Electronic Supplementary Information (ESI)

N-heterocyclic carbene-catalyzed synthesis of polyurethanes

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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 (tBuNHC) was synthesized as described in the literature.

Instrumentation
Size-exclusion chromatography (SEC) was used to determine number-average molar masses (\(M_n\)) and dispersities (\(D = M_w/M_n\)) 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 tBuNHC (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-\(d_6\) at room temperature, residual signal of DMSO was used as reference.
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 \( m/z = 312.20n + 22.99(\text{Na}^+) \) corresponds to the expected polyurethane with 1,4-butanediol and IPDI groups at both ends. A second distribution (S2) at \( m/z = 90.07 + 312.20n + 22.99(\text{Na}^+) \) 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.

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