Electronic Supplementary Information

Identifying competitive tin- or metal-free catalyst combinations to tailor polyurethane prepolymer and network properties

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Determination of NCO-terminated prepolymers kinetics by infrared spectroscopy

To monitor the isocyanate consumption during the synthesis of NCO-terminated prepolymers between 4,4'-MDI, diol and triol pol(propylene glycol)s, infrared spectroscopy with ATR mode are used (Figure S1).

Due to the excess of isocyanate in the medium (NCO/OH ratio equal to 1.83), the following normalization of NCO consumption is used to determine the kinetics:

 $x = 1 - \frac{A(NCOt) - A(NCOf)}{A(NCO0) - A(NCOf)}$

With x represents the normalized area of the NCO peak at 2270cm⁻¹

A(NCO_t) the NCO peak area at time t

A(NCO_f) the NCO peak area at the end of the prepolymerization

 $A(NCO_0)$ the NCO peak area at the beginning of the prepolymerization $t_{=0}$

The difference kinetics can be compared due to the similar value of NCO peak area at $t_{=0}$ and $t_{=f}$ for all syntheses.

In our case, FTIR analysis is considered quasi-quantitative due to the homogeneity of our samples. This hypothesis has been verified by monitoring the evolution of NH urethane signal and CH in α position of urethane signal during the NCO-terminated prepolymerization synthesis by ¹H-RMN (Figure S2).

The satisfactory correlation between kinetics obtained by ¹H-NMR and FTIR confirmed that FTIR analysis is quasi-quantitative in our system (Figure S3).



Figure S1. Evolution of FTIR-ATR spectra of the reaction medium at different times during the prepolymerization stage catalyzed with Sn 6ppm



Figure S2. Evolution of ¹H-NMR spectra of the reaction medium at different times during the prepolymerization stage catalyzed with Sn 6ppm



Figure S3. Comparison of urethane formation kinetics during the prepolymerization stage in presence of Sn 6ppm monitored by ¹H-NMR and FTIR





Figure S4. Evolution of prepolymerization kinetics in function of metallic catalysts and their concentration compared to Sn 6ppm by FTIR analysis

This screening of catalyst amounts allowed us to adjust the kinetics in order to obtain similar kinetics as Sn 6ppm and compare the different catalyst activities.



Figure S5. ¹H NMR spectra of NCO-terminated prepolymers obtained with different catalysts in acetone-d6.

Calibration of SEC-THF for residual isocyanate titration

To independently synthesize this organic molecule di(MeOH)-MDI, 4,4'-MDI is quenched by an excess of anhydrous methanol at room temperature during one night. ¹H NMR spectra are recorded in DMSO_{d6} to confirm the structure of this quenched residual monomer.



Figure S6. ¹H NMR spectra of 4,4'-MDI quenched with anhydrous methanol for SEC-THF analysis.

In order to determine residual isocyanate, a titration of di(MeOH)-MDI was conducted to provide a relationship between the area of this peak by SEC-THF and the concentration of free MDI at the end of the prepolymerization stage. A solution of 1 mg/ml of 4,4-MDI quenched with methanol in THF and different volume of this solution are injected in the column of SEC-THF. The equation of the curve which represented the concentration of remaining MDI in function of the signal area by SEC allows for precise quantification the residual isocyanate present in prepolymers.



Figure S7. Calibration curve represented concentration of free di(MeOH)-MDI in function of the area of its corresponding

signal in SEC-THF.



Figure S8. Treatments of NCO-terminated prepolymers for SEC-THF analysis.



Figure S9. Reproducibility of the molar-mass distribution trends between different sets of prepolymer syntheses (a and b) in presence of different catalysts (A- or B-type): the A-type leads to less chain extension than the B-type (no presence of fraction of higher molar masses), with usually a distribution even narrower than the uncatalyzed prepolymer.



Figure S10. Mechanism of organic catalyst DABCO during the synthesis of polyurethane.¹



Figure S11. Possible mechanism of tin catalysts during the synthesis of polyurethane.²⁻⁵



Figure S12. Formation of urea by reaction of isocyanate with water at the crosslinking stage.

				DMA		DSC
NCO/OH prepolymers	P(catalyst)	C(catalyst)	Height tan δ	<i>Τ</i> α (°C)	Width tan δ (°C)	<i>Т_g</i> (°С)
	DABCO 45ppm	-	1.26	-30.2	19.1	-44.7
1.83	Sn 6ppm	-	1.25	-30.2	19.0	-45.9
	Sn 6ppm	1 wt% Sn	1.24	-30.8	20.3	-53.1

Table S1. DMA and DSC experiments to assess the influence of prepolymerization and crosslinking catalysts on materials properties.

Spectroscopic study to evaluated the optimal concentration of DMSO to shield urea H-bonding

DMSO was added at the crosslinking stage in order to shield intra- and intermolecular H-bonding and only observe the influence of catalysts. In presence of this polar solvent, chain conformations were independent of H-bonding and we would be able to only observe the influence of catalysts on the 3D-network architectures. First of all, the molar amount of DMSO compared to the molar amount of urethane functions necessary to shield H-bonding was determined by ¹H NMR in benzene-d₆.



Figure S13. Evolution of chemical shift of urethane function on ¹H-NMR spectrum in function of DMSO quantity.

 Table S2. Comparison of catalysts influence on mechanical properties of polyurethane materials with or without fillers determined by tensile test.

		P(catalyst)	C(catalyst) (0.2wt%)	Elongation at break (%)	Modulus at 100% elongation (MPa)	Ultimate tensile strength (MPa)
NCO/OH prepolymers ratio 1.83	Without	Sn 6ppm	-	255.3 ± 35.7	1.19 ± 0.08	2.09 ± 0.3
		Sn 600ppm	-	266.1 ± 35,9	1.18 ± 0.07	2.08 ± 0.1
	fillers	DABCO 90pm	-	255.3 ± 19.6	1.19 ± 0.04	2.06 ± 0.1
		DABCO 4500ppm	-	257.6 ± 16.1*	1.02 ± 0.06*	1.78 ± 0.2*
	With	Sn 7.7ppm	Sn	544	1.02	1.32
	fillers	DABCO 95ppm	DMDEE	376	1.29	1.54

* Average values of two dumbbells instead of three

	Composition of formulation (%wt)				
	Formulation P(Bi 6.3ppm)+ C(DMDEE 0.2 wt%)	Formulation P(Bi 6.3ppm)+ C(DABCO 0.2 wt%)	Formulation P(DABCO 95ppm)+ C(DMDEE 0.2 wt%)		
NCO-terminated prepolymers (catalysed with Bi 6.3ppm or DABCO 95ppm)	32.6 32.6		32.6		
Fillers ¹	43.6	43.6	43.6		
Plasticizers (DIDP, bis-urea) ²	20.9	20.9	20.9		
Other (H ₂ O and CO ₂ scavenger, solvent)	2.7	2.7	2.7		
DMDEE (catalyst for crosslinking)	0.2	-	0.2		
DABCO (catalyst for crosslinking)	-	0.2	-		
¹ Example of fillers:					
Inorganic fillers (CaCO ₃ , TiO ₂ , additives)	29.7	29.7	29.7		
Organic fillers (PVC powder)	13.9	13.9	13.9		

Table S3. Composition of polyurethane materials with fillers.⁶

² DIDP (diisodecyl phtalate)

Bis-urea





Figure S14. Solid-state ¹H-NMR spectra of crosslinked-PU thin film without fillers a) in the case of P(Sn 6ppm)+C(1wt% Sn) and b) in presence of different catalysts and catalyst combinations.



Figure S15. Solid-state ¹³C-NMR spectra of crosslinked-PU thin film without fillers a) in the case of P(Sn 6ppm)+C(1wt% Sn) and b) in presence of different catalysts and catalyst combinations.



Figure S16. Stress-strain curve for polyurethane materials with fillers in the case of P(Bi 6.3ppm)+C(DABCO 0.2wt%) obtained by tensile test (Table 6, example 3).

Entry	P(catalyst)*	C(catalyst) (0,2%wt)	Tensile test Elongation at break (%)	<i>Τ</i> α (°C)	DMA Height tanδ	Width tanδ (°C)	Integral tanδ At 25°C ±5°C ^{**}
1	Sn 7,7ppm	Sn	544	-43.6	1.12	22.7	1.15
2	Bi 6,3ppm	DMDEE	391	-45.5	1.08	22.2	0.94
3	DABCO 95ppm	DMDEE	376	-45.6	1.03	23.1	1.00

 Table S4. Comparison of tensile test and DMA analyses of crosslinked poly(urethane-urea) with fillers and different catalysts combinations.

* NCO-terminated prepolymers obtained at NCO/OH ratio equal to 1.83

^{**} Integration of tan δ curve in the temperature range of 20 to 30°C (experimental condition for tensile test)

The heterogeneity hypothesis is confirmed by DMA (see Table S4 above to exemplify these network heterogeneities depending on chosen catalyst). We indeed see that P(**Sn** 7.7 ppm)+C(0.2 wt% **Sn**) (entry 1) has a better damping ratio that the two other formulations (entries 2 & 3) through the higher integral value of tan δ over the temperature range of the tensile test. This formulation thus translates into a more homogeneous network that also give significantly higher elongation-at-break (~550% compared to <400%, see Table S4) using international standard ISO 37 – 2011 (min. 5 dumbbells tested to give an average value for each formulation). This network heterogeneity hypothesis is also suggested by the new DMA results (deeper analysis using tan δ integrals) of Table 5 for the DMSO study (main text).

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