Functional regioregular (poly)urethanes from soft nucleophiles and cyclic iminocarbonates

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Abstract

The catalyst-free synthesis of urethanes from cyclic iminocarbonates, used as masked isocyanates, and soft nucleophiles (i.e. carboxylic acids and thiols) has been studied. Remarkably, the ring-opening reaction occurred fully site-selective (i.e. methylene). The disclosed method showed a high functional group tolerance towards carboxylic acids bearing alkyl-, alkenyl-, ketone-, pyrone- and hydroxyl groups. The methodology was further applied for the construction of regioregular functional polyurethanes by step-growth copolymerization of cyclic bisiminocarbonates and dicarboxylic acids or dithiols. M_w up to 34,000 g/mol were obtained in a fully atom economical manner using equimolar amount of both monomers.

Introduction

Isocyanates are highly reactive electrophilic compounds that received huge interest in organic and polymer synthesis.[1] These amine surrogates could for example be coupled with carboxylic acids to generate a large diversity of amides, which are key structural motifs for biological systems, active pharmaceutical ingredients and agrochemicals.[2–5] This condensation reaction proceeds either through the formation of an acyl carbamate

intermediate that affords after decarboxylation the corresponding amide (**Scheme 1**, **path a**) [6,7] or *via* a Pd-mediated CO_2 extrusion from an aromatic carboxylic acids followed by insertion of an isocyanate (**Scheme 1**, **path b**).[8] The reaction of isocyanates with carboxylic acids has only limitedly been explored in macromolecular sciences. Only rare examples describe the generation of aromatic or aliphatic poly(amide)s with M_n up to ~ 19,000 g/mol by the direct decarboxylative polycondensation of dicarboxylic acids and diisocyanates (**path a**).[9] More recently, sequential self-repetitive reactions that involve the catalytic condensation of two isocyanates with a *N*-acylurea, generated from a carbodiimide and a carboxylic acid, have been reported.[10–12] The *N*-acylurea subsequently expels one isocyanate fragment to provide the desired amide backbone. This requires a high temperature (T > 180-200 °C) which is a drawback.[13]

In contrast to carboxylic acids, the condensation of isocyanates with alcohols (**Scheme 1**, **path c**) to construct urethanes or diisocyanates with diols delivering polyurethanes (PU) is of major industrial importance as the value of the polyurethane market was estimated to be around USD 65.5 billion in 2018.[14] PUs are one of the most widely used commodity polymers for everyday life, and have found applications in coatings, adhesives, sealants, foams, medical devices, and textiles. The condensation between isocyanates and alcohols is often driven by organometallic complexes, with dibutyltin dilaurate as the most employed catalyst, and could nowadays proceed under mild operating conditions (at room temperature and/or ambient atmosphere).[15] However, isocyanates are subjected to REACH restrictions due to their significant toxicity causing skin allergy, asthma or occupational disease.[16] It is thus attractive to find methods to generate isocyanates and let them react *in situ* to the target compound/polymer without isolation. To address this issue, masked/blocked isocyanates have been introduced. Conceptually, the isocyanate functional group is reversibly protected by a compound containing an active hydrogen (e.g. phenol, oxime, ε-caprolactam, amides, imidazoles, pyrazoles) producing a new adduct which is stable at room temperature.[15,17] Pleasingly, it yields again a reactive isocyanate functionality at elevated temperatures. The nature of the masking agent dictates at which temperature this occurs, generally between 120 and 200 °C. Unfortunately, these blocked isocyanates share the disadvantage of releasing an equimolar amount of masking agent during polymerization, which is undesirable from an atom-economical perspective. To overcome these hurdles and as part of our research programs on C_1 chemistry and sustainable methodology development,[18–20] we envisioned an alternative approach for urethane (**Scheme 1**, **path d**) and PU (**Scheme 1**, **path e**) synthesis based on cyclic (bis)iminocarbonates and soft nucleophiles (e.g. (di)carboxylic acids and (di)thiols) in the absence of a catalyst. Cyclic iminocarbonates can be seen as masked isocyanates under the form of their corresponding acetals and which offer the opportunity to incorporate the masking moiety in the (poly)urethane backbone, thereby delivering functional (poly)carbamates in a fully atom-economical method. Interestingly,

the chemistry of iminocarbonates is so far a curiosity in polymer sciences and to the best of our knowledge only rare and ancient works have been reported for the construction of polymers based on these monomers. Sixty years ago, the group of Hyugaji reported in a vague study the basic coupling of *N,N'*-phenylene bis(ethylene iminocarbonate) with terephthalic or adipic acid, however no information has been provided regarding the polymerization features (polymer microstructure, molar masses, regioselectivity, …).[21] At the end of the 60's, Mukaiyama fabricated poly(ethylene carbamate) by the cationic room temperature ring-opening polymerization of a 5-membered cyclic *N*-chloroiminocarbonate using boron trifluoride etherate or sulfuric acid as catalyst, followed by hydrolysis of the *N*-chloro carbamate moiety using arsenic trioxide or zinc powder/butanol mixture.[22] The polymerization was slow (10 days) and produced an amorphous, tough elastomer which decomposed in air into a brittle, pumiceous polymer. In a third and final example Hayashi and co-workers described in the late 70thies the alternating ring-opening copolymerization of 2-phenylimino-1,3-dioxolane with β-propiolactone.[23] The polymerization manifold proceeded through the formation of zwitterionic intermediates and provided chains with M_n up to 13,000 g/mol at 35 °C in 65 h when nitromethane was used as the solvent. Herein, we revisit the utilization of cyclic (bis)iminocarbonates in step-growth manifold with various dicarboxylic acids to fabricate novel regioregular polyurethanes. We first studied in detail the regioselectivity of the ring-opening of a model cyclic iminocarbonate and its functional group tolerance prior investigation of the polymerization features. Furthermore, we demonstrate the versatility of our concept by investigating for the first time the step-growth copolymerization of cyclic bisiminocarbonates with dithiols soft nucleophiles to furnish PUs with thioether moieties

Previous work: isocyanates for amide and urethane synthesis
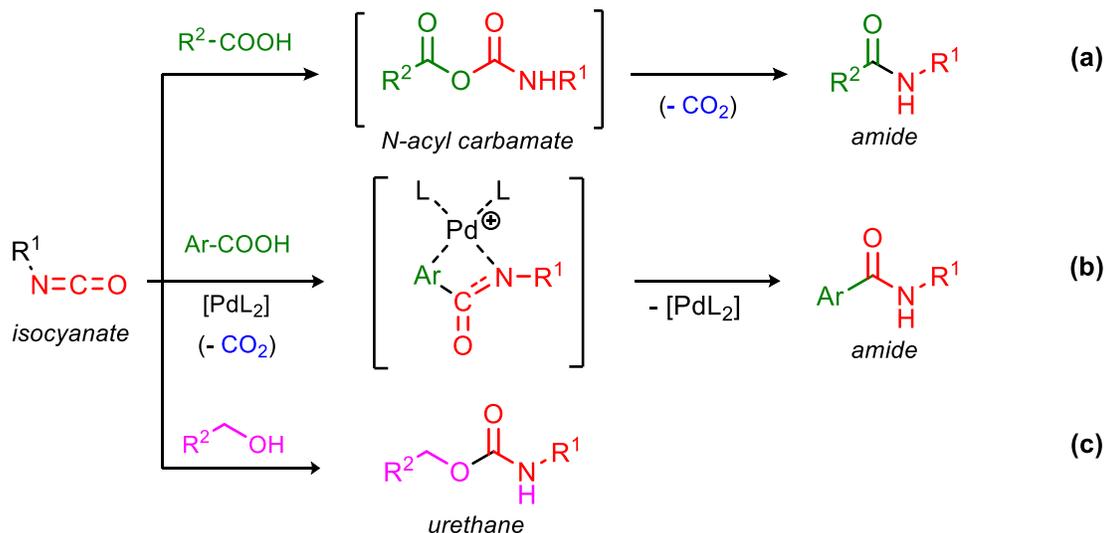
This work: cyclic iminocarbonates for regioselective (poly)urethane synthesis
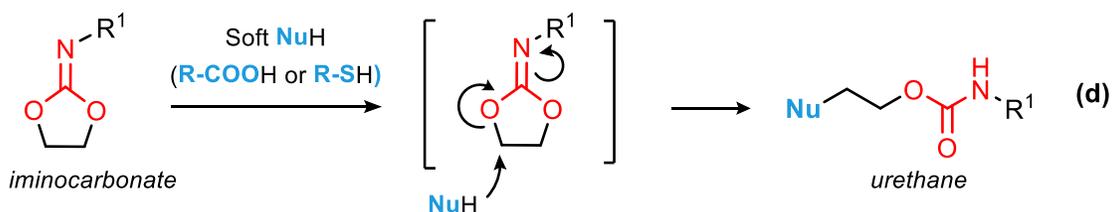
- ✔ exclusive methylene attack
- ✔ full atom economy
- ✔ catalyst-free
- ✔ high functional group tolerance
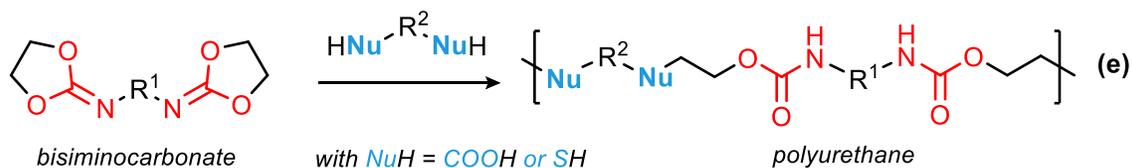
Scheme 1: Top: Amide (a-b) and urethane (c) synthesis from isocyanates and carboxylic acids or alcohols. Bottom: Urethane (d) and polyurethane synthesis (e) form regioselective ring-opening of cyclic iminocarbonate or cyclic bisiminocarbonates

Results and discussion

Synthesis of iminocarbonates

Although iminocarbonates have attracted the attention of organic chemists for decades, only a limited number of methods to synthesize them are known (**see Supporting Information**, **Page S2**). For this work a model iminocarbonate was prepared *via* the most general two-step procedure involving the synthesis of *n*-butylcarbonimidic dichloride from sulfuryl chloride and *n*-butylisocyanide, followed by the imidoylation with vicinal 2-methylpropane-1,2-diol under reflux to obtain, *N*-(4,4-dimethyl-1,3-dioxolan-2-ylidene)butan-1-amine (**1**, **Scheme 2**, mixture of *Z* and *E* isomers) with a yield of 72%. Switching from *n*-butylisocyanide to 1,4-diisocyanobutane gave access to the corresponding diiminophosgene used as precursor for the construction of a polymerizable cyclic bisiminocarbonate (**6**).

Model cyclic iminocarbonate
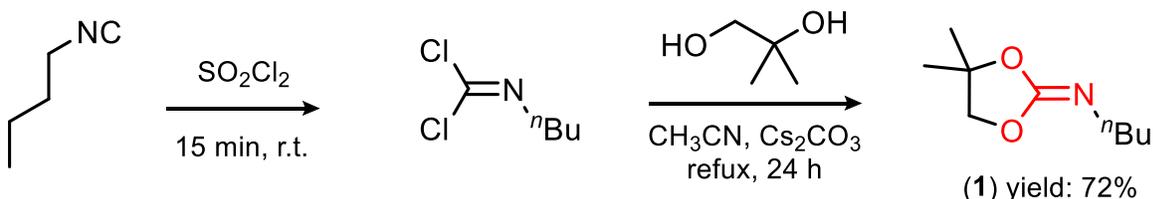
imidoylation
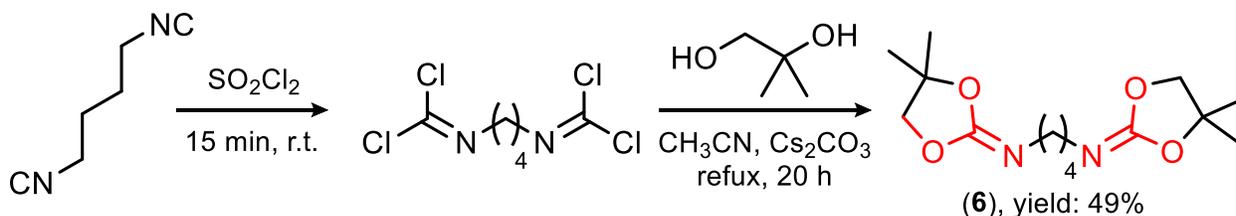
Polymerizable bicyclic iminocarbonate

Scheme 2: General strategy for the synthesis of cyclic (bis)iminocarbonates

Model Reactions

Five-membered cyclic iminocarbonates display two electrophilic sites, i.e. the methylene and the imine carbon atom. To determine which of these two sites preferentially reacts with soft nucleophiles, such as carboxylic acids, cyclic iminocarbonate *N*-(4,4-dimethyl-1,3-dioxolan-2-ylidene)butan-1-amine (**1**) was treated with glacial acetic acid (pKa = 4.76)

in DMSO-d_6 (C = 1.2 M, dry) at 80 °C under N_2 atmosphere (**Figure 1**). Pleasingly, the ring-opening of this model iminocarbonate was fully regioselective and only occurred at the methylene position to deliver 2-[(butylcarbamoyl)oxy]-2-methylpropyl acetate (**2a**). The structure of this compound was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS analysis (see ESI). **Figure 1** illustrates the conversion of cyclic iminocarbonate **1** in function of time, as monitored by ^{1}H NMR spectroscopy by comparing the relative intensity of the methylene protons from iminocarbonate **1** (δ = 4.00 - 4.08 ppm) with the methylene protons of compound **2** (δ = 2.93 ppm) (For ^{1}H NMR spectra, see **Figure S1A**). The selectivity towards 2-[(butylcarbamoyl)oxy]-2-methylpropyl acetate (**2a**) remained unchanged throughout the entire time span of the reaction and the conversion of **1a** was higher than 98% after 8 h. At a lower reaction temperature of 40 °C, the conversion of **1** only reached 14% in 8 h. Remarkably, with a stronger carboxylic acid such as benzoic acid (pKa = 4.2), the reaction proceeds much faster with a conversion up to 98% in just 90 minutes at 80 °C. In that case 2-[(butylcarbamoyl)oxy]-2-methylpropyl benzoate (**2b**) was formed with a selectivity higher than 95% (**Figure 1** and **S1B**).
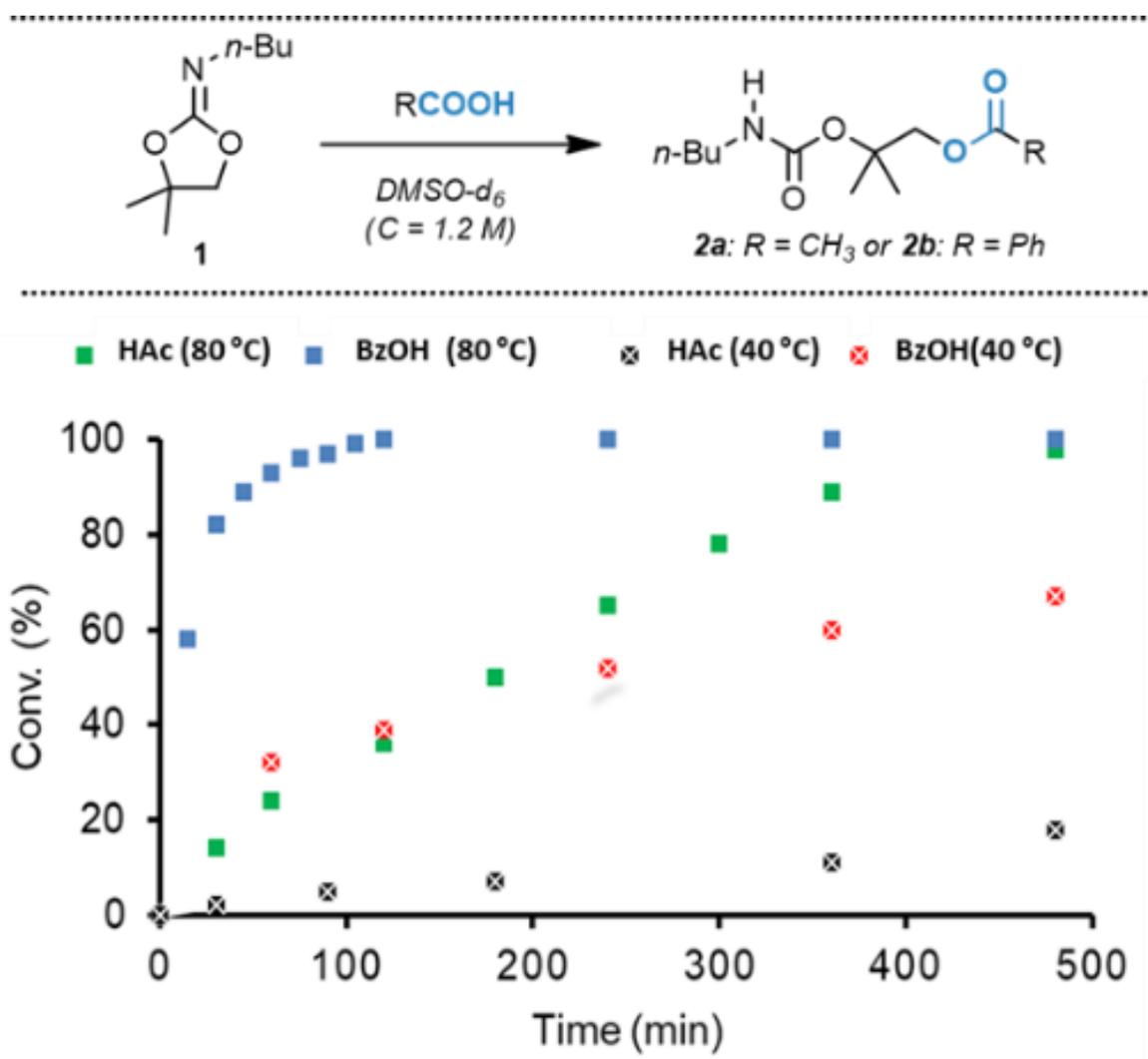
Figure 1: Evolution of the conversion of N-(4,4-dimethyl-1,3-dioxolan-2-ylidene)butan-1-amine (**1**) in the presence of acetic acid (HAc) or benzoic acid (BzOH) into **2a** and **2b** respectively at 40 °C and 80 °C. Reaction conditions: [1]/[carboxylic acid] = 1, C = 1.2 M in DMSO-d6 (dry).

The higher reactivity of BzOH compared to HAc could be explained by its stronger acidity, which allows an easier imine protonation and thereby ring opening of iminocarbonate 1 with the liberated carboxylate anion (**Scheme 3**).
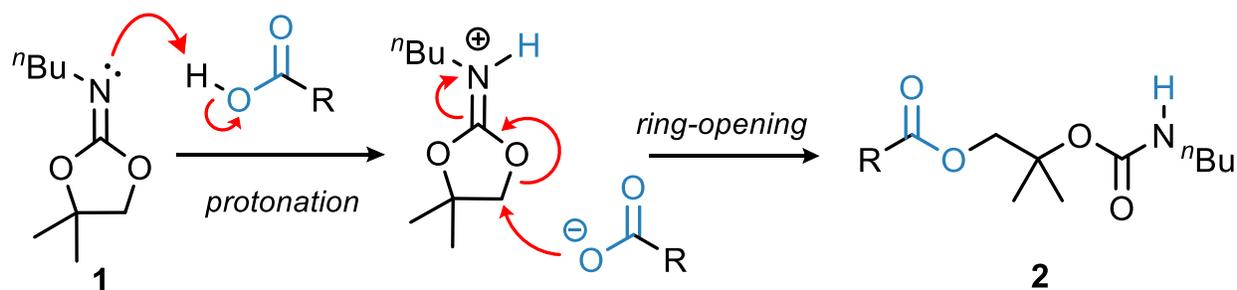
Scheme 3: Urethane **2** synthesis by ring-opening of iminocarbonate **1** with carboxylic acids

Although the reaction for model substrate **2a** is finished after 8 h (see **Figure 1**), a reaction time of 18 h was selected for the scope to assure full conversion for all carboxylic acids. We were delighted to observe a broad acid scope featuring various functional groups (**Scheme 4**). In all cases high selectivities were obtained in generally high yields.

Unsubstituted aliphatic and aromatic carboxylic acids delivered the desired urethanes **2a-c**. Functionalized carboxylic acids such as acrylic, 3-butenoic, coumalic or levulinic acid also provided the corresponding urethanes (**2d-g**). Interestingly, this chemistry is also compatible with unprotected hydroxyl groups at the carboxylic acid moiety as illustrated by L-lactic, L-leucic or 2,2-bis(hydroxymethyl)propionic acid, delivering the desired urethanes (**2h-j**). These experiments also suggest that aliphatic alcohols that may be viewed as a harder nucleophile than carboxylic acids according to the hard and soft (Lewis) acids and bases theory of Pearson would not ring open iminocarbonate **1** *via* attack onto the soft methylene site under the investigated conditions. This was confirmed by treating **1** with 1-butanol under identical reaction conditions with full recovery of **1** after 18 h. Even in the presence of a superbase (DBU, 5 mol%) that is known to catalyze the ring-opening of α-alkylidene cyclic carbonates by alcohols,[24,25] 1-butanol did not react with **1** (**Figure S2**). On the other hand, an acidic catalyst such as methanesulfonic acid, led to a mixture of products as shown by a very complex NMR spectrum (**Figure S3**).
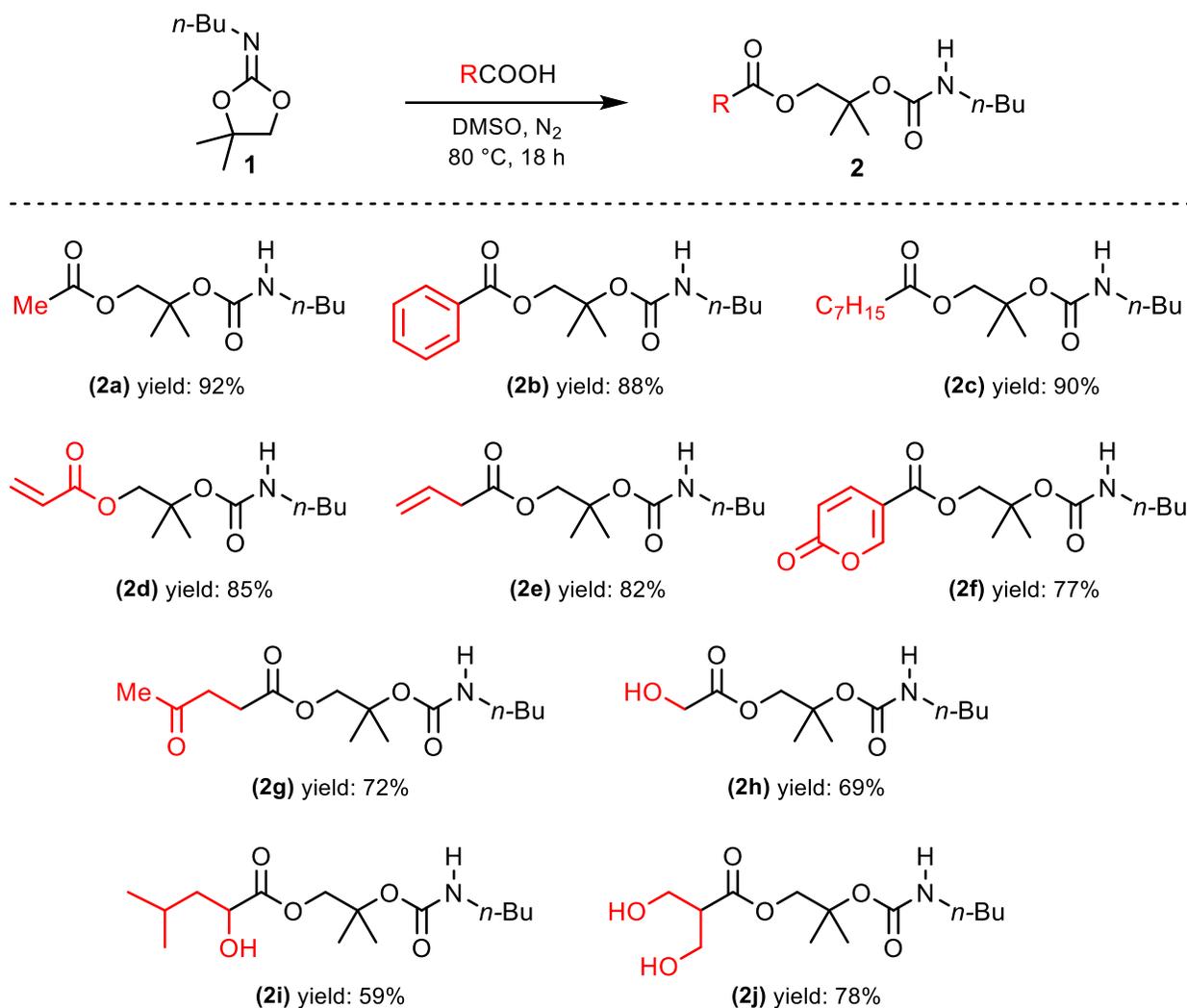
Scheme 4: Carboxylic acid scope. Reaction conditions: **1** (5.1 mmol, 1.0 equiv), carboxylic acid (1.0 equiv), DMSO (3 mL, dry), 18 h, 80 °C, N2 atmosphere. Conversion and selectivity determined from crude ^1H NMR. Yield after isolation

It has to be noted that a selectivity lower than 99% in **Scheme 4** was the result of acid-promoted hydrolysis of the cyclic iminocarbonate **1** by the residual water in the carboxylic acids, generating the corresponding *gem*-dimethyl substituted cyclic carbonate 4,4-dimethyl-1,3-dioxolan-2-one (**3**) and *n*-butylamine (**4**) as side products. However, these did not hamper the purification of the desired carbamates **2** by flash chromatography. To confirm the hydrolysis hypothesis, product 1 was treated with 1.0 equivalent of water in DMSO (C = 1.2 M) for 18 h at 80 °C, but in the absence of acid no reaction occurred (**Scheme 5a**). However, when the same experiment was carried out under a CO2

atmosphere (50 bar), 3 and 4 were quantitatively formed in 18 h (**Scheme 5b**). The *in-situ* formation of carbonic acid, from CO_2 and water, was sufficient to catalyze the hydrolysis of **1**.
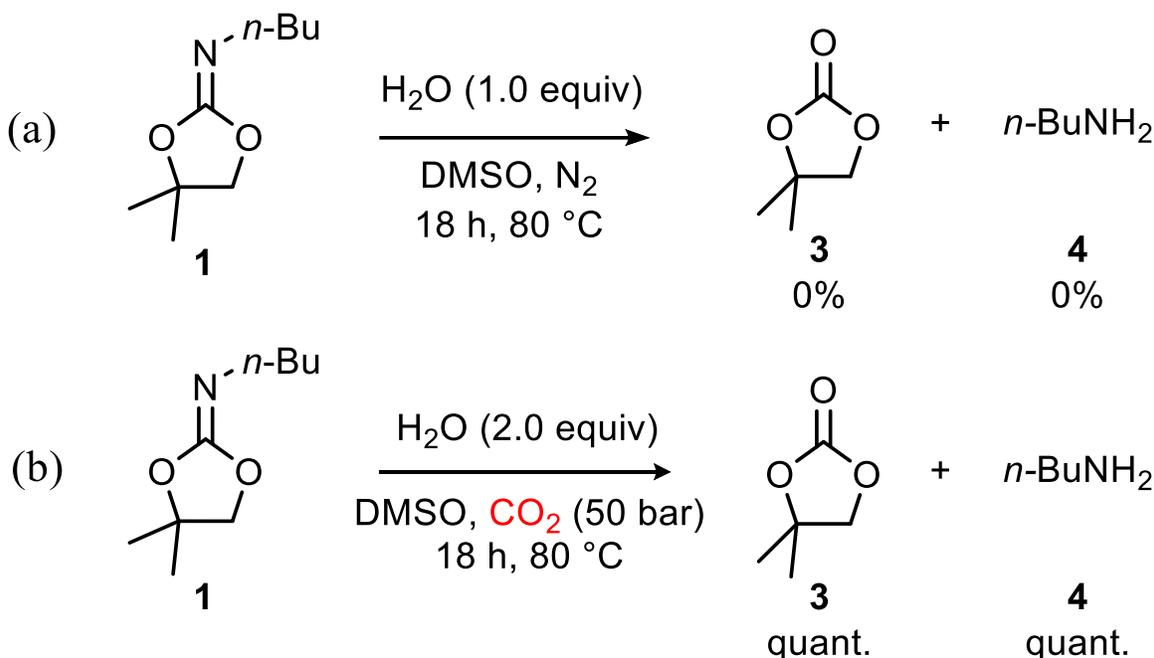
Scheme 5: Stability of iminocarbonate **1** towards hydrolysis in the absence of acid (**a**) or with *in-situ* generated carbonic acid (**b**)

The ring-opening of **1** was subsequently examined with different other aromatic nucleophiles including aniline (pKa = 4.6), phenol (pKa = 9.95) and thiophenol (pKa = 6.61) for 8 h at 80 °C in DMSO (C = 1.2 M, dry). While the *N*- and *O*-nucleophiles did not react (even with a prolonged reaction time of 48 h), *S*-alkylation of thiophenol by **1** was found complete and selective (> 99%, 5a in **Scheme 6**). This is in accordance with the pKa of the three aromatic nucleophiles evaluated and the critical role of substrate protonation in the reaction mechanism. Interestingly, attempts to perform kinetic studies revealed that thiophenol was instantaneously consumed even at room temperature (an exothermic reaction) to deliver urethane 5a in less than 1 minute! Unexpectedly, the thiol scope could also be extended to aliphatic derivatives, i.e. benzyl mercaptan (pKa = 9.43) and 1-butanethiol (pKa = 10.78) (**Scheme 6**).[26] With benzyl mercaptan, the conversion of **1** reached 77 % after 8 h at 80 °C, while delivering 5b in excellent selectivity. Extension of the reaction time to 24 h or 48 h did however not improve the yield. With 1-butanethiol as coupling partner, the conversion of **1** dropped to 52% and dibutyl disulfide was observed as by-product, which formation might be due to the possible presence of residual oxygen within the reaction medium. Based on the pKa values alone we would not predict

this reaction to occur. Therefore, we believe that the reactivity of the *S*-nucleophiles towards **1** is dictated by an interplay between the acidity and the charge delocalization of the sulfur electrons (3d orbitals) that modulates their reactivity versus oxygen nucleophiles, thiophenol offering the best compromise.
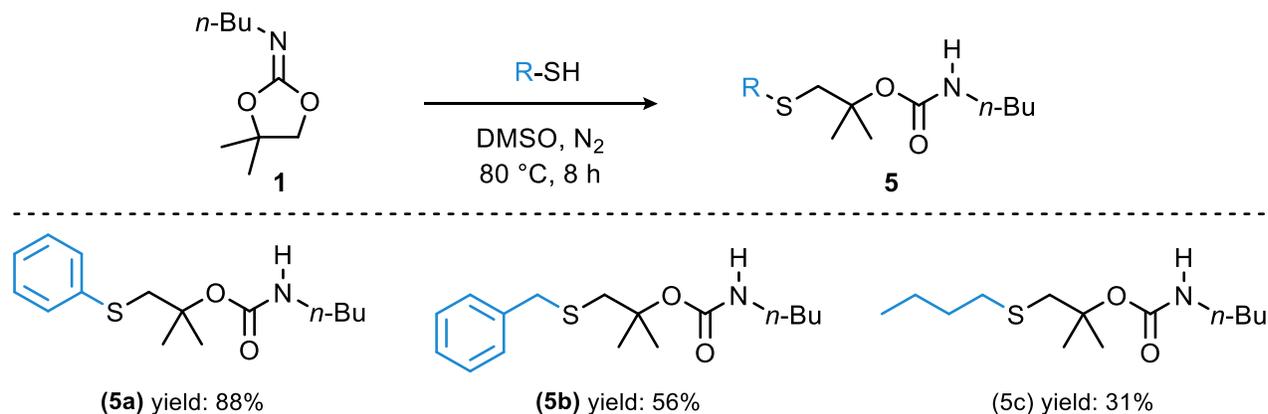
Scheme 6: Thiol scope. *Reaction conditions:* **1** (5.1 mmol, 1.0 equiv), thiol (1.0 equiv), DMSO (3 mL, dry), 8 h, 80 °C, N2 atmosphere. Conversion and selectivity determined by crude ^{1}H NMR. Yield after isolation

Polymer synthesis

We exploited the developed chemistry for the polyaddition of model cyclic *gem*-dimethyl substituted bisiminocarbonate **6** derived from butane-1,4-diamine with a biorenewable dicarboxylic acid, such as succinic acid (7a) (Table 1, entries 1-3). For the first set of experiments, all monomers were vacuum dried (p = 3 x 10^{-2} mbar) at 25 °C for 16 h prior to the polymerization that was conducted at 80 °C by using an equimolar amount of the comonomers in DMSO (dry). To ensure an initial homogeneous polymerization system, the medium was diluted to a concentration of 0.7 M. After 24 h, the regioregular microstructure of the poly(urethane-*co*-ester) chains was confirmed by ^{1}H and ^{13}C NMR spectroscopy, as illustrated in **Figure S4**. The ^{1}H NMR spectrum shows methylene peaks adjacent to the newly formed linkages, i.e. at δ = 2.61 ppm or 4.19 ppm for the methylenes (peaks A : -CH$_2$-C=OO- and B : -C=OO-CH$_2$- in **Figure S4**) adjacent to the ester bonds and at δ = 2.89 ppm for the methylene (peak E in **Figure S4**, -CH$_2$-NH-COO-) attached to the urethane unit. This observation is in line with the regioselective ring-opening of iminocarbonate **1** (*vide supra*). Unfortunately, the obtained polymer was characterized by a rather low weight-average molar mass (*M*$_w$) of 4,400 g/mol due to a termination reaction (**Table 1**, **entry 1**). Careful analysis of the ^{1}H NMR spectrum of the crude polyurethane revealed the presence of additional peaks, i.e. two singlets at δ = 4.23 ppm and δ = 1.45 ppm as well as a shoulder at δ = 2.96 ppm of the methylene signal of the urethane linkage

(δ = 2.89 ppm) (**Figure S5**). This termination reaction was caused by the hydrolysis of some cyclic iminocarbonate rings, either from the monomer or from the polymer chain-end. It delivered the *gem*-dimethyl substituted ethylene carbonate, i.e. 4,4-dimethyl-1,3-dioxolan-2-one 3 and a polymer chain end-capped by an amine moiety unreactive against the cyclic iminocarbonate (**Figure S5**). This side hydrolysis is estimated to 13% by comparing the relative integration of the methylene signals at 4.23 (methylene typical of 3) and 4.18 ppm (methylene adjacent to the urethane linkage of the polymer) in the ^{1}H NMR crude spectrum. Consequently, it induces a deviation from the initial 1:1 stoichiometry between cyclic bisiminocarbonate **6** and succinic acid (**7a**), causing termination of the step-growth copolymerisation. The vacuum drying of the comonomers prior to polymerization was clearly insufficient to remove all residual water. Drying by three azeotropic distillations from toluene was then investigated to remove the water, however it was found unsatisfactory as well, delivering once again oligomers with low M_w of 3,800 g/mol and 14% of hydrolysis of the cyclic iminocarbonate (**Table 1**, **entry 2**). Therefore, the polymerization procedure was adapted and solutions of bisiminocarbonate 6 and succinic acid (**7a**) were prepared in DMSO (C = 1.4 M, dry) and further dried *via* molecular sieves. Titrations of solutions of **6** and **7** *via* the Karl Fisher method enabled quantifying the residual water content to respectively 26 and 27 ppm. Gratifyingly, after mixing an identical volume of both solutions, a polyurethane with M_w up to 15,800 g/mol was generated at 80 °C for 24 h, with only 4 % of hydrolysis of the cyclic bisiminocarbonate **6**.

Table 1: Synthesis of polyurethanes from equimolar ratio of cyclic bisiminocarbonate **6** and dicarboxylic acids **7a-d** by step-growth copolymerization. Conditions: C = 0.7 mol/L, DMSO (dry), 80 °C, 24 h
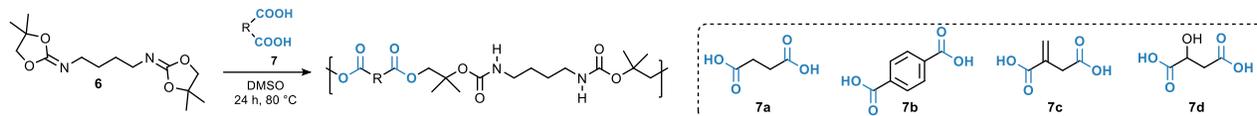
Entry	Polymer	Dicarboxylic acid	Drying method	$M_n{}^a$ (g/mol)	$M_w{}^a$ (g/mol)	Đ	Hydrolysis of **6** (%)[b]	T_g/T_m (°C)[c]
1	**P1**		Vacuum	3,300	4,400	1.34	13	n.d.
2	**P2**	**7a**	Azeotropic distillation	2,800	3,800	1.33	14	n.d.
3	**P3**		Molecular sieves (3 Å)	8,000	15,800	1.96	4	-45
4	**P4**		Vacuum	2,900	4,200	1.45	11	n.d.
5	**P5**	**7b**	Azeotropic distillation	3,500	5,300	1.53	8	n.d.
6	**P6**		Molecular sieves (3 Å)	3,900	6,000	1.56	5	21/120
7	**P7**		Vacuum	3,000	4,800	1.62	10	n.d.
8	**P8**	**7c**	Azeotropic distillation	2,600	3,800	1.46	11	n.d.
9	**P9**		Molecular sieves (3 Å)	3,200	5,800	1.6	4	-38
10	**P10**		Vacuum	1,100	1,800	1.63	15	n.d.
11	**P11**	**7d**	Azeotropic distillation	/	/	/	/	n.d.
12	**P12**		Molecular sieves (3 Å)	2,900	3,500	1.20	4	n.d.

[a] Apparent molar masses determined by SEC using DMF/LiBr as eluent and a calibration of standards with PS.

[b] Calculated from the crude samples by comparison of the relative intensities of the CH$_2$ signals of 4,4-dimethyl-1,3-dioxolan-2-one (**3**) at δ = 4.23 ppm (or the methyl signals at δ = 1.46 ppm) and the polymers (4.18 < δ < 4.45 ppm, depending on the dicarboxylic acid)

^c Determined by modulated differential scanning calorimetry (heating ramp of 5 °C/min, amplitude = 1 °C, period of 60 seconds)

n.d. not determined

This copolymerization was then extended to other dicarboxylic acids such as terephthalic (**7b**), itaconic (**7c**) and malic acid (**7d**). In line with the synthesis of PUs from succinic acid (**7a**), the preliminary drying of these diacids/bisiminocarbonate comonomer mixtures under vacuum at 25 °C for 16 h or *via* three azeotropic distillations from toluene was insufficient and only enabled to build low molar mass polymers (**Table 1**). With terephthalic acid (7b), chains with M_w of 4,200 and 5,300 g/mol were produced (**Table 1**, **entries 4-5**). M_w remained similar with values of 3,800 or 4,800 g/mol when itaconic (**7c**) was used (**Table 1**, **entries 7-8**). With D,L-malic acid (**7d**), M_w of the oligomers did not exceed 3,500 g/mol (**Table 1**, **entry 10**). Whatever the comonomers formulation, both drying methods seemed insufficient as 10 to 15 % of 4,4-dimethyl-1,3-dioxolan-2-one (**3**) were identified within the crude reaction medium. The level of hydrolysis was again decreased to 4-5% by using molecular sieves as desiccant, which increased M_w of the PUs (**Table 1**, **entries 6, 9** and **12**) though not so much as observed with dicarboxylic acid **7a** due to a higher residual water content, e.g. 49 ppm for the itaconic solution. ¹H and ¹³C NMR spectra confirmed the structure of the copolymers (**Figure S6**). From these experiments, it appeared that the hydrolysis of cyclic iminocarbonate units in the inherently acidic conditions when dicarboxylic acids are used as comonomers interferes with the construction of high molar mass polyurethanes. Capitalizing on the quantitative and selective *S*-alkylation of thiophenol by model compound **1** (*vide supra*), this hydrolysis issue was completely circumvented by synthesizing PUs from 6 and aromatic dithiols **8a-c** (**Table 2**, **entries 1** and **2**). Pleasingly, with 1,4-benzenedithiol (**8a**), polymer chains were constructed with M_w up to 34,000 g/mol after 24 h at 80 °C (C = 0.7 M in dry DMSO) (**Table 2**, **entry 1**). It has to be noted that the so-produced PU precipitated during its formation and was only partly soluble in common organic solvents (including those known to solubilize conventional PUs, such as *N,N*-dimethylacetamide (DMA), hexafluoroisopropanol or dimethylformamide (DMF)). Therefore, the estimated molar mass reported in **Table 2**, **entry 1** only reflects the value of the soluble chains (in DMF) and M_w is thus underestimated. The polymer fractionation was confirmed by the low dispersity of 1.34 instead of usual values closed to ~2 for step-growth copolymerizations.

By using 4,4′-thiobisbenzenethiol (**8b**), soluble chains with M_w of 12,500 g/mol were produced (**Table 2**, **entry 2**). With benzylic 1,4-benzenedimethanethiol (**8c**) (**Table 2**, **entry 3**), only a polymer with a low molar mass of 3,100 g/mol was fabricated, which is not surprising regarding the lower conversion and yield of *S*-alkylation obtained with

iminocarbonate **1** and benzyl mercaptan (**Scheme 6**). ^{1}H and ^{13}C NMR spectra of the obtained polymers are in line with their expected structure (**Figure S7**).

Thermal analyses of selected polymers (previously purified by precipitation in diethyl ether and dried under high vacuum) were realized by modulated differential scanning calorimetry (mDSC, **Figures S8-S13**). With the exception of the poly(urethane-*co*-ester) P6 made from terephthalic acid 7b that displayed a semi-crystalline nature (T_m = 120 °C), all polymers were amorphous. **P3** and **P9** were low viscous materials with T_g's of -45 and -38 °C, respectively. Such low values are not surprising regarding the low molar masses and aliphatic nature of the chains. Despite the partial aromatic nature of the sulphur containing polyurethanes **P14** and **P15**, both polymers also displayed low T_gs of respectively 26 and -25 °C. Such low values may be explained by the low molar masses of the chains, especially for **P15**, and it has been demonstrated previously that the presence of in-chain thioether linkages within the main polymer skeleton decreased their T_g values.[27] **P13** is characterized by two endothermic transitions, at -21 and 70 °C. The occurrence of two distinct T_g's is amazing for homopolymers as this behavior is expected for blends or block-structured scaffolds. Further analyses would be required to comprehend the origin of such phenomena, this curious behavior has also been observed recently for sulfur-containing poly(hydroxyoxazolidone)s.[28]

Table 2: Synthesis of polyurethanes from equimolar ratio of cyclic bisiminocarbonate **6** and dithiols **8a-c** by step-growth copolymerization. Conditions: C = 0.7 M, DMSO (dry), 80 °C, 24 h
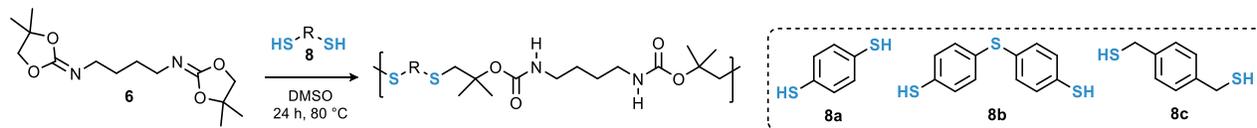
Entry	Polymer	Dithiol	Drying method	$M_n{}^a$ (g/mol)	$M_w{}^a$ (g/mol)	Đ	T_g (°C)[b]
1*	**P13**	**8a**	Molecular sieves (3 Å)	22,000	34,000	1.34	T_{g1} = -21 T_{g2} = 70
2	**P14**	**8b**	Molecular sieves (3 Å)	6,900	12,500	1.81	26
3	**P15**	**8c**	Molecular sieves (3 Å)	1,600	3,100	1.96	-25

[a] Apparent molar masses determined by SEC using DMF/LiBr as eluent (and a calibration of standards of PS) on crude polymers.
* The polymer was only partly soluble in DMF. Only the soluble fraction was analyzed by SEC
[b] Determined by modulated differential scanning calorimetry (heating ramp of 5 °C/min, amplitude = 1 °C, period of 60 seconds)

Conclusions

Herein, we investigated the use of cyclic iminocarbonates for the construction of unprecedented functional carbamates and regioregular polyurethanes by a ring-opening reaction with soft nucleophiles, including carboxylic acids and thiols. Through model reactions, we highlighted the remarkable selectivity in the ring-opening of the cyclic iminocarbonate by the nucleophile that occurred exclusively *via* the methylene site under catalyst-free conditions, both with carboxylic acids and thiols. We also illustrated the excellent functional group tolerance within carboxylic acids displaying an alkyl-, alkenyl-, acrylate-, pyrone-, ketone- or hydroxyl-moiety. Even in the latter case, no protecting group was needed to avoid side reactions with the hydroxyl moieties present on the carboxylic acid reactant. All carbamates were synthesized with a high conversion and selectivity (90-99%), opening new perspectives for the production of diversified functional carbamates from cyclic iminocarbonates that are perceived as masked isocyanates. The extension of the concept to difunctional precursors opened a fully atom economical route towards polyurethanes from dicarboxylic acids or dithiols by a facile step-growth copolymerization process. Regioregular PUs with M_w up to 15,000 g/mol (with succinic acid) or up to 34,000 g/mol (with 1,4-benzenedithiol) were successfully constructed, with an alternating urethane and ester or thioether linkage in the polymer backbone. However, one should take care to dry all reactants and solvents, especially carboxylic acids, as cyclic iminocarbonates were found highly sensitive to hydrolysis under acidic conditions. Current

work is devoted to explore the properties and applications of these novel polyurethanes. It has to be noted that, although iminophosgenes used for the synthesis of the cyclic iminocarbonates are toxic, sensitive to hydrolysis and poorly stable just as phosgene, a new methodology has recently been developed to prepare iminophosgene-free cyclic iminocarbonates.[29] Adaptation and optimization of these procedures for the preparation of bisiminocarbonates would therefore be highly desirable to give access to greener polyurethanes described in this work.

Experimental

Experimental protocols and additional products characterizations are provided in the supporting information section available free of charge on the website of the editor.

Conflict of interest

There are no conflicts of interest to declare.

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