Electronic Supplementary Material (ESI) for RSC Advances.
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Solvent- and catalyst-free synthesis of fully biobased nonisocyanate polyurethanes with different macromolecular architectures.

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Supporting Information

1. Titration methods

In order to calculate the NCO:OH molar ratio required for PU synthesis, preliminary titrations were realized to determine the hydroxyl index (I_{OH}) of the polyol and the NCO content (*NCO%*) of the isocyanate.

1.1. Hydroxyl index (I_{OH}) determination

I_{OH} is a key parameter in the characterization of polyols. This value is the amount of potassium hydroxide (KOH), in milligrams, equivalent to the number of OH groups in 1 g of polyol.

I_{OH} was determined by the standard esterification method using phthalic anhydride. Polyol (1 g) and the reactive solution (20.0 mL, phtalic anhydride 1 M in pyridine) were heated at 130°C for 45 minutes, and then cooled to room temperature. Pyridine (30 mL) was then added, followed by water (30 mL). The solution was then titrated with a 1 M sodium hydroxide (NaOH) solution.

Hydroxyl index (I_{OH}), in mg KOH/g, was determined from Eqn (S1) where, V_b and V_{eq} are the volumes in milliliter of the NaOH titration solution required respectively for blank and polyol sample titrations, C is the NaOH solution concentration in mol.L^{-1}, and w_P is the polyol weight in grams.

$$I_{OH} = \frac{(V_b - V_{eq}) * C * 56.1}{w_P} \quad \text{(S1)}$$

1.2. NCO content (*NCO%*) determination

NCO% is a key parameter in the characterization of isocyanates. This value is the percent by mass of the NCO groups present in the sample. *NCO%* was determined by indirect titration of dibutylamine in excess with a hydrochloric acid (HCl) solution.

In a flask, isocyanate (1 g), toluene (30 mL) and a 1 M solution of dibutylamine (20.0 mL) were added. This flask was closed and then stirred during 15 minutes at room temperature. Methanol (30 mL) was then added. The solution was finally titrated with a 1 M HCl solution. A blank sample without isocyanate was also titrated in order to determine the total quantity of dibutylamine introduced. *NCO%* was determined according to Eqn (S2) where, V_b and V_{eq} are the volumes in milliliter of the HCl titration solution required respectively for blank and isocyanate sample titrations, C is the HCl solution concentration in $mol.L^{-1}$, and w_P is the isocyanate weight in grams.

$$NCO\% = \frac{(V_b - V_{eq}) * C * 4.2}{w_P} \quad \text{(S2)}$$

2. DFA chemical characterization

2.1. FTIR, ^{1}H- and ^{13}C-NMR analyses

Chemical characterizations were performed on DFA in order to define its chemical structure. FTIR and ^{1}H-NMR analyses are presented in Figures 3 and 4. Additional ^{13}C-NMR spectrum (Figure S1) can be found below.

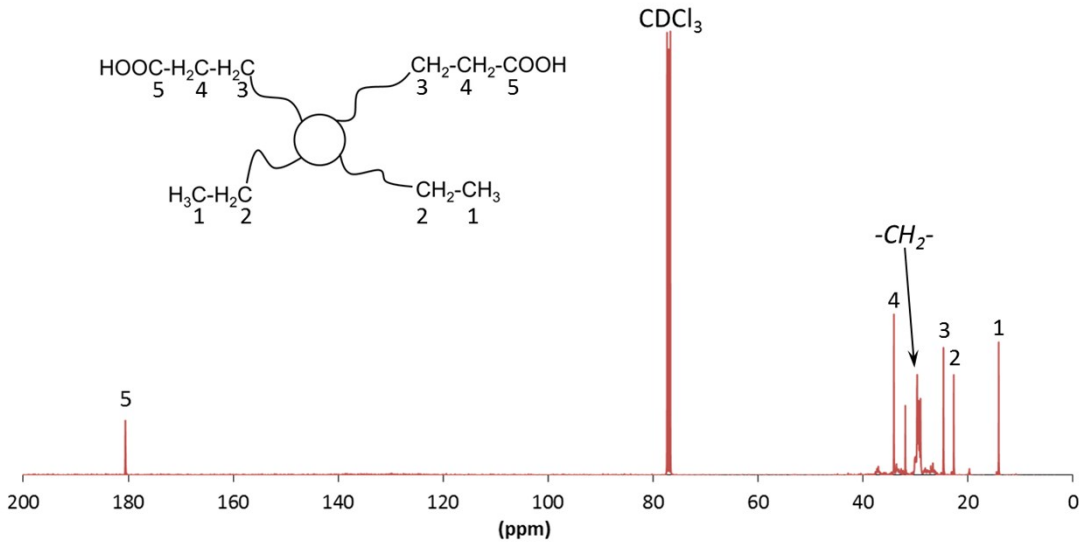

Figure S1. ^{13}C-NMR spectrum of DFA.

2.2. SEC analysis of DFA

SEC analysis was achieved to evaluate the average molar masses of DFA and observe its dispersity (Figure S2).

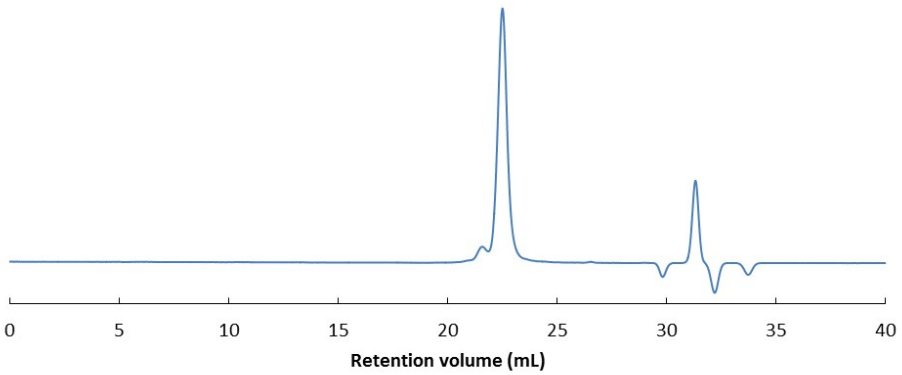

Figure S2. SEC chromatogram of DFA obtained with RI detector (PS standard calibration).

2.3. DOSY NMR analysis of DFA

Molecules are differentiated according to their self-diffusion coefficient (D), related to their hydrodynamic radius. NMR spectra of molecules presenting sufficiently different sizes can be

isolated. DOSY is a two-dimensional (2D) NMR experiment with a frequency dimension (^{1}H-NMR chemical shifts) and a dimension related to a D coefficient. D measurement is based on the use of magnetic fields gradients. This results in a 2D map displaying spots, which correlate each NMR signal to a D coefficient. It is thus possible to isolate the NMR spectrum of each compound of the mixture. D measurement is based on the use of magnetic fields gradients.

DOSY spectra were generated by using the program NMRNotebook and the DOSY Module from NMRTEC (NMRNotebook, http://www.nmrtec.com/software/nmrnotebook) using inverse Laplace Transform (M. A. Delsuc and T. E. Malliavin, *Anal. Chem.*, 1998, **70**, 2146) driven by Maximum Entropy, to build the diffusion dimension. For each data set, 8192 complex points were collected for each 20 experiments in which the gradient strength was linearly incremented from 0.5 to 45 G.cm^{-1}. The gradient duration δ/2 was adjusted to observe a near complete signal loss at 45 G.cm^{-1}. A 1 s recycle delay was used between scans. The number of scan was set to 64. The total experiment time, including a 20 min temperature equilibration step, is close to two hours. For each data set, the spectral axis was processed with sine-bell, and Fourier transform was applied in order to obtain 4096 real points. A spline baseline correction was finally applied. The columns (axis of varying gradient) of the datasets were then processed for Inverse Laplace transform using the Inverse Laplace Technique using the NMRNotebook software (NMRTEC-France). The DOSY reconstruction was performed with 256 points in the diffusion dimension and a maximum of 100,000 MaxEnt iterations.

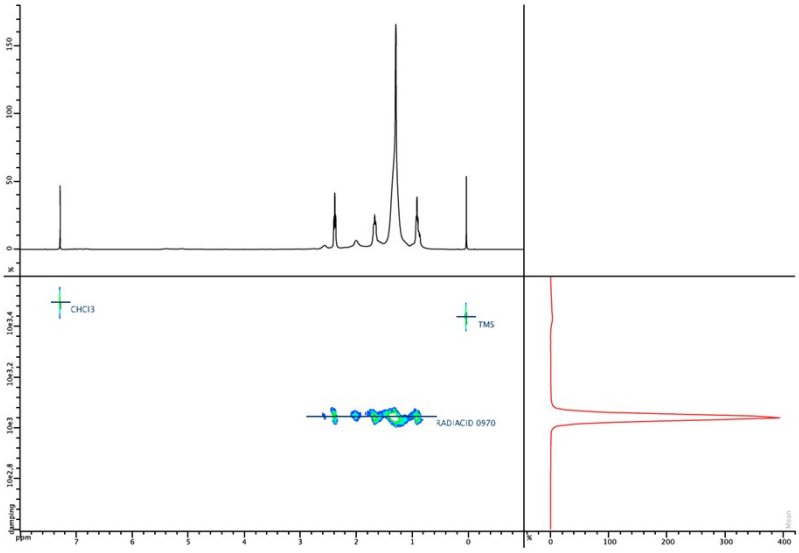

Figure S3. DOSY NMR spectra of DFA in $CDCl_3$.

3. Characterization of intermediates based on DFA

In order to complete ^{1}H-NMR analyses, ^{13}C-NMR analyses were also performed on DFA intermediates (Figures S4 and S5).

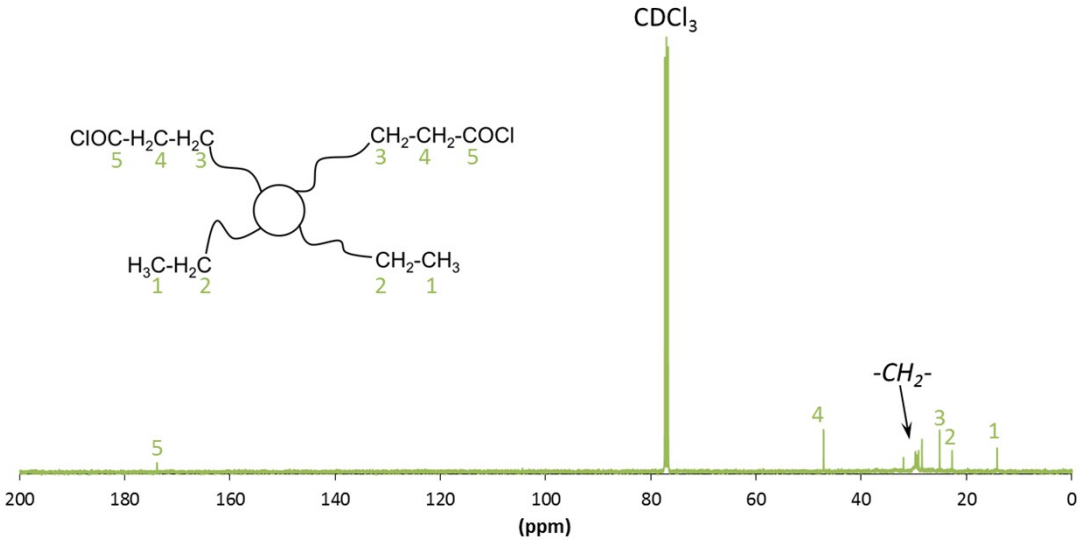

Figure S4. ^{13}C-NMR spectrum of DCl.

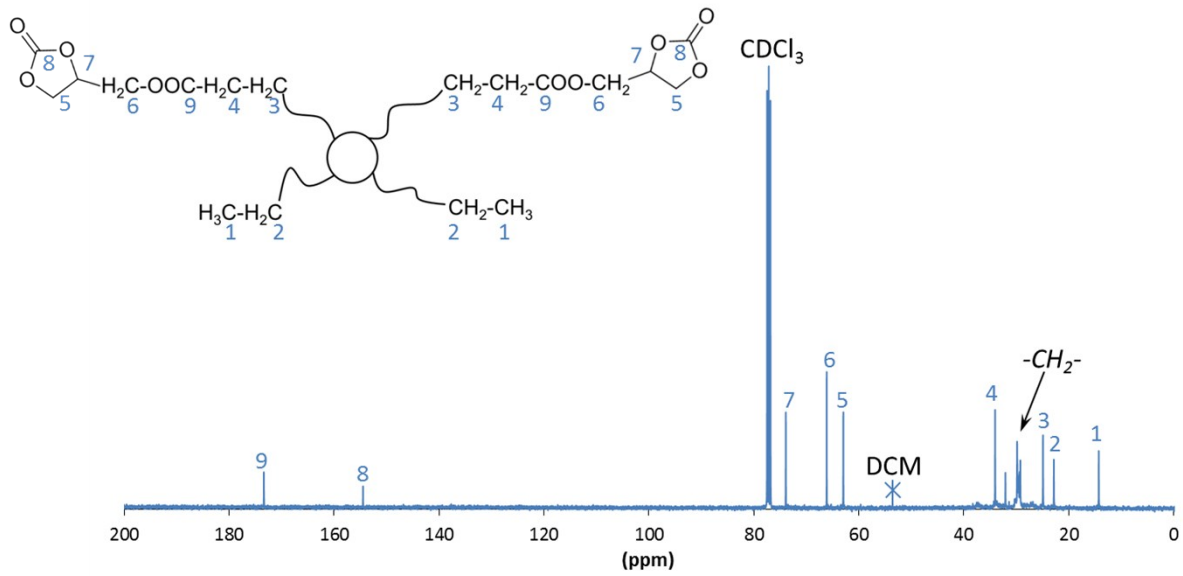

Figure S5. ^{13}C-NMR spectrum of DBisCC.

4. Synthesis and characterization of DNIPU

4.1. Effect of the DBisCC:diamine molar ratio

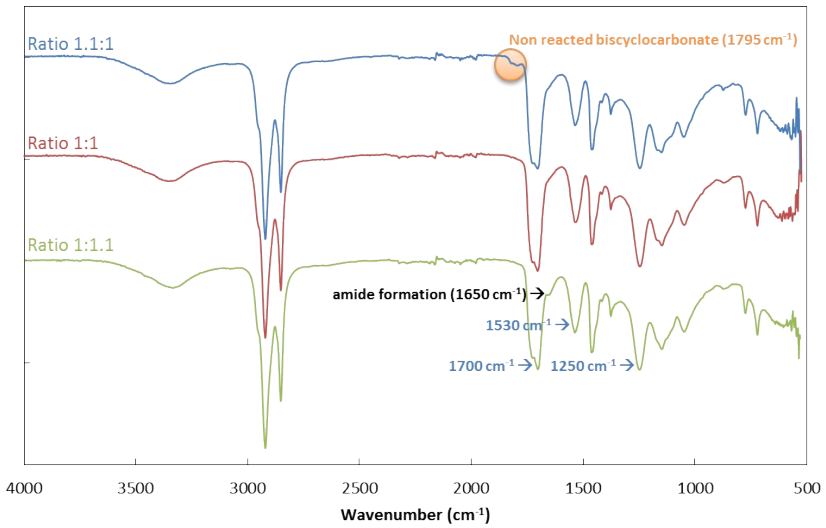

Figure S6. FTIR spectra of DNIPU-fn=2.0 at different carbonate:amine ratios.

4.2. Effect of the average amine functionality of DNIPU samples

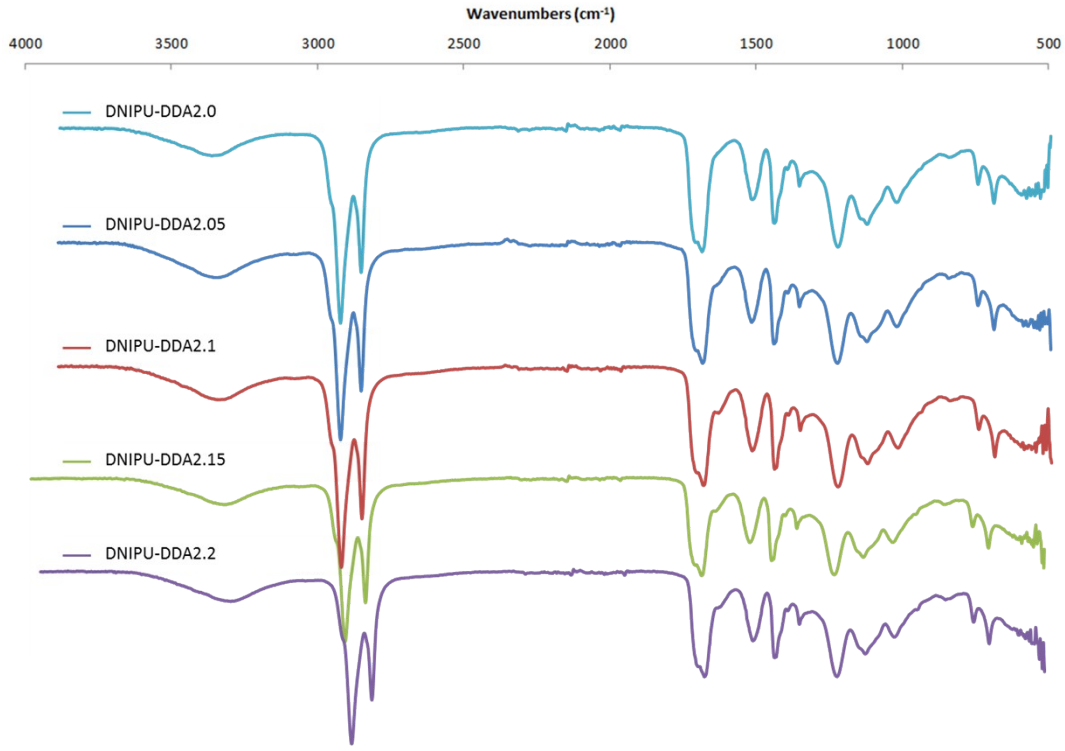

Figure S7. FTIR spectra of DNIPU samples.

Table S1. Main degradation temperatures of the different DNIPUs.

Samples	$T_{98\%}$ (°C)	$T_{50\%}$ (°C)	$T_{2\%}$ (°C)	T_{max} (°C)
DNIPU-DDA2.0	245	437	479	452
DNIPU-DDA2.05	201	426	467	445
DNIPU-DDA2.1	240	434	488	444
DNIPU-DDA2.15	246	433	544	442
DNIPU-DDA2.2	251	436	514	444

4.3. Particular case: DNIPU-fn=2.0, study of its mechanical properties

Figure S8 displays the mechanical behaviour of NIPU-fn=2.0 sample under uniaxial tensile test. Three samples were tested and show a similar behaviour typical of elastomeric materials. The sample picture after breaking indicates that no necking phenomenon occurred.

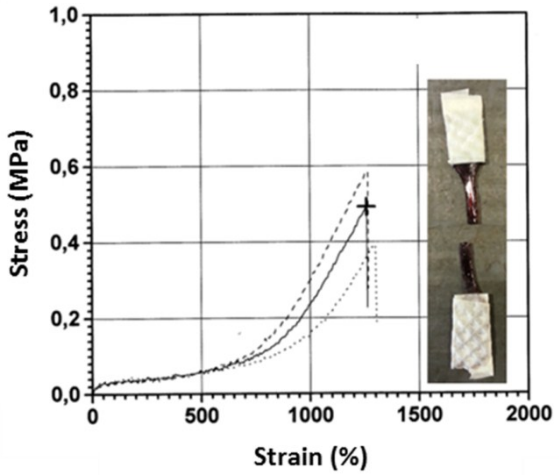

Figure S8. Stress-strain curve of DNIPU-DDA2.0.