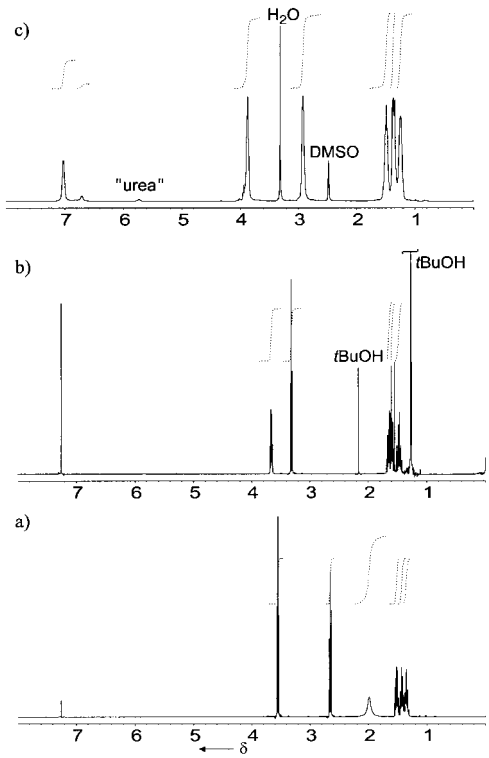

Figure 1. ^{1}H NMR spectra of a) 5-aminopentanol, b) 5-isocyanato-1-pentanol, c) [6]-polyurethane.

were characterized by NMR and FT-IR spectroscopy, elemental analysis, size exclusion chromatography (SEC), viscometry, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). According to NMR and FT-IR spectroscopy and elemental analyses, all polymers possess a very uniform microstructure; the results are in agreement with the assigned structures. Detailed analyses by ^{1}H NMR spectroscopy (Figure 1c) showed that the polymers contain a very small amount (less than 2%) of urea linkages, and both the *cis* and *trans* carbamate conformations are observed.

Table 1 shows the yields of the [*n*]-polyurethanes and some of their characteristics. The molecular weights of the polymers are fairly high to respectable, despite the precipitation of the polymers from the poor solvent during preparation. The data obtained with SEC correlates nicely with the values found by viscometry using the Mark–Houwink parameters of the known [*m,n*]-polyurethanes.[1] Performing the polymerization in THF, DMSO, or *N*-methylpyrrolidine (NMP), or at reflux temperature in chloroform, does not significantly change the molecular weight of the polymer, as investigated for the [6]-polyurethane.

The thermal properties of the polymers were studied by DSC, which indicated that all polymers are highly crystalline. Melting points of the polymers are given in Table 1, and plotted in Figure 2. They are much lower than the melting points of the [*n*]-nylons, as is also observed for [*m,n*]-polyurethanes compared to [*m,n*]-nylons. It is evident from Figure 2 that these [*n*]-polyurethanes display a strong odd–even effect in their melting points. As with other polymers, for example [*n*]-nylons,[9] the [*n*]-polyurethanes with an odd number of methylene units in the monomeric main chain melt at lower temperatures than the [*n*]-polyurethanes with an even number of methylene units.[10] The observed melting points are 10 to 20 °C lower than those predicted by the additive group theory as developed by van Krevelen.[11] Noteworthy is that the melting points can be raised by approximately 5 °C by extensive Soxhlet extraction of the lower molecular weight fractions with hot methanol.

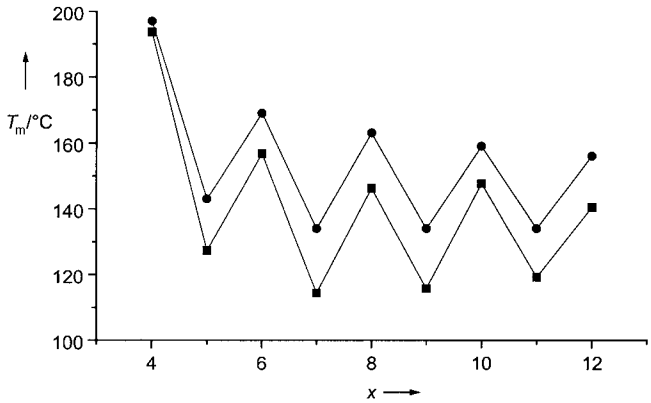

Figure 2. Melting points T_m of [*n*]-polyurethanes; (■): experimental, (●): calculated.

A random copolymer derived from 5-isocyanatopentanol and 6-isocyanatohexanol in a 1:1 molar ratio was prepared in the same way as the homopolymers. In contrast to the homopolymers, the random copolymer is soluble in chloroform, and is completely amorphous with a glass transition temperature of 8 °C according to DSC. According to TGA, all polymers are stable up to 200 °C, after which they decompose due to the reversibility of the urethane entities.

The facile synthesis of the aliphatic [*n*]-polyurethanes by using di-*tert*-butyltricarbonate to prepare the appropriate monomers has yielded a general class of polymers. These structures are especially interesting for biodegradable polymers, since the synthetic procedure is applicable to all amino alcohols with a spacer of at least four carbon atoms between both functionalities. Finally, this study shows that the use of new synthetic methodologies from organic chemistry is highly favorable for the area of polymer synthesis as well.

Table 1. Characteristics of [*n*]-polyurethanes **4**.

x	Yield [%]	M_w [kg mol^{-1}][a]	M_w/M_n[a]	$[\eta]$ [dL g^{-1}]	M_w [kg mol^{-1}][b]	T_m [°C][c]
4	61	18.9	1.4	0.16	16	194
5	63	22.3	1.5	0.17	18	127
6	65	34.4	1.4	0.22	25	157
7	56	26.5	1.5	0.24	29	114
8	55	30.5	1.6	0.24	29	146
9	61	67.4	1.6	0.43	64	116
10	57	32.6	1.7	0.30	39	148
11	63	20.3	1.5	0.18	19	119
12	59	21.4	1.6	0.26	32	141
5-*co*-6	48	22.7	1.4			–

[a] Measured by SEC, with NMP as solvent, relative to polystyrene standards. [b] Calculated from intrinsic viscosity in *m*-cresol at 25 °C; $K = 1.34 \times 10^4$, $a = 0.73$. [c] Measured by DSC at a heating rate of 10 K min^{-1}.

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Experimental Section

The synthesis of [6]-polyurethane is given as a typical example: A solution of 5-amino-1-pentanol (9.69 mmol, 1.00 g) in chloroform (2 mL) was injected by a syringe under the surface of a stirred solution of di-*tert*-butyltricarbonate (10.66 mmol, 2.80 g) in chloroform (30 mL). The solution was stirred for 10 min at room temperature under an argon atmosphere. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 3.67$ (q, $^3J = 6.0$ Hz, 2H; CH_2OH), 3.32 (t, $^3J = 6.6$ Hz, 2H; CH_2NCO), 1.55 (br.m; 4H; $CH_2CH_2OH + CH_2CH_2NCO$), 1.40 (m, $^3J = 6.7$ Hz, 2H; CH_2 $CH_2CH_2CH_2$ CH_2); IR ($CHCl_3$): $\tilde{\nu} = 3396$ (br.s), 2971 (m), 2274 (s) cm^{-1}.

Zirconium(IV) acetylacetonate (0.1 mol%) was added, and the polymerization was carried out for 20 h with continuous stirring under argon at room temperature. The turbid reaction mixture was precipitated in diethyl ether (150 mL), and the polymeric product was collected by suction filtration in a yield of 0.81 g (63%). M.p. 127 °C; decomposition at 200 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 20 °C, TMS): $\delta = 7.04$ (br.t, 0.9H; N*H trans* conformer), 6.72 (br.m, 0.1H; N*H cis* conformer), 3.89 (t, $^3J = 6.2$ Hz, 2H; CH_2O), 2.95 (q, $^3J = 6.0$ Hz, 2H; CH_2N), 1.50 (m, $^3J = 7.2$ Hz, 2H; CH_2CH_2O), 1.40 (m, $^3J = 7.7$ Hz, 2H; CH_2CH_2N), 1.28 (m, $^3J = 6.6$ Hz, 2H; $CH_2CH_2CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 100 °C, TMS): $\delta = 156.4$ (*C*=O), 63.5 (CH_2O), 40.1 (CH_2N), 29.4 (CH_2CH_2O), 28.7 (CH_2CH_2N), 26.0 ($CH_2CH_2CH_2CH_2CH_2$); IR (KBr): $\tilde{\nu} = 3318$ (br.s), 2944 (m), 2870 (w), 1684 (s), 1535 (s), 1263 (s) cm^{-1}; elemental analysis (%) for $(C_6H_{11}NO_2)_n$ calcd: C 55.80, H 8.58, N 10.85; found: C 55.46, H 8.67, N 10.55.

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Isoporphycene: The Fourth Constitutional Isomer of Porphyrin with an N_4 Core—Occurrence of *E*/*Z* Isomerism**

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Dedicated to Professor Satoru Masamune on the occasion of his 70th birthday

The synthesis of porphycene (**1**) in 1986[1] led to the realization that, in principle, no less than seven constitutional isomers of porphyrin with an N_4 core are possible.[2] Unlike porphyrin, its constitutional isomers contain one or two formal double bonds and may therefore give rise to *E*/*Z* isomerism. After **1** was shown to match porphyrin in many of its properties, it was clear that the isomers open a promising new chapter of porphyrin chemistry.[3] If a further incentive for the synthesis of the isomers was needed, this was provided by the inverted porphyrins discovered simultaneously by a Japanese and a Polish group.[4]

Porphycene (**1**), which is approximately 2 kcal mol^{-1} more stable than porphyrin according to ab initio calculations (BLYP/6-31G** method), has meanwhile been joined by hemiporphycene (**2**)[6] and corrphycene (**3**; each as octaalkyl derivatives).[7] Compounds **2** and **3** follow **1** on the stability scale of the constitutional isomers and are 5 and 12 kcal mol^{-1}, respectively, higher in energy than porphyrin.[5] Similar to porphyrin, **1** – **3** (see Scheme 1) are excellent complexing agents; this could not be predicted with certainty as the N_4 core of the three isomers covers a smaller area and deviates more or less strongly from the square shape. Thus, a multitude of comparative investigations of the metal complexes of the isomers and the corresponding metalloporphyrins suggested itself.

The isoporphycenes [porphyrins-(3.0.1.0)] **4** and **5** (Scheme 1), in fourth place on the stability scale of the isomers,[5] are not only interesting as complexing agents and for other porphyrin-relevant properties, but also demand attention under the aspect of stereoisomerism. Other than in the case of the constitutional isomers **1** – **3**, for which the *Z* isomer is strongly favored energetically over the *E* isomer, the two isoporphycene isomers only differ slightly (PM3) or

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