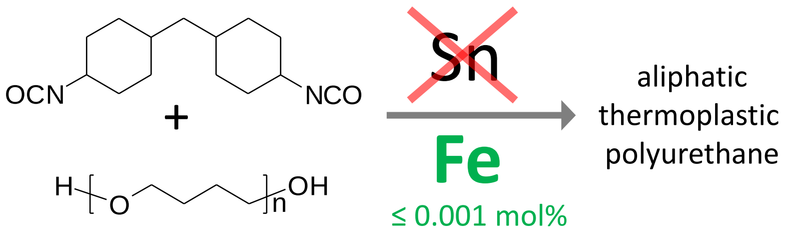
Graphical Abstract, Schellekens et al.



Short text for the Table of contents:

Iron compounds, such as $FeCl_3$, are highly active and temperature resistant catalysts for the solventless reaction of polyols with aliphatic diisocyanates to form thermoplastic polyurethanes.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Tin-free catalysts for the production of aliphatic thermoplastic polyurethanes

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Polyurethanes based on aliphatic isocyanates are of great interest for industrial applications that require UV-stability. To overcome the low reactivity of (cyclo)aliphatic diisocyanates a catalyst is usually added to accelerate urethane formation. In most applications, organotin-based compounds are used; however, due to growing concerns about the toxicity of organotin compounds, their use is being restricted and the need for alternative catalysts is growing. This paper investigates the catalytic activity of several non-tin catalysts in the formation of (poly)urethanes based on cycloaliphatic diisocyanates. Initial screening in a small-scale solvent-free model system under mild conditions shows that several Lewis acid catalysts remain highly active at very low concentrations. Additional screening in a 40 g polymer system under harsher conditions demonstrates that Fe(III)-based compounds, in particular $FeCl_3$ may serve as viable alternatives to the currently used organotin compounds.

Introduction

Ever since their discovery by Otto Bayer in the 1930s[1-3], polyurethanes (PU) have gained increasing interest from industry due to the wide array of products that can be made from them, ranging from soft foams for automotive and building applications to hard wear-resistant materials used in sports articles and industrial applications. The versatility of polyurethanes can be attributed to the large number of monomers available, which in turn results in products with different physical and chemical properties.

The main reaction taking place during polyurethane formation is the polyaddition of alcohols and isocyanates. To accelerate this reaction, one or more catalysts may be added, depending on the desired end product[2]. Usually, catalysts for urethane formation are subdivided into two main categories: metal-based catalysts, typically accelerating the gelling reaction between isocyanate and alcohol, and (tertiary) amine-based catalysts, mostly used at 1-2 mol % in foaming reactions as these catalysts also promote the isocyanate-water reaction[4-5]. Research into organocatalytic PU formation was revived by a recent report on the use of sulphonic acid catalysts for PU formation[6]. In this paper, the focus is on the first group of metal-based catalysts, in particular on alternatives for the widely used organotin catalysts. The latter provide very short reaction times for the isocyanate-hydroxyl reaction when used under typical industrial processing conditions. A broad range of organotin catalysts is available, allowing the polyurethane chemist to select the optimal catalyst for each application, e.g. delayed-action catalysts with thioglycolate ligands, or hydrolytically stable mercaptide-based catalysts for water-blown foam applications. However, due to the high stability of the covalent alkyl-tin bond against hydrolysis and both thermal and oxidative degradation, organotin compounds may end up in the environment[6]. Their toxicity depends on several factors, the number of alkyl groups on Sn being the most important one. Both di- and in particular trisubstituted compounds display the highest toxicity. Apart from the degree of alkyl substitution, the toxicity also depends on the length of the alkyl side chain, with increasing toxicity for shorter side chains. As a consequence, research efforts are being conducted towards finding alternative catalysts for the urethane formation.

Zr catalysts with 2,4-pentanedionate (acetylacetonate; acac) ligands have been proposed for crosslinking reactions in coating applications, using a trimerized aliphatic diisocyanate[7]. It was found that alkyl substitution on C1 and C5 of the acac-backbone led to an improved catalytic activity, as measured by the gelling time of the reaction mixture under mild conditions (62 °C) in a solvent mixture (butyl acetate/xylene). Due to the sensitivity to moisture of the Zr-compounds, it was suggested to use a large excess of 2,4-pentanedione to protect the catalyst against hydrolysis. Additional research[8] on the catalytic activity of acetylacetonate salts of Cr(III), Fe(III), Cu(II) and Sn(II) showed a difference in activity depending on the NCO:OH ratio and the polyol type (polyether *vs.* polyester). For an NCO:OH ratio of 1, DBTDL, $Sn(acac)_2$ and $Cr(acac)_3$ appeared to be the most active catalysts. The reactions were carried out under mild conditions (30 °C) in acetone, using 1 – 2 mol% of catalyst. Patents by Hofacker et al. [9-10] suggest the use of 0.12 mol% of rare earth (Ho, Er, Yb, Lu) acetylacetonate salts as catalysts for PU formation, using an aliphatic isocyanate (isophorone diisocyanate, IPDI) in mild solvent-free conditions (60 °C; 2 h).

An entirely different catalyst type was proposed by Bantu et al. [11-12], using CO_2 and metal (Zn, Mg, Al) adducts of N-heterocyclic carbenes (NHCs) under mild conditions (0.004 mol% catalyst; 65 °C; reactants in butyl acetate). The newly synthesized catalysts proved very promising as delayed-action catalysts, combining the catalytic power of the NHC as such with a traditional Lewis acid catalyst. More recently, MoO_2Cl_2 and its DMF adduct were shown to be active in synthesis of mono- and oligocarbamates under mild conditions (0.1 – 1.0 mol% catalyst; room temperature; 2 h maximum) in solution[13-14].

Summarizing, while several alternatives to organotin catalysts have been proposed, most of these have been tested in solvents, using monofunctional reactants. Few have actually been evaluated at very low concentrations and elevated temperatures, which are the typical process requirements for applications.

In this paper the catalytic activity of tin-free catalysts in a solvent-free reaction between a cycloaliphatic diisocyanate and several alcohols is investigated. Such conditions exclude any possible solvent effects that may affect the reactivity of the isocyanate in particular. An initial screening, using a monofunctional alcohol, uncovers several tin-free catalysts that remain highly active at very low concentrations (0.001 mol% of catalyst per mol hydroxyl groups) under mild temperature conditions. Based on this screening a selection of catalysts is then subjected to additional testing in a more realistic polymeric setup, using a mixture of diols and diisocyanate at autogenous temperature. Finally, the thermal robustness of the catalysts is evaluated by preheating the catalyst stock solutions prior to using them in the actual polymerization.

Results and discussion

Screening in 1-butanol

In a first screening stage, the catalytic activity of the metal compounds was tested in a small-scale solvent-free setup, using an aliphatic diisocyanate (methylene-bis-4,4'-(cyclohexylisocyanate), $H_{12}MDI$) and a monofunctional alcohol (1-butanol), maintaining an NCO:OH ratio of 1 (Scheme 1). In order to perform the screening in a relatively quick and safe way, Near Infrared spectroscopy was applied.

Concentration series of each individual reactant were made by dissolution in THF. THF is preferred, as it is able to dissolve both reactants and the urethane product, and has moreover an open spectral window in the regions of interest. Figure 1 shows the NIR spectra in the 4000 – 7500 cm^{-1} region for a concentration series of 1-butanol (Fig. 1a) and $H_{12}MDI$ (Fig. 1b), both corrected for a THF blank. The 1-butanol concentration series clearly shows an increase in absorbance at 4880, 6370 and 6800 cm^{-1}, while $H_{12}MDI$ displays characteristic bands at 5200, 5570 and 5700 cm^{-1}. To assess the effect of urethane formation on the spectra, two reaction mixtures containing a 1:2 molar mixture of $H_{12}MDI$ and 1-butanol were heated for 15 min at 60°C, either in the absence of a catalyst, or in the presence of dibutyl tin dilaurate (DBTDL; 0.1 mol% with respect to 1-butanol).

When comparing the spectra of the uncatalyzed mixture with those of the sample containing 0.1 mol% of tin catalyst (Figure 1c) it is clear that the hydroxyl-alkyl combination band ($\nu_{O\text{-}H}$ + $\nu_{C\text{-}H}$; 6800 cm^{-1}) and the isocyanate:alkyl combination band ($\nu_{N=C=O}$ + $\nu_{C\text{-}H}$; 5200 cm^{-1}) disappear; at the same time, a carbonyl:alkyl combination band ($\nu_{C=O}$ + $\nu_{C\text{-}H}$) appears at 4650 cm^{-1} as a result of urethane formation. Neither longer reaction

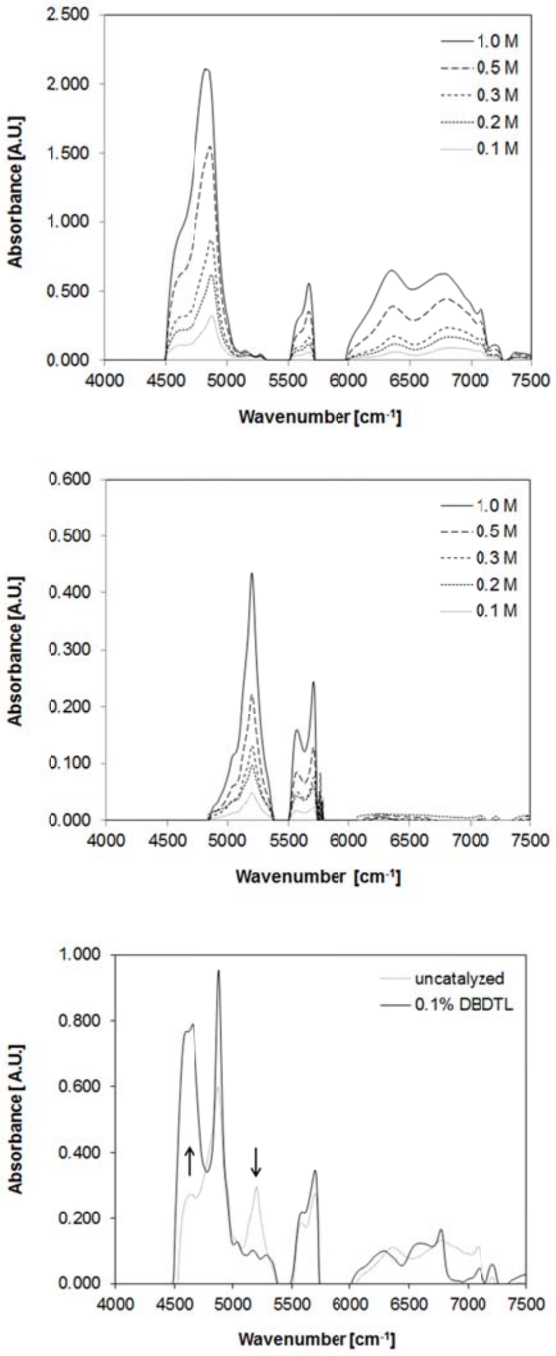
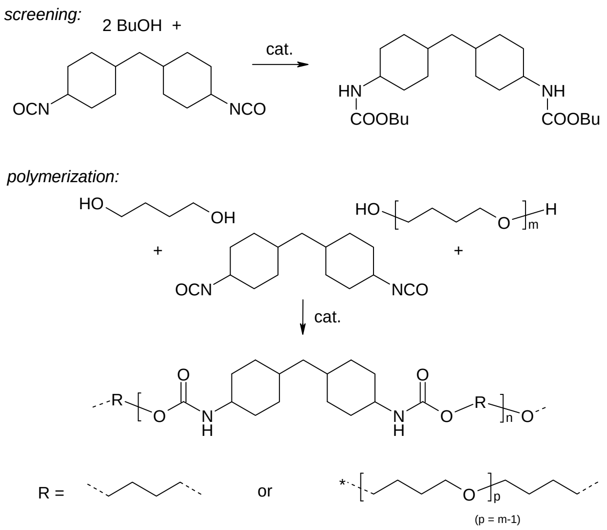


Fig. 1 NIR spectroscopy for monitoring urethane formation from of 1-butanol and $H_{12}MDI$. (a) concentration series (0.1 – 1 M) for 1-butanol; (b) concentration series (0.1 – 1 M) for H_{12}-MDI; (c) reaction mixture in the absence of a catalyst (dotted line) and reaction mixture containing 0.1 mol% of DBTDL as a catalyst. Peaks that are diagnostic for urethane formation and isocyanate consumption are marked.



Scheme 1

times, nor higher catalyst concentrations, nor higher temperatures resulted in any further changes of the spectrum for the DBTDL catalyzed reaction, implying that a reaction of 15 min at 60°C with 0.1 mol% DBTDL reaches essentially complete conversion, within the precision limits of the detection method. Therefore, the activity of a catalyst can be determined by measuring the absorbance of the sample at 4650 cm^{-1}, using the DBTDL-catalyzed reaction as the 100% conversion benchmark. While the NIR analysis only evidences urethane formation, detailed ^{1}H and ^{13}NMR studies have evidenced that under these conditions, urethane formation is effectively the only significant reaction. Ureas would only be formed when the water content of the reaction mixture is higher; allophanate and triisocyanurate formation would require much higher temperatures and an excess of isocyanate, which is not available in the stoichiometric screening reaction. The conversions (X) obtained with various catalysts are calculated using Equation 1 (see experimental section) and are listed in Table 1 below.

In selecting the candidate catalysts in Table 1, compounds with a suspected toxicity or with environmental hazards were excluded *a priori* (e.g., Cr, Ni, Co, Cd). This narrows down the potentially suitable metals to some elements from groups III and XII, to early transitions metals with the d^0 configuration, to middle transition metals with the d^5 configuration, or to rare earths. As the catalysts are eventually to be used in a concentration range below 100 ppm in the finished polymer, their performance at high dilution is an important criterion. While DBTDL is able to reach complete or near-complete conversion at 0.1 and 0.01 mol%, conversion is incomplete at 0.001 mol%. Stannous octoate, which is an industrially widely used Sn(II) compound, is clearly less active than the Sn(IV) compounds DBTDL and UL-22. Several non-tin catalysts offer an alternative to catalyze the urethane formation under these mild reaction conditions, the most active catalysts being soluble diketonate compounds of Fe(III), Zn(II), Ga(III), Zr(IV) and Hf(IV). However, not all di-, tri- or tetravalent cations give rise to suitable catalysts: acetylacetonate-based catalysts like $Ru(acac)_3$, $Al(acac)_3$ and $In(acac)_3$ show negligible activity, while others such as $Fe(acac)_3$, $Zn(tmhd)_2$ and $Mn(acac)_2$ remain highly active even at very low concentrations.

Table 1 Conversions (X, %) for tested catalysts. [a]

Catalyst	X, % [b, c]		
	0.1	0.01	0.001
DBTDL	100	96	32
$Sn(octoate)_2$	99	28	-
UL-22 [d]	100	99	50
$Mn(acac)_2$	96	93	73
$Fe(acac)_3$	95	94	90
$Fe(tmhd)_3$ [e]	100	100	98
$FeCl_3$	91	90	14
$Ru(acac)_3$	5	-	-
$Ti(^{i}OPr)_2(acac)_2$ [f]	91	81	69
$Zr(acac)_4$	95	92	68
$Hf(acac)_4$	100	96	82
$Al(acac)_3$	2	-	-
$Ga(tmhd)_3$ [e]	100	100	51
$In(acac)_3$	93	40	-
$Zn(acac)_2$	98	39	-
$Zn(tmhd)_2$ [e]	99	95	68
$ZnCl_2$	53	12	-
$Zn(OTf)_2$ [g]	67	13	-
$Sc(OTf)_3$ [g]	37	-	-
$La(OTf)_3$ [g]	41	-	-
$Fe(OTf)_3$ [g]	84	28	-

[a] General reaction conditions: 1.31 g H_{12}-MDI, 0.74 g 1-butanol, 15 min, 60°C. [b] Conversion X calculated based on reactions without catalyst and with 0.1 mol% DBTDL as references for 0% and 100% conversion; additional dilutions tested only if conversion at 0.1 mol% (or 0.01 mol %) was 50% or more. [c] concentration in mol%, mol catalyst per mol hydroxyl. [d] Fomrez® UL-22 = bis(dodecylthio)dimethyl tin (CAS 51287-84-4) [e] tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionate. [f] ^{i}OPr = isopropoxide. [g] OTf = trifluoromethanesulfonate ($CF_3SO_3^-$).

While the cation choice seems to have the largest impact, there are some clear trends for the ligand as well. Thus, significantly better results are obtained with $Fe(tmhd)_3$ in comparison with $Fe(acac)_3$, with 98 vs. 90 % conversion at 0.001 mol %. While it might prove difficult to disentangle electronic, steric and solubility effects, it should be remarked that the reaction mixture containing the diisocyanate H_{12}MDI is rich in aliphatic moieties, and $Fe(tmhd)_3$ with its 18 methyl groups around the metal ion, is likely to be mixed very well into the H_{12}MDI background. Similarly, $Zn(tmhd)_2$ is at high dilution more performant than $Zn(acac)_2$. Diketonates in general give much better performance than triflates, proving that many other factors are at play than just creating open coordination sites on the metal ion. Thus, Zn triflate even at 0.01 % gives little conversion. Similar poor performance is noted for trivalent triflates of La, Sc and Yb, despite the well-known Lewis acid character of these compounds.[16]

Catalyst activity in polymer system

In a next testing stage, the highly active catalysts from the system with a monofunctional alcohol are tested in a more realistic polymer system, using a mixture of both long and short chain diols (Scheme 1). The molar ratio of poly(tetramethylene)glycol (PTMEG) and 1,4-butanediol is decisive for the eventual physical properties of the polymer: increasing the 1,4-butanediol content generally gives more rigid materials, while mixtures rich in PTMEG lead to softer, more elastic materials. In the present experiments, 1,4-butanediol accounts for 55.3 % of the hydroxyl groups. As a most direct expression of the progress of the polymerization, the reaction is monitored by following the temperature of the mixture as the exothermic polymerization ($\Delta_r H$ = 84 kJ mol^{-1}) proceeds. When comparing the temperature profiles of an uncatalyzed system and a system with 0.1 mol% DBTDL (Figure 2), it is clear that – under the given reaction conditions – a large temperature increase is observed for the catalyzed system as a result from the urethane formation. The temperature reached is indicative for the eventual conversion level reached, while steeper slopes correspond to faster reactions.

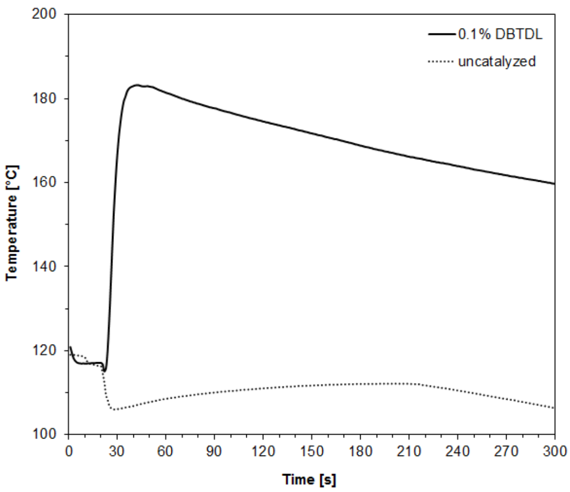


Fig. 2 Exotherm profiles of uncatalyzed *vs.* catalyzed (0.1 mol% DBTDL) reaction mixtures. Sequential addition of BDO/catalyst (80 °C) and $H_{12}MDI$ (80 °C) to PTMEG-1000 (120 °C) under constant stirring (400 rpm).

Effect of catalyst concentration and catalyst type on exothermic profile

As an extrusion process is typically used to make TPUs on industrial scale, the homogeneous catalyst is not separated or recycled from the solid polymer. For these reasons, it is a prerequisite that the catalyst is highly active at very low concentrations. In order to evaluate the catalytic activity at such low concentrations, additional dilutions of the catalyst solution were prepared and tested per the standard protocol. As expected, the generated reaction heat becomes less pronounced for lower catalyst concentrations as shown in Figures 3 and 4 for DBTDL and $Fe(acac)_3$, respectively.

When lowering the catalyst concentration to 0.001 mol% the difference between DBTDL and $Fe(acac)_3$ becomes very pronounced. While DBTDL seems to lose most of its catalytic activity (Figure 3), $Fe(acac)_3$ remains highly active. Even at extremely low concentrations of 0.00025 mol% polymerization takes place, albeit to a clearly smaller extent as the reaction mixture is still liquid after 5 minutes (Figure 4). A hypothetical explanation for this remarkable difference in activity may be that DBTDL is more susceptible to hydrolysis than $Fe(acac)_3$ as trace amounts (up to 100 ppm) of water may be present in the 1,4-butanediol, which is also the case in a typical industrial production environment.

Figure 5 provides an overview of the exothermic profiles of a selection of catalysts at 0.001 mol% concentration. Upon comparing both organotin catalysts, the hydrolytically more

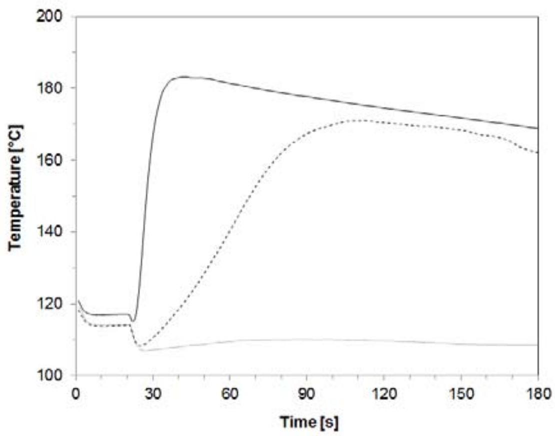


Fig. 3 Effect of DBTDL concentration on exotherm profile: 0.1 mol% (full); 0.01 mol% (dashed) and 0.001 mol% (dotted). Sequential addition of BDO/catalyst (80 °C) and $H_{12}MDI$ (80 °C) to PTMEG-1000 (120 °C) under constant stirring (400 rpm).

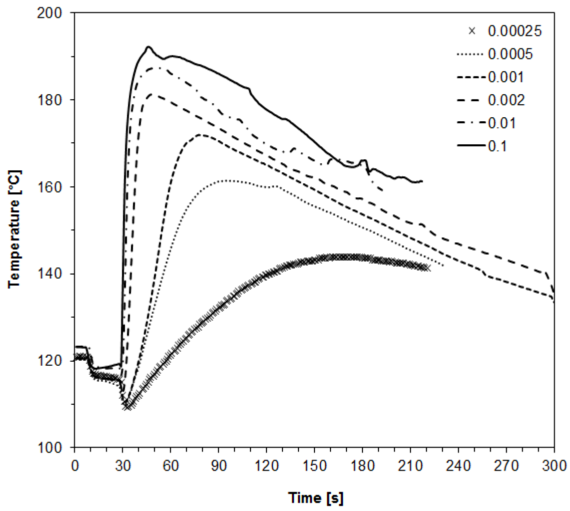


Fig. 4 Effect of $Fe(acac)_3$ concentration (mol%; catalyst per hydroxyl) on exotherm profiles. Sequential addition of BDO/catalyst (80 °C) and $H_{12}MDI$ (80 °C) to PTMEG-1000 (120 °C) under stirring (400 rpm).

stable UL-22 greatly outperforms DBTDL, which is unable to form a solid polymer within a predetermined 3 minute time frame. Taking a closer look at the non-tin catalysts, it is clear that the Fe(III)-based compounds manage to maintain their activity at this very low concentration, whereas other acetylacetonate-based catalysts such as $Mn(acac)_2$, $Zr(acac)_4$ and $Hf(acac)_4$ show a negligible activity, despite their high catalytic activity in the initial screening. This significant loss in activity may be attributed to the catalyst proneness to hydrolysis, which has already been documented for Zr-diketonates[7]. Another possible explanation may be the sensitivity of the catalyst to the harsher reaction conditions, causing partial detachment of the ligand and subsequent catalyst deactivation by cluster formation with minute amounts of water or carboxylate impurities in the reaction mixture.

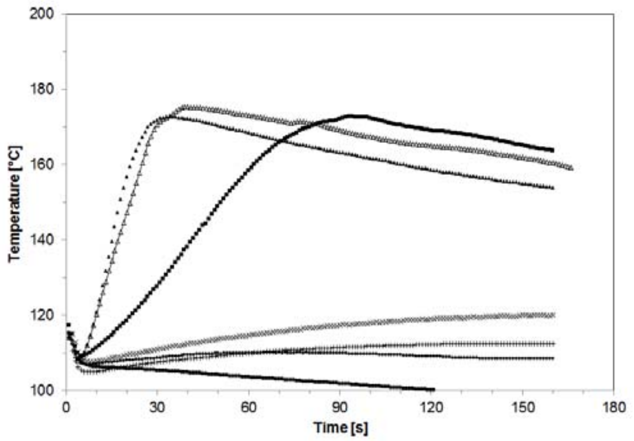


Fig. 5 Effect of catalyst on exotherm profile, at 0.001 mol% catalyst on total hydroxyl basis. DBTDL (◆); UL-22 (■); Fe(acac)$_3$ (▲); Mn(acac)$_2$ (✕); Hf(acac)$_4$ (+); Zr(acac)$_4$ (●); $FeCl_3$ (-▵-). Sequential addition of BDO/catalyst (80 °C) and H_{12}MDI (80 °C) to PTMEG-1000 (120 °C).

Thermal robustness of the catalysts and their effect on molecular weight of the polymer

As the catalysts are eventually to be used under typical TPU processing conditions, thermal stability of the compound is of paramount importance as temperatures of 200 °C and higher are not uncommon in a standard extrusion process. To assess the thermal robustness the BDO/catalyst mixture was preheated at 180 °C for 30 minutes after which the catalyst solution was used as per standard procedure. It is clear from Figure 6 that the catalytic activity of Fe(acac)$_3$ undergoes a tremendous decrease after this harsh thermal pretreatment. A possible explanation is that the acetylacetonate ligands are unable to maintain their protective role under these conditions, causing deactivation of the central Fe-ion, most likely by oxyhydroxide cluster formation. This decrease in catalytic activity is translated into a massive drop in the molecular weight (Table 2).

Taking a closer look at the $FeCl_3$ exotherms, it is clear that this catalyst is much less susceptible to deactivation by the same thermal pretreatment. The ability of the catalyst to withstand deactivation by heat is also reflected in the fact that the molecular weight of the polymer remains the same (within the experimental margin of error). We hypothesize that one or more of the chloride anions stay bonded on the iron atom, maintaining its catalytic activity and protecting it from degradation by heat.

When subjecting the hydrolytically stable tin catalyst UL-22 to the same preheating procedure, the exotherms show only a moderate decrease in catalytic activity. This thermal robustness may result from a combination of the strong alkyl-tin bonds (two methyl groups for UL-22) and the long aliphatic dodecylthio side chains, providing additional strong sulphur-metal bonds. However, some deactivation seems to take place as the molecular weight obtained is distinctly lower when using the preheated UL-22 sample than using the freshly prepared catalyst solution. DSC measurements showed that polymers produced using either UL-22 or $FeCl_3$ displayed similar T_m (peaks at 178-180°C) and T_g (peaks around -55, -50°C).

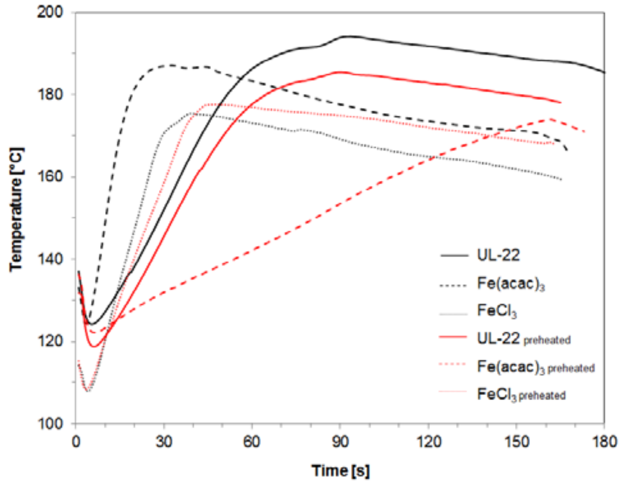


Fig. 6 Effect of preheating on catalytic activity of UL-22 (full line), Fe(acac)$_3$ (dashed line) and $FeCl_3$ (dotted line). Sequential addition of BDO/catalyst (80 °C) and H_{12}MDI (80 °C) to PTMEG-1000 (120 °C). Catalyst concentration of 0.001 mol%.

Table 2 Molecular weights of formed polymers with and without thermal pretreatment of the catalyst stock solutions

Catalyst [a]	M_w (x1000 g . mol^{-1}) [b] no preheating	preheating [c]
Fe(acac)$_3$	19	4
$FeCl_3$	59	56
UL-22	63	49

[a] 0.001 mol% catalyst per mol hydroxyl groups. [b] Determined by GPC based on polystyrene (PS) standards. [c] Catalyst stock solution preheated for 30 min at 180 °C.

General discussion and conclusion

In our search for non-toxic, tin-free catalysts several compounds were initially found to be very active at very low concentrations (down to 0.001 mol%) in a model reaction with 1-butanol at 60°C. A more detailed study offered some insight into the complexity of the effects of both ligand and metal center on the catalytic activity. As evidenced by the varying activities of several Zn(II) and Fe(III) compounds, it is clear that both parameters play an important role. As for the anion, comparison between triflates and acetylacetonates of the same metals clearly showed a much lower activity for the weakly-coordinating triflates, suggesting that a strongly coordinating ligand greatly aids in improving and maintaining the catalytic activity.

Additional screening in a 40 g polymer formulation indicates that several inorganic compounds are able to enhance the formation of thermoplastic polyurethane. It is remarkable that several highly active compounds from the 1-butanol screening – such as Zr(IV), Hf(IV), Zn(II), Mn(II) salts – fail to display the same activity at low concentrations in the polymeric system. Given the harsher reaction conditions (120 – 180 °C), this may be an indication that thermal stability and catalyst deactivation also play a significant role.

After submitting several catalyst stock solutions to a severe thermal pretreatment, the importance of the thermal robustness of the catalyst became even more obvious. $FeCl_3$ remains highly active even after the severe thermal pretreatment, resulting in a TPU with a molecular weight within the same range as obtained with the tin-based UL-22. Gratifyingly, at the very low effective concentrations (e.g. 0.001 mol%), the Fe catalyst hardly confers any colour to the polymer product. At the same time, the commonly used DBTDL appeared unable to accelerate the reaction at very low catalyst concentrations.

Experimental

Materials

Methylene-bis-4,4'-(cyclohexylisocyanate) ($H_{12}MDI$) was purchased under its trade name Desmodur® W from Bayer AG. 1-Butanol, tetrahydrofuran (THF), 1,4-butanediol (BDO) and poly(tetramethylene)glycol (PTMEG-1000; MW 1000 g/mol) were purchased from Sigma-Aldrich. All reactants and solvents were used as received from the respective suppliers. The catalysts were purchased from Sigma-Aldrich and Strem, and were used as received. As $H_{12}MDI$ has a very low vapor pressure under ambient conditions, any manipulations involving unreacted isocyanate were performed in a fume hood to minimize exposure to possible vapors.

Standard procedure for screening in 1-butanol

First, a stock solution of the catalyst in 1-butanol is prepared by weighing 10 – 100 mg of catalyst (depending on the molecular weight of the catalyst) in a 12 ml crimp-cap vial, followed by adding 2 – 5 g of 1-butanol to obtain a mixture with a concentration greater than 0.1 mol% (catalyst per hydroxyl functional group). The catalyst:butanol mixture is stirred and heated if necessary (< 80 °C) to ensure complete catalyst dissolution. From this stock solution a series of 3 dilutions is prepared (0.1, 0.01 and 0.001 mol% catalyst).

Next, a magnetic stirring bar is placed in a 22 ml screw-cap vial after which 1.31 g (5 mmol; 10 mmol NCO functional groups) of $H_{12}MDI$ is added. Subsequently, 0.74 g (10 mmol) of 1-butanol containing the catalyst is added to the $H_{12}MDI$ after which the vial is placed in a heating block at 60 °C. After 15 minutes, the vial is taken out of the heating block, placed on ice for 5 minutes to stop the reaction, and 5 ml of tetrahydrofuran (THF) is added to dissolve the formed product. The clear solution is then transferred to a quartz cuvette for NIR analysis. All NIR-spectra are recorded using a Varian Cary5000 spectrophotometer. The absorbance at 4650 cm^{-1} of a blank sample without catalyst ($A_{\mathrm{uncatalyzed}}$) serves as the 0 % benchmark, while the absorbance of a sample containing 0.1 mol% of DBTDL (A_{DBTDL}) is used as a 100 % reference. Conversions X are calculated using equation 1:

$$X = \frac{A_{sample} - A_{uncatalyzed}}{A_{DBTDL} - A_{uncatalyzed}} \qquad (1)$$

Standard procedure for screening in polymer system

Prior to the actual polymerization, a catalyst stock solution is prepared by dissolving 5 – 20 mg catalyst in 5 – 10 g of 1,4-butanediol (BDO). This stock solution is subsequently diluted with BDO until the desired concentration is obtained. Next, 2.84 g of this diluted catalyst-in-BDO solution is weighed in a crimp cap vial, after which the vial is capped and placed in a heating block at 80.0 ± 0.5 °C. Next, 14.32 g of $H_{12}MDI$ is weighed in a 22 ml screw cap vial, after which the vial is closed and placed in the same heating block at 80 °C.

23.76 g of PTMEG-1000 was weighed in a tin can, which served as an open reactor, and heated to 120 °C, while being stirred continuously at 400 rpm using an IKA Eurostar power control-visc overhead stirrer equipped with a 3-blade 45 mm diameter stainless steel R1381 propeller stirrer. As soon as the PTMEG-1000 reaches a temperature of 120 °C, the heated BDO/catalyst solution is added to the reactor by pouring from the vial; immediately after adding the BDO/catalyst solution, the heated $H_{12}MDI$ is added to the reactor by emptying the vial. The temperature change of the reaction is then monitored *in situ* by a Testo temperature probe connected to a laptop on which the Comfort Software X35 has been installed. After 3 minutes of reaction the stirrer is turned off and the reaction mixture is poured out onto a cooled Teflon plate.

The final monomer composition was 53.1 mmol $H_{12}MDI$, 29.3 mmol BDO and 23.8 mmol PTMEG-1000, with relative errors on the quantities below 0.5 %. The highly reproducible nature of the procedure was confirmed by repetitions of a standard procedure using 0.001 mol% DBTDL.

Molecular weights of the polymers were determined using Gel Permeation Chromatography (GPC) on a Shimadzu 10A GPC. All samples were analyzed over a PLgel 5 µm mixed-D column using a Refractive Index Detector (RID); the final molecular weight was determined based on a polystyrene (PS) standard. 5 mg of TPU was dissolved in 2 ml THF and allowed to dissolve completely, which may require overnight stirring. Prior to injecting on the GPC, the sample was filtered over a 0.45 µm Teflon filter.

Acknowledgements

The authors would like to thank IWT Flanders and the Lubrizol Corporation for the financial support.

Notes and references

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