

# Supporting Information

to

## Polymerization of $\epsilon$ -Caprolactam by Latent Pre-Catalysts

### Based on Protected N-Heterocyclic Carbenes

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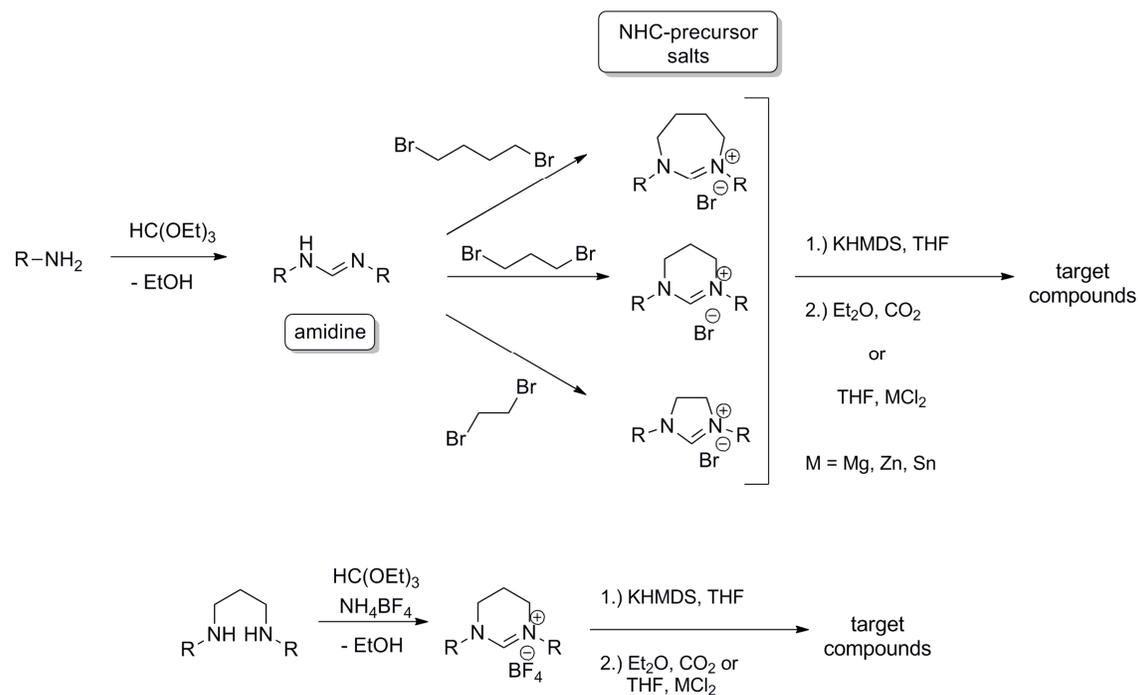
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## Experimental Part

### Materials and Synthesis

The synthesis of the NHC-precursors was performed without special precautions under air. All manipulations involving free carbenes, i.e. the formation of NHC-carboxylates, NHC-metal salt complexes and polymerizations, were conducted in a nitrogen-filled glove box (MBraun Lab Master 130, MBraun, Garching, Germany) or by standard Schlenk techniques. CH<sub>2</sub>Cl<sub>2</sub>, diethyl ether, toluene, pentane and THF were dried by a solvent purification system (SPS, MBraun). KOtBu was purified by sublimation; all other starting materials and chemicals were purchased from Sigma-Aldrich, TCI Europe, ABCR or STREM and used without further purification.  $\epsilon$ -Caprolactam was a gift from L. Brüggemann KG (Heilbronn, Germany). The sample was a commercial grade monomer designated for anionic polymerization (dried, packed in air-tight foliage) and used without any further purification. NMR measurements were recorded on a Bruker Avance III 400. IR spectra were measured on an IFS 28 (Bruker) using NaCl cuvettes. GC-MS data were recorded on an Agilent Technologies device consisting of a 7693 autosampler, a 7890A GC and a 5975C quadrupole MS. A SPB-5 fused silica column (34.13 m x 0.25 mm x 0.25  $\mu$ m film thickness) was used. All non-commercial amidines, NHC-precursors, NHC-carboxylates and NHC-metal complexes were synthesized as described in the literature<sup>[i-vii]</sup>, where more details and spectra can be found. Preparation

followed a simple route as shown in Figure S1. The NHC-precursor salts were received either by cyclization of the corresponding amidines or by cyclization of diamines. These salts were then deprotonated using KHMDS (potassium hexamethyldisilazide) and reacted with a suitable protecting group like CO<sub>2</sub> or metal salts.



**Figure S1:** General route for the preparation of protected N-heterocyclic carbenes by cyclization of amidines (top) and diamines (bottom).

### Characterizations

The molecular weights of the PA 6 samples were determined by viscosimetric measurements using a Ubbelohde Ic at T = 20°C (phenole:1,1,2,2-tetrachloroethane = 1:1, concentration = 0.5 g sample per 100 mL of solvent mixture or 1.0 g per 100 mL of solvent mixture) with  $\alpha = 0.685$  and  $K = 7.55 \cdot 10^4$  mL/g.

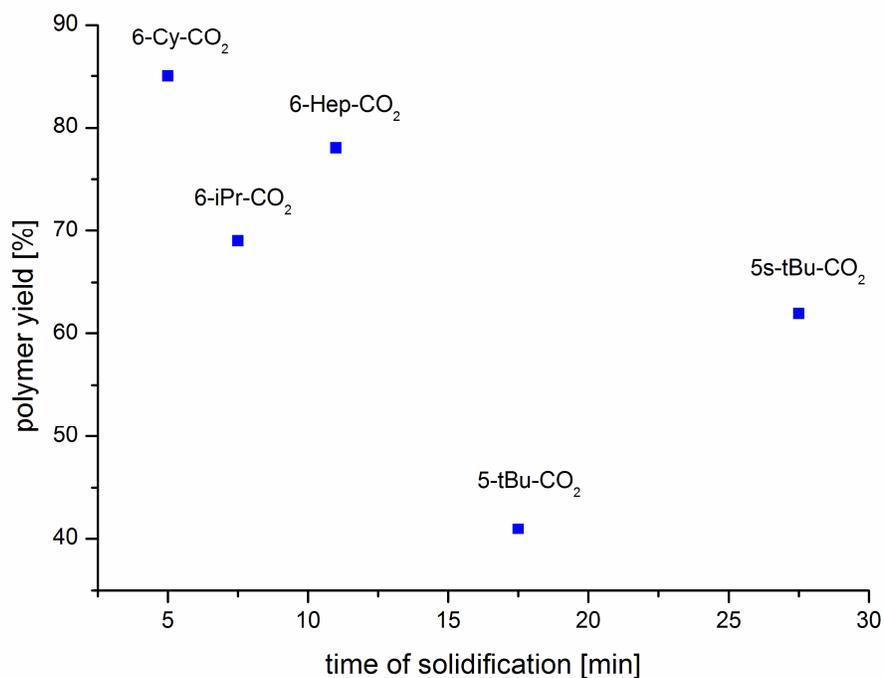
Rheological investigations were conducted on a RMS 800 (Rheometric Scientific). During the measurements, a nitrogen atmosphere was applied. Prior to addition of the pre-mixed initiator/monomer-sample the plates were heated to the desired reaction temperature. About 2 mL of melt were necessary for each measurement.

## **Polymerizations**

Inside a glove box, 0.5-5.0 g of  $\epsilon$ -caprolactam were mixed with the desired amount of initiator (5-50 mg) and put into a Schlenk tube equipped with a magnetic stirrer. The sealed reaction vessel was then removed from the glove box and placed into a pre-heated oil bath. Within a short time (< 60 s) a stirred melt formed. In case no polymerization occurred, the reaction mass remained liquid and was soluble in acetone or chloroform after cooling. If polymerization took place, rapid solidification was observed. The polymer was dissolved in formic acid and precipitated in acetone. After washing with acetone, the remaining substance was dried in vacuo. The resulting amount of PA 6 was used to calculate the isolated yields listed in Table 1.

## **Solidification times and yields**

The onset of polymerization is marked by a sharp increase in viscosity. This caused stirring to slow and eventually stop. In Figure S2 the times of solidification are plotted against the yields of PA 6 after 45 minutes of heating at 180°C. Though no exact tool, this plot reveals again that the more basic tetrahydropyrimidine-2-ylidenes are more suitable to provide fast polymerizations in higher yields than the corresponding imidazolium- or imidazolinium-derivatives.



**Figure S2:** Correlation of polymer yield (taken from Table 1) and solidification, stressing the observation that tetrahydropyrimidin-2-ylidenes deliver higher yields in shorter time.

## References

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