Electronic Supplementary Information (ESI)

N-heterocyclic carbene-catalyzed synthesis of polyurethanes

Olivier Coutelier[a], Mohammad El Ezzi[a], Mathias Destarac*[a], Fabien Bonnette[a], Tsuyoshi Kato[a], Antoine Baceiredo[a], Gopakumar Sivasankarapillai[b], Yves Gnanou[b]and Daniel Taton[b]

Summary of the Supplementary Information document

[a] *Université de Toulouse, UPS, LHFA, CNRS, UMR 5069 118 route de Narbonne, F-31062 Toulouse, France Fax: 33 (0)5 61 55 82 04; Tel: 33 (0)5 61 55 63 54; E-mail: destarac@chimie.ups-tlse.fr*
[b] *Laboratoire de Chimie des Polymères Organiques (LCPO) - ENSCBP - CNRS, Université Bordeaux 1, 16 avenue Pey Berland, 33607 Pessac Cedex 9, France. Fax: XX XXXX XXXX; Tel: XX XXXX XXXX; E-mail: xxxx@aaa.bbb.ccc*

I Experimental

Materials

Isophorone diisocyanate (IPDI, 98%, Aldrich), bisphenol-A 99+% (Aldrich), 1,6-diisocyanatohexane (HDI, 98%, Aldrich), 2,2-dimethylpropane-1,3-diol (Fluka) were used as received. 1,4-butanediol (99% Acros) was stored on molecular sieves 3A , polyethylene glycol 200g/mol (PEG-200, Aldrich) was stored on molecular sieves 3A and heated at 110°C under vacuum for 1 day. *N*,*N*-di(*tert*-butyl)imidazol-2-ylidene (*t*BuNHC) was synthesized as described in the literature.[i]

Instrumentation

Size-exclusion chromatography (SEC) was used to determine number-average molar masses (M_n) and dispersities ($Đ = M_w/M_n$) of polymer samples with respect to polystyrene standards (Polysciences Corporation) using a refractive index detector (Waters 2414) where THF was used as eluent at a flow rate of 1ml/min, with a set of two columns (Shodex KF-804 and KF 802.5), maintained at 35°C. Weight-average molecular masses (M_w) were determined by multi angles light scattering analysis (MALS) on a MiniDawn TREOS (Wyatt Technology Corporation). dn/dc of polymers were measured in THF at 35°C on a PSS dndc-2010 apparatus. FT-IR spectroscopy was performed on a PERKIN 1760 spectrometer using a diamond compression cell.

General protocol for the NHC-catalyzed polymerization of diols with diisocyanates

In a 100 mL round-bottom flask under argon, are successively added diol (1.10^{-2} mol), THF (25 mL), and the reaction mixture is then heated to the polymerization temperature. Diisocyanate (1.10^{-2} mol) is then added, followed by 1 mL of THF solution of *t*BuNHC (1.10^{-4} mol). The reaction is allowed to proceed for 1 h. The polymer is then precipitated in pentane, filtered under vacuum, and dried in a vacuum oven at 80 °C. The polymer is then analyzed by SEC.

II. NMR spectroscopy of 1,4-butanediol/IPDI polyurethane.

Polymer was characterized by NMR spectroscopy. Analyses were performed in DMSO- *d6* at room temperature, residual signal of DMSO was used as reference.

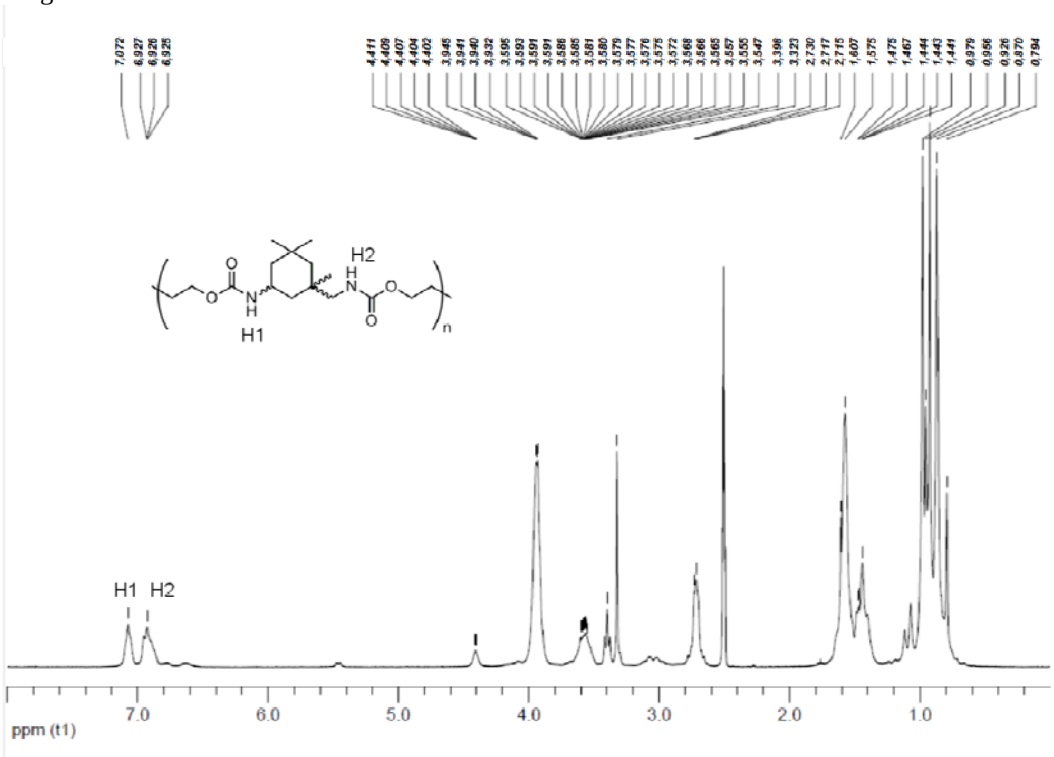

Fig.S1. ^{1}H NMR spectrum

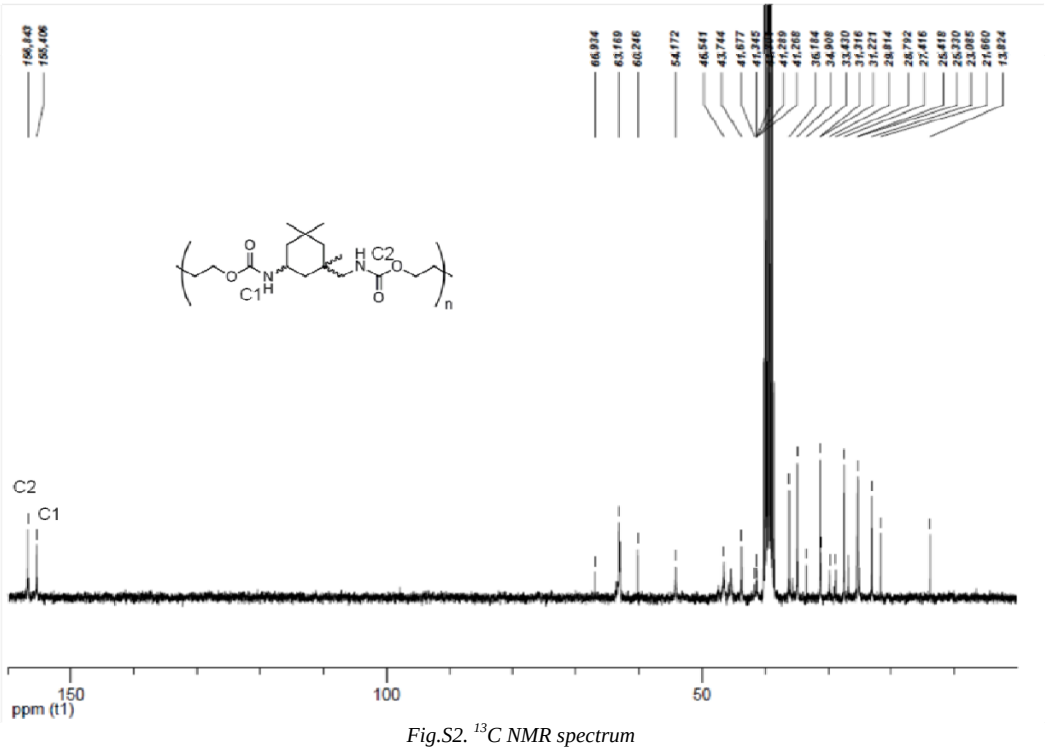

Fig.S2. ^{13}C NMR spectrum

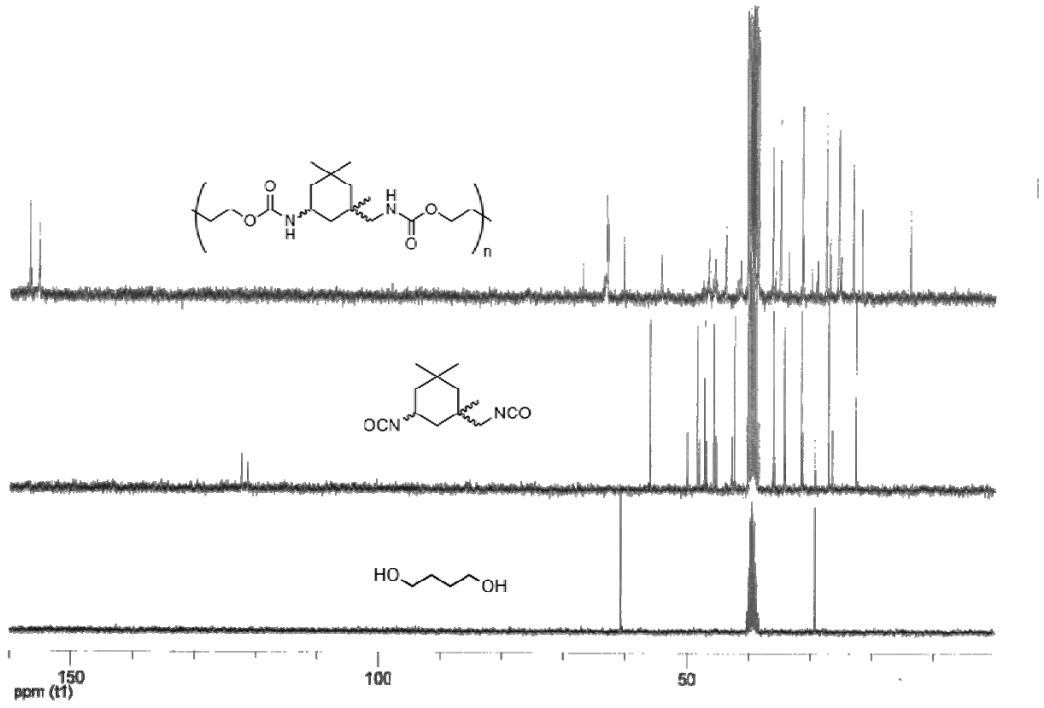

Fig.S3. ^{13}C NMR spectrum comparison between monomers and final polymer

III. MALDI-TOF mass spectrometry of 1,4-butanediol/IPDI polymer

The MALDI-TOF mass spectrum of polyurethane was obtained through the use of a dithranol matrix and sodium iodide salt as the cationization reagent. Fig. S4 shows the MALDI-TOF spectrum of the 1,4-butanediol/IPDI polyurethane after the deisotoping procedure. The MALDI-TOF spectrum contains three mass distributions in the range 400-3600 Da with mass intervals corresponding to the molar mass of the repeating unit (312.20 u). The most intense distribution (S1) at m/z = 312.20n + 22.99(Na^+) corresponds to the expected polyurethane with 1,4-butanediol and IPDI groups at both ends. A second distribution (S2) at m/z = 90.07 + 312.20n + 22.99(Na^+) was

attributed to the polyurethane with 1,4-butanediol at both ends. A third (minor) distribution (S3) is also present at m/z = 160 + 312.20n+22.99(Na^+) but could not be attributed.

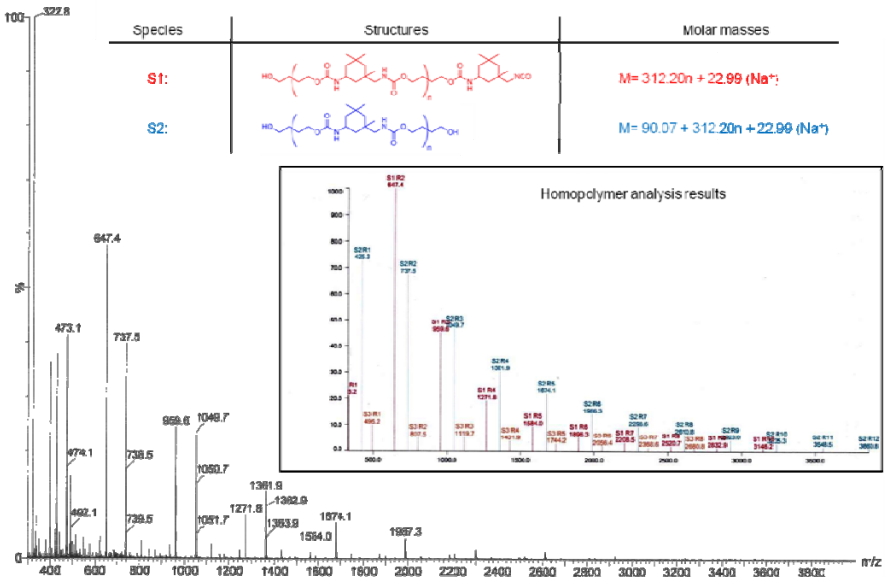

Fig.S4. MALDI-TOF mass spectrum of 1,4-butanediol/IPDI polyurethane after deisotoping procedure

IV. FTIR spectroscopy of 1,4-butanediol/IPDI polymer

FT-IR analysis was performed on a PERKIN 1760 spectrometer using a diamond compression cell.

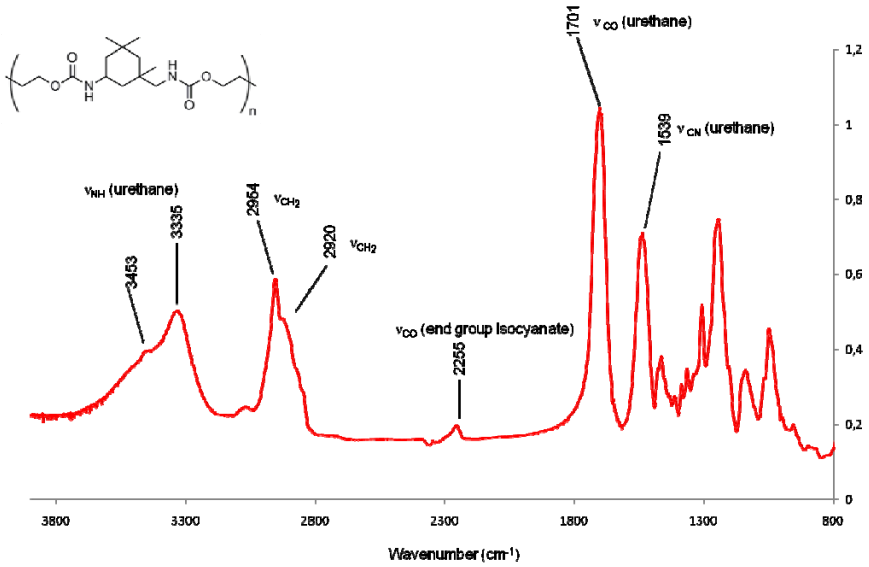

Fig. S5. FTIR spectroscopy of 1,4-butanediol/IPDI polymer

[i] Scott, N.M.; Dorta, R.; Stevens, E.D.; Correa, A.; Cavallo, L.; Nolan,S.P. *J. Am. Chem. Soc*. **2005**, *127*, 3516.