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Low temperature amino-based catalyst activation for on-demand polyurethane synthesis

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Thermo-latent catalyst for the “on-demand” PU synthesis

Keywords

Polyurethane, latent catalyst, activation, organic catalyst

Abstract

A new latent catalyst, based on 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), has been specifically designed to be thermally deprotected at low temperature. More generally, specific isocyanurates based on the reaction of two substituted isocyanates and DBN are used as pre-catalyst for polyurethane synthesis. The activation temperature of the pre-catalysts is determined by DSC and resulting free catalysts activity is demonstrated through a catalysis cycle on a PU model reaction.

Introduction

For almost a century, the synthesis of polyurethane never stops to be studied and their field of application continues to widen.^{1,2} Discovered by Bayer and co-workers in 1937,³ the reaction

between a diisocyanate and a diol (typically a polyester diol) catalyzed by a metal/amine couple allows to design polymers ranging from thermoplastics with tailored mechanical properties to functional foams thanks to the multitude of available substituents.^{4,5} The main advantage of the use of isocyanates is their high reactivity even at low temperatures or in highly viscous systems, ensuring a rapid conversion.⁶ For some industrial application, this high reactivity can also be a major drawback since specific applications need latency in order to allow delivery and shaping of the mixture into a mold or template. In this perspective, some strategies appear in the literature based on blocked isocyanate,⁷ or on catalyst modification⁸ with the aim to design a stimuli-responsive mixture able to switch on the polymerization by simple external request. In an industrial context, the catalyst modification appears as the most promising strategy because the lower quantity used and, de facto, the lower cost involved.

A strategy described by Landais and coworkers consists in the use of two equivalents of monoisocyanate to mask the aminated co-catalyst through the formation of an isocyanurate derivative.⁹ They observed cleavage temperature from 69°C to 176°C depending on amine and isocyanate nature and from 72°C to 162°C only focusing on the 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) amine.

Based on this approach we performed polyurethane (PU) synthesis by working with selected functionalized isocyanate in order to decrease the cleavage temperature. In this perspective, amine has been fixed on DBN^{10,11} and electronically attractive groups are added to isocyanate structure in order to decrease the strength of the C-N bonds of isocyanurate moieties (Figure 1, 4a-c). In addition to the simplest aromatic isocyanate, two chemical groups such as nitro and fluoride were selected because of their -M effect and high intrinsic electronegativity, respectively (Figure 1, compounds 1-3).

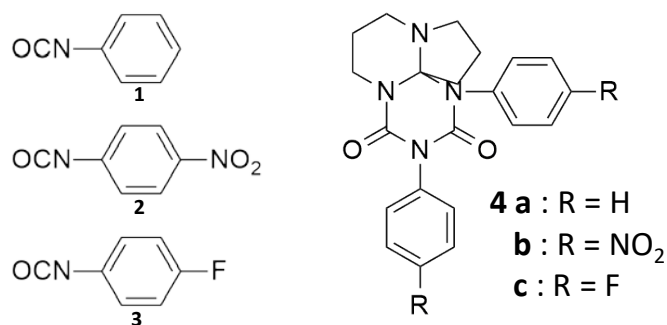


Figure 1: Isocyanates used (1-3) for the synthesis of isocyanurate derivative pre-catalysts (4a-c)

Experimental

Materials

Isocyanates including phenylisocyanate (99%, Acros Organics), 4-nitrophenylisocyanate (97%, Sigma Aldrich) and 4-fluoroisocyanate (99% Acros Organics), were used directly as received. 1,5-Diazabicyclo[4.3.0]non-5-ene (98%, DBN) was used as received from ABCR. Toluene was received from Sigma Aldrich, dried under polystyryllithium seeds and distilled prior to use. Hydroxy-telechelic polybutadiene (HTPB) and 4,4-dicyclohexylmethane diisocyanate (MDCI, 90%) were purchased from Sigma Aldrich and used directly as received.

Instruments

NMR: ¹H NMR spectra were recorded on a Bruker AC-400 spectrometer in appropriate deuterated solvents. All ¹³C measurements were performed at 298 K on a Bruker Avance III 400 spectrometer operating at 100.7 MHz. To describe the multiplicities of the signals, the following abbreviations were used: s: singlet, bs: broad signal, d: doublet, t: triplet, q: quartet, m: multiplet.

DSC: Differential scanning calorimetry analyses (DSC) were carried out on a DSC Q100 LN2 TA Instrument. The DBN derivatives (10 mg) were heated from -50 °C to 150°C at a rate of 10 °C.min⁻¹. The instrument was calibrated with indium sample.

FT-IR: Fourier transform infrared spectra were recorded using a Bruker FT-IR spectrometer (Vertex 70) in transmission mode using ATR equipment. All spectra were recorded between 400 to 4000 cm^{-1} , with a resolution of 4 cm^{-1} and 64 scans. To compare samples, the same baseline correction was used and the spectra were normalized to the signal at 2930 cm^{-1} , which was not affected by the chemical modifications. The isocyanate band at 2280 cm^{-1} was selected to determine the conversion. The calculation of conversion is obtained as follow: t_0 is admitted as 0% conversion and the baseline as 100% conversion. The ratio of the peaks area leads to the conversion for each sample.

Synthesis of precatalyst 4a-c: A solution of 15 mmol of DBN in 15 mL of dry diethyl ether was added drop-wise to an ethanol-cooled solution (-30 °C) of 30 mmol of the selected isocyanate in 40 mL dry toluene. The solution was stirred for 24 h at room temperature. After removing the solvent at 25°C under vacuum for 12h, targeted products 4a, 4b and 4c were obtained in yields ranging from 76 to 84% and stored at 4°C.

NMR (CDCl_3 , δ ppm): 4a, ^1H : 7.2-7.4 (m, Ar, 10H), 4.3 and 3.1 (dd, N- CH_2 , 2x1H), 2.9 and 2.3 (dd, N- CH_2 , 2x1H), 2.7 (m, - CH_2 -, 4H), 2.9 (m, - CH_2 -, 2H), 2.9 and 2.3 (dd, - CH_2 , 2x1H). ^{13}C : 151, 152, 147, 148, 128-130 (Ar), 92, 50.5, 48.5, 47.5, 34, 19.8, 21.5.

4b, ^1H : 7.1-7.3 (m, Ar, 4H), 4.3 and 3.1 (dd, N- CH_2 , 2x1H), 2.9 and 2.3 (dd, N- CH_2 , 2x1H), 2.7 (m, - CH_2 -, 4H), 2.9 (m, - CH_2 -, 2H), 2.6 and 2.3 (dd, - CH_2 , 2x1H). ^{13}C : 151, 152, 147, 148, 128-130 (Ar), 92, 50.5, 48.5, 47.5, 34, 19.8, 21.5.

4c, ^1H : 6.9 -7.3 (m, Ar, 4H), 4.3 and 3.1 (dd, N- CH_2 , 2x1H), 3.0 and 2.5 (dd, N- CH_2 , 2x1H), 2.8 (m, - CH_2 -, 4H), 2.9 (m, - CH_2 -, 2H), 2.7 and 2.5 (dd, - CH_2 , 2x1H). ^{13}C : 151, 152, 147, 148, 128-130 (Ar), 92, 50.5, 48.5, 47.5, 34, 19.8, 21.5.

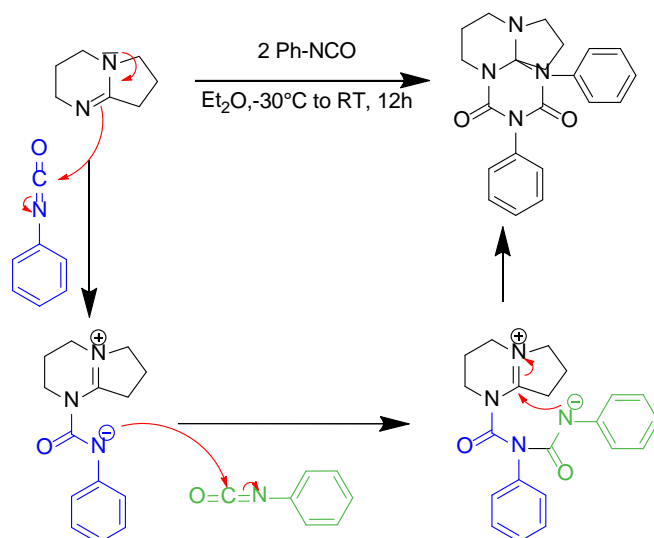
PU synthesis example: HTPB (10g) was put in a glass flask containing magnetic bar and was dried 1h at 70°C under high vacuum. MDI (1,17g) was then added and stirred for 10 min.

DBTL (0.1%) and catalyst 4b (0.5%) were then added and the mixture stirred at 20°C for 1h and then 6h at 60°C. Kinetic profile was followed by FT-IR analysis.

Results and discussion

The reaction of isocyanates with DBN proceeds immediately by the formation of a 2:1 adduct at room temperature (see experimental section). As the reaction is fast and exothermic, the pre-catalyst synthesis was carried out at low temperature to avoid side-reaction or premature cleavage reaction. The adducts were obtained with high yields around 80% and directly used without any purification step. The mechanism of this reaction was first described by Richter et al. and is illustrated in Scheme 1.^{12,13}

They suggested a two steps addition with the formation of zwitterionic intermediate. The first step consists in an addition of the DBN on the carbon of the isocyanate function of the first phenyl isocyanate moiety. The resulting zwitterionic intermediate is then added to a second phenyl isocyanate entity in order to form a second zwitterionic species. By an intramolecular cyclisation the anionic nitrogen is bonded to the sp² carbon of DBN to form the neutral isocyanurate moiety. This mechanism also illustrates the impossibility to directly use diisocyanate as masking agent as intermolecular side-reactions could not be avoided.



Scheme 1: Proposed mechanism for the formation of the 2:1 adduct between DBN and isocyanate moieties.^{12,13}

Pre-catalysts were fully characterized by ^1H and ^{13}C NMR on which all expected chemical shifts could be observed. Indeed, aromatics from isocyanate appears from 7 to 7.4 ppm on ^1H NMR spectrum and from 128 to 140 ppm on ^{13}C NMR spectrum in the same way that carbons characteristics to the C=O functions of the isocyanurate are identified around 152 ppm (Figure 2).

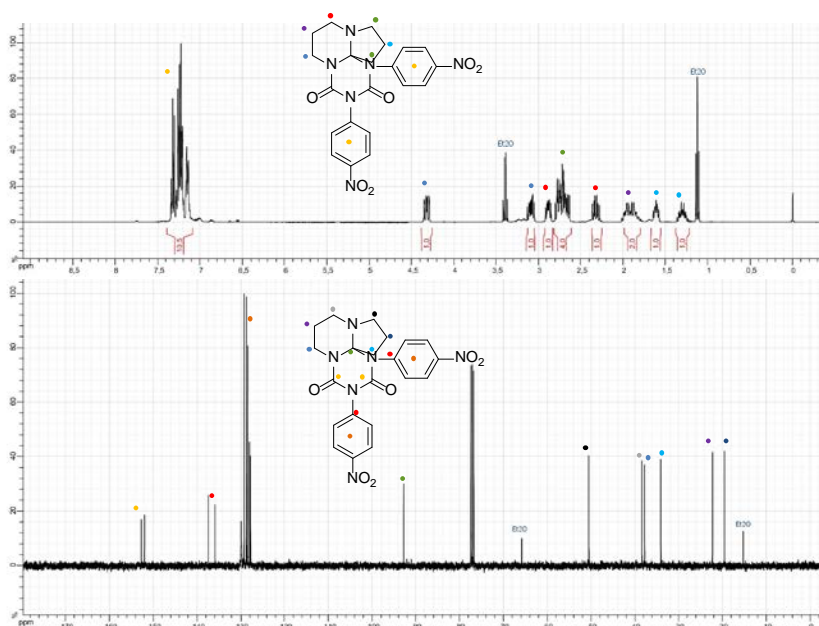


Figure 2: ^1H and ^{13}C NMR spectra of **4b** performed in CDCl_3

The cleavage temperature was then probed by differential scanning calorimetry analyses (Figure 3). The thermograms presented are therefore enlarged to the endothermic peak region. Thermograms of 4a-c showed peaks ranging from 60 to 90°C for pre-catalyst 4a, 10°C to 80°C for 4b, and 80 to 115°C for 4c. The optimums of these curves were considered as the cleavage temperature and were determined at 85°C for 4a, 46°C for 4b and 112°C for 4c, knowing that cleavage can occur below those temperatures.

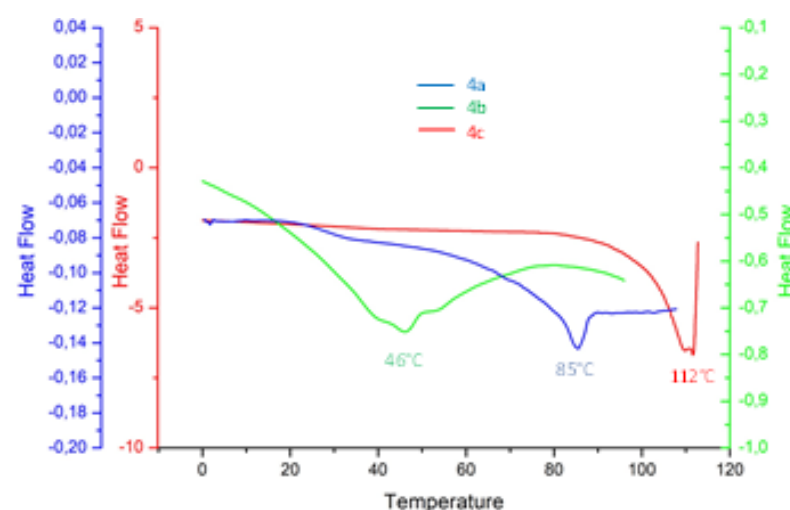


Figure 3: DSC curves (enlargement on the endothermic signal) of 4a (blue), 4b (green) and 4c red)

The range of cleavage temperature is in good agreement with the electronic effects induced by the chemical substituents in para of the isocyanate function with respectively $-H$, $-NO_2$. Concerning the fluoride substituent, the expected $-I$ inductive effect has been outperformed by the $+M$ mesomeric effect, leading to the higher cleavage temperature observed in this study.¹⁴ Thereby, the nitro group -which combined both inductive and mesomeric effects is the most efficient to decrease the cleavage temperature.

To illustrate the applicability of such an efficient system, pre-catalyst 4b –the most effective- was used to catalyse the polymerization of HTPB and MDI (Figure 4a). In line with

industrial processes bulk reaction using a small amount of tin derivative (0.1% of DBTL) was used. A low amount of latent aminated pre-catalyst (0.5%) was then added. The reaction was monitored using IR spectroscopy, regarding the disappearance of the signal of the isocyanate bond at 2280 cm^{-1} (Figure 4b). The reaction was first stirred at 20°C for 1 hour using 4b (grey line) to show its low catalytic activity in its masked form since only 5% of conversion was reached and as compared with the 40% conversion obtained with free DBN (yellow line) at the same temperature (Figure 4c). The mixture was then placed at 60°C in order to deprotect the aminated co-catalyst. A significant increase of the kinetic was observed since the conversion increased from 5 to 54% in the following hour, attesting the release of free DBN in the mixture. As a point of comparison, catalyst 4b in its masked form could only yield to low conversion (10%) after 5h (grey line), demonstrating again its poor activity. Conversely, free DBN (orange and red lines) exhibits a high reactivity at 20°C and even more at 60°C . The conversion vs time profile of 4b after 1h (blue line) is quite similar to the free DBN one at the same temperature (60°C).

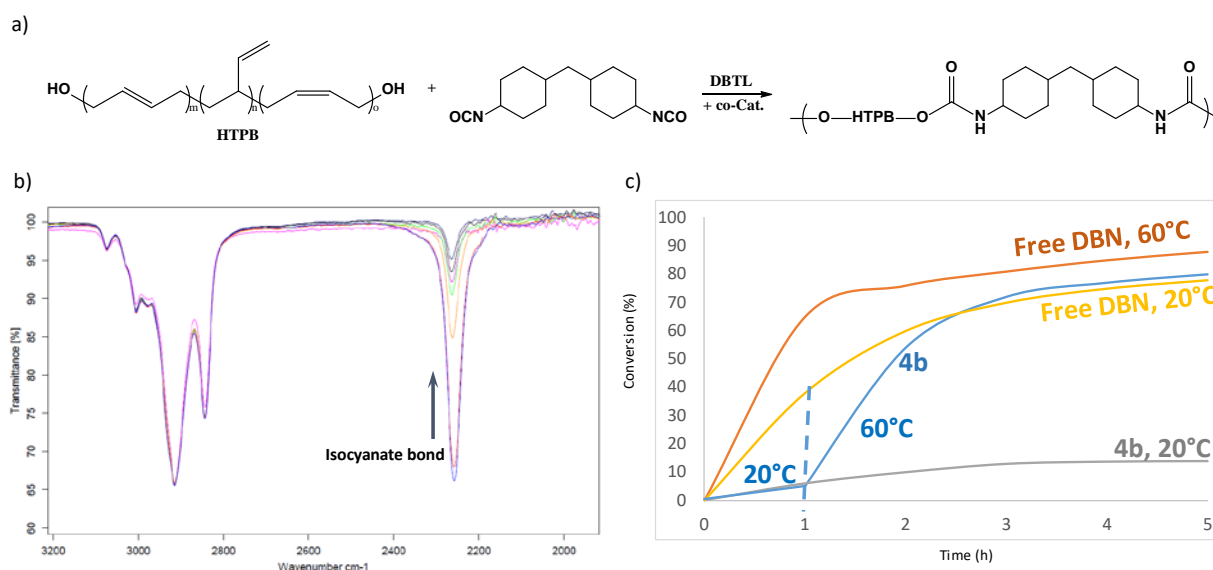


Figure 4: (a) Reaction studied (PU synthesis), (b) conversion measurement by FT-IR analysis and (c) conversion vs time profile of the HTPB/MDCI reaction performed using DBTL, for all systems, and unprotected co-catalyst (free DBN) at 60°C (orange) and 20°C (yellow), 4b co-catalyst at 20°C and 60°C after 1h (blue) and 4b at 20°C (grey).

Conclusions

New thermo-latent catalysts are used for the “on-demand” synthesis of polyurethanes. These compounds are easily prepared from DBN and two equivalents of substituted isocyanates. After storage at low temperature, they appear very efficient when reaching a certain temperature. The nitrophenyl-based isocyanurate co-catalyst was exhibiting the lower cleavage temperature starting at about 10°C. The thermo-latent characteristic was demonstrated through model reaction between HTPB and MDCI at 60°C by a poor catalytic activity of the masked catalyst at 20°C as compared to DBN-free system, and a high activity at 60°C.

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Figure Legends

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Graphical Abstract

