

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263940158>

Anionic Ring-Opening Homo- and Copolymerization of Lactams by Latent, Protected N-Heterocyclic Carbenes for the Preparation of PA 12 and PA 6/12

ARTICLE in MACROMOLECULES · OCTOBER 2013

Impact Factor: 5.8 · DOI: 10.1021/ma4018586

CITATIONS

9

READS

54

7 AUTHORS, INCLUDING:



Friedrich Georg Schmidt

Evonik Industries

38 PUBLICATIONS 337 CITATIONS

SEE PROFILE



Stefan Epple

Universität Stuttgart

8 PUBLICATIONS 22 CITATIONS

SEE PROFILE



Christian Bonten

Universität Stuttgart

90 PUBLICATIONS 46 CITATIONS

SEE PROFILE



Michael R Buchmeiser

Universität Stuttgart

330 PUBLICATIONS 7,620 CITATIONS

SEE PROFILE

Anionic Ring-Opening Homo- and Copolymerization of Lactams by Latent, Protected N-Heterocyclic Carbenes for the Preparation of PA 12 and PA 6/12

Stefan Naumann,[†] Friedrich Georg Schmidt,[‡] Maria Speiser,[†] Margit Böhl,[‡] Stefan Epple,[§] Christian Bonten,[§] and Michael R. Buchmeiser^{†,‡,*}

[†]Institute of Polymer Chemistry, University of Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

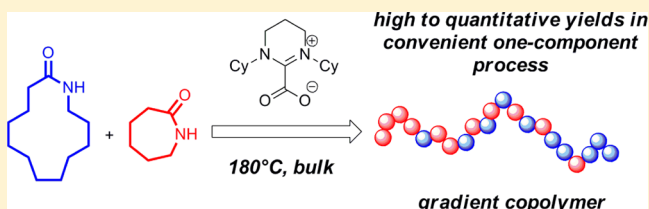
[‡]Evonik Industries AG, Paul-Baumann-Strasse 1, D-45764 Marl, Germany

[‡]Institute of Textile Chemistry and Chemical Fibers, Körschtalstrasse 26, D-73770 Denkendorf, Germany

[§]Institut für Kunststofftechnik, University of Stuttgart, Böblingerstrasse 70, D-70199 Stuttgart, Germany

S Supporting Information

ABSTRACT: Laurolactam (LL) is polymerized in the bulk using strongly basic N-heterocyclic carbenes (NHCs) as initiators at temperatures of 180–200 °C to prepare the corresponding polyamide (PA 12). In-situ rheology of the polymerization progress reveals that an anionic mechanism is active, which is supported by the strong dependence of initiator activity on the basicity of the NHCs. GPC data and kinetic investigations show the process to be moderately controlled and fast, allowing high or quantitative yields in short polymerization times. Fifteen different NHC–CO₂–adducts and NHC–metal complexes were used as thermally labile but room temperature stable NHC-precursors. Depending on the ring size and N-substituent, some of these protected NHCs allow forming a mixture of monomer and NHC-precursor that is suitable for long-term storage and readily polymerizable by simple heating. All polymerizations are executed without activator or other additives and thus represent a true one-component system for the production of PA 12. Finally, LL is copolymerized with ϵ -caprolactam (ϵ -CLA). It is found that a copolymer with a considerable gradient is formed, with ϵ -CLA being incorporated preferentially at the onset of the polymerization.



INTRODUCTION

Far from being mere ligands for transition metals, N-heterocyclic carbenes (NHCs) are ever more recognized as powerful organocatalysts on their own.¹ Because of their nucleophilicity² they can bring about a wealth of organic transformations, like umpolung reactions or transesterifications.³ NHCs are also bases, though there are much less examples of their application as such,⁴ which is probably related to the frequent use of imidazol-2-ylidenes and imidazolin-2-ylidenes. These compounds are much weaker bases than for example tetrahydropyrimidin-2-ylidenes.⁵ Both types of NHCs are part of this work, and special emphasis is put on their use as bases. Combined with the aforementioned properties, the flexibility with regard to ring-size, N-substituents, and backbone, as well as the relative ease of preparation,⁶ have won NHCs a prominent position in polymerization chemistry.⁷ Among others, methyl methacrylate was polymerized both directly or via a group transfer mechanism.⁸ Epoxides,⁹ lactones,¹⁰ lactides,¹¹ and cyclosiloxanes¹² were successfully ring-opened to give the corresponding polymers. In most cases excellent yields and good control of polydispersity were achieved.

However, disadvantages of free NHCs are the limited stability and storability and also the awkward handling of free carbenes since they are often of oily consistence. Consequently much effort has been put into research concerning compounds that exist in the form of adducts or complexes but can release the active NHC after warming (“protected NHCs”) or by solvent effects. Examples for this type of chemistry are azolium hydrogenates,¹³ CO₂-, COS- or CS₂-adducts,¹⁴ Sn-, Zn- or Mg-based complexes,¹⁵ and isothiocyanate-,¹⁶ alcohol-¹⁷ and chloroform-adducts.¹⁸ A range of differently substituted CO₂- and metal-salt protected NHCs was therefore synthesized (Figure 1). These initiators have been used in the polymerization of methyl methacrylate¹⁹ or ϵ -caprolactone,²⁰ where in both cases no reaction at room temperature occurred, but could be induced by heating. Compounds of this type were also used as latent precatalysts for the synthesis of polyurethanes.¹⁵ Recently, we also extended this principle to ϵ -caprolactam (ϵ -CLA).²¹ It was demonstrated for the first time that NHCs can effectively deliver poly(ϵ -caprolactam) (PA 6), if they are basic

Received: September 6, 2013

Revised: October 10, 2013

Published: October 23, 2013

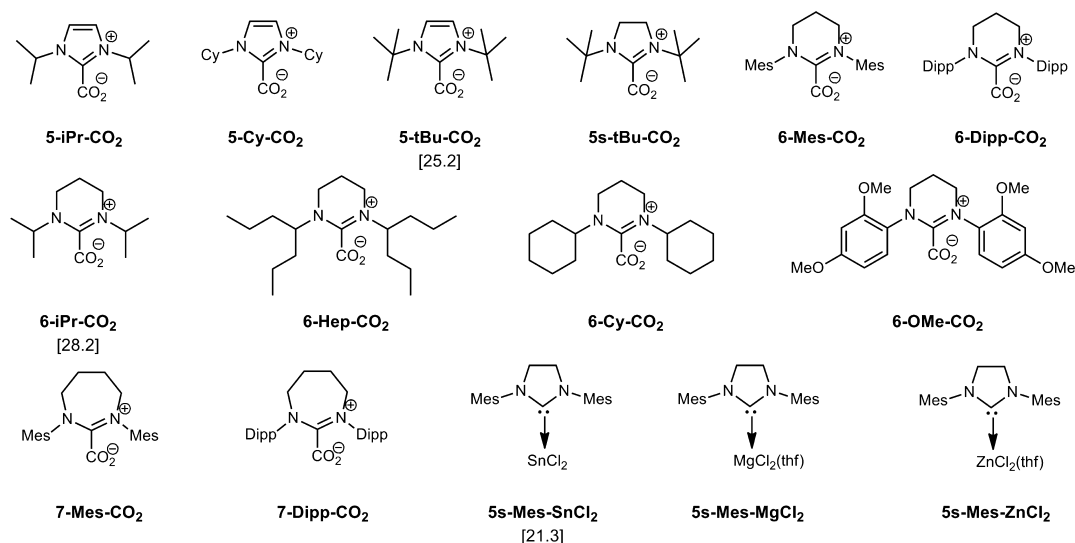
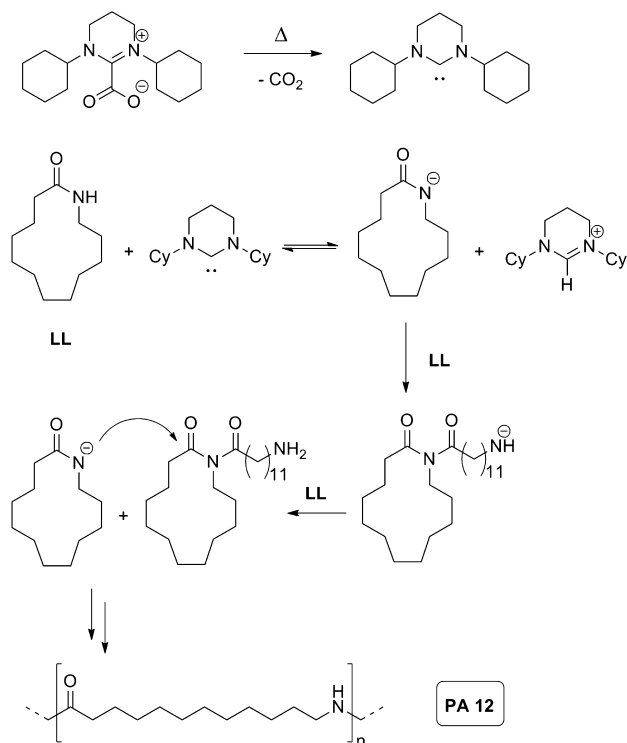


Figure 1. NHC-carboxylates and NHC-metal complexes used in the present work. Brackets: pK_a -values of the parent NHCs (aqueous solution at 25 °C).³¹ Cy = cyclohexyl, Mes = 2,4,6-trimethylphenyl, Dipp = 2,6-diisopropyl-phenyl.

enough. This rendered especially *N*-alkyl bearing tetrahydropyrimidinium-based initiators the most suitable. The polymerizations displayed characteristics typical for anionic lactam polymerization and yields were high, though not quantitative. These promising results indicate that NHC-catalysis may be applied to other lactams as well and has the potential to compete successfully with other organic-based initiators like phosphazenes.²² Accordingly, in the present work the NHC-initiated homopolymerization of lauro lactam (LL) to PA 12 as well as the copolymerization of LL and ϵ -CLA are presented (Scheme 1). Its many methylene linkages and accordingly low

Scheme 1. Thermal deprotection of the initiator (top) induces anionic ROP of LL



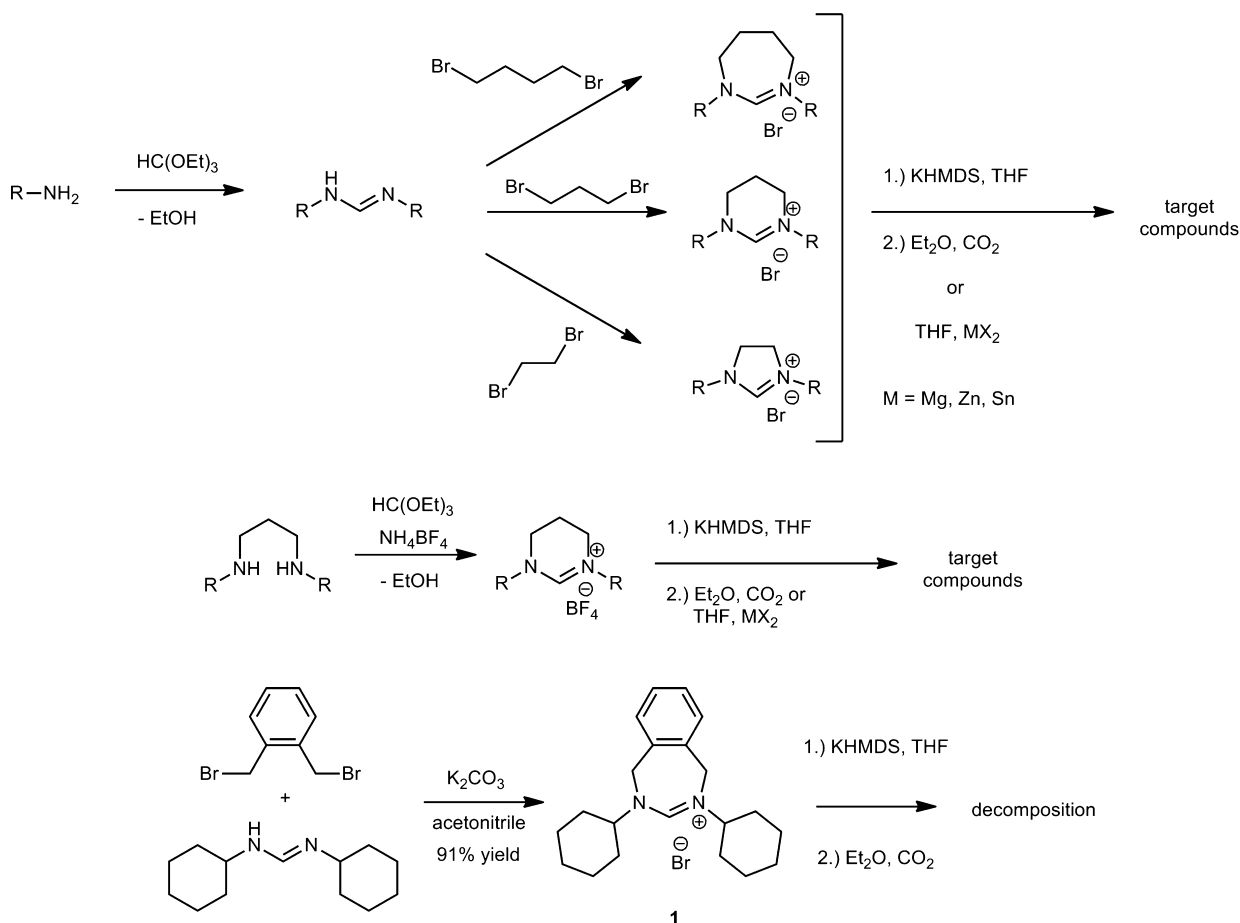
amide density make PA 12 a much less polar polyamide than PA 6. The consequence is that PA 12 is much less prone to water uptake than PA 6, a property that is much desired since it promotes dimensional stability in a polymer body.²³ The downside is the lower melting point ($T_m = 180$ °C) compared to PA 6 ($T_m = 225$ °C). As a result, copolymers of LL and ϵ -CLA have been investigated to combine high melting points with lowest possible water uptake,²⁴ resulting in various types of commercially important PA 6/12.²⁵

Mechanistically, LL can be expected to polymerize following the well-known anionic ring-opening of ϵ -CLA,²⁶ as depicted in Scheme 1, where it is proposed that the *N*-heterocyclic carbene is acting as base. Generally, anionic lactam polymerization displays an induction time, but is in sum much faster than hydrolytic polymerization of lactams.²⁶ This allows the use of reactive extrusion techniques, where usually the monomeric melt is combined with initiator/catalyst (organic or inorganic bases) and activator (such as *N*-acyl lactam or cyclohexyl isocyanate) and polymerized within seconds or few minutes to the polyamide. A reduction of necessary components considerably simplifies the technical realization, and for PA 12 the reduction to a two-component system combined with reactive extrusion has been successfully executed by Månson et al.²⁷ The system consisting solely of a protected NHC and LL discussed below is thought to be applied in this kind of technique, the more so since it allows a further reduction of polymerization components.

EXPERIMENTAL SECTION

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 glovebox (MBraun Lab Master 130, MBraun, Garching, Germany) or by standard Schlenk techniques. CH_2Cl_2 , 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. ϵ -Caprolactam was a gift from L. Brüggemann KG (Heilbronn, Germany). The sample was a commercial grade monomer designated for anionic polymerization (dried, packed in airtight foliage). Lauro lactam was bought from

Scheme 2. Preparation of the Initiators via Amidines (Top) or via Cyclization of Diamines (middle) and Synthesis of Diazepinium-Derivative **1**^a (Bottom)



^aThis compound decomposed when reacted with KHMDS.

Aldrich (98%). Both lactams were stored under nitrogen and used without further purification. All noncommercial amidines, NHC-precursors, NHC-carboxylates and NHC-metal complexes were synthesized as described in the literature.^{19,20,28} NMR measurements were recorded on a Bruker Avance III 400. IR spectra were measured on an IFS 28 (Bruker) using KBr pellets or via ATR on a Bruker Alpha instrument. GC-MS data were recorded on an Agilent Technologies device consisting of a 7693 autosampler, a 7890A GC and a 5975C quadrupole MS. An SPB-5 fused silica column (34.13 m \times 0.25 mm \times 0.25 μ m film thickness) was used. For GPC, a column set by PSS Polymer Standard Service (Mainz, Germany) was used (precolumn PSS SDV, 20 μ m, 8 \times 50 mm, column SDA 0830201E3, PSS SDV, 1000 \AA , 20 μ m, 8 \times 300 mm, column SDA 0803201E5, PSS SDV, 10 000 \AA , 20 μ m, 8 \times 300 mm). The GPC system was maintained at 70 $^\circ$ C and a flow rate of 1 mL/min using PS standards and *m*-cresol as a solvent. DSC measurements were conducted using a DSC 4000 by Perkin-Elmer (software: Pyris) and heating rates of 20 $^\circ$ C/min in a range of -50 to $+250$ $^\circ$ C. Rheology was measured using an RMS 800 (Rheometric scientific). During the measurements, a nitrogen atmosphere was applied. Prior to addition of the premixed initiator/monomer-sample the plates were heated to the desired reaction temperature. About 2 mL of melt was necessary for each measurement.

2,4-Dicyclohexyl-4,5-dihydro-1H-benzo-1,3-diazepinium Bromide (1). *N,N'*-Di(cyclohexyl)formamidinium¹⁹ (14 mmol, 2.92 g), 1,2-bis(bromomethyl)benzene (15.53 mmol, 4.10 g, 1.1 equiv), and potassium carbonate (7.16 mmol, 0.99 g, 0.5 equiv) were suspended in 130 mL of acetonitrile. The mixture was refluxed for 5 h, while the reaction progress was monitored via 1H NMR. Then all volatiles were removed by evaporation, and the residue was dissolved in dichloro-

methane. After filtration, diethyl ether was added to the clear solution, which resulted in the precipitation of a white solid. Yield: 5 g (12.8 mmol, 91%). 1H NMR ($CDCl_3$, δ): 8.85 (s, 1H), 7.36 (m, 2H), 7.20 (m, 2H), 4.73 (s, 4H), 4.05 (m, 2H), 1.08–2.00 (m, 20H). ^{13}C NMR ($CDCl_3$, δ): 154.5, 134.8, 129.9, 128.2, 67.6, 47.3, 30.9, 24.94, 24.86. IR (ATR, cm^{-1}): 2928 (s), 2856 (m), 1660 (s), 1449 (m), 1072 (m), 752 (s), 610 (m). HRMS (ESI) m/z calcd for $C_{21}H_{31}N_2Br$, 390.1671; found, 311.2489 $[M - Br]^-$.

Homopolymerization of LL. For polymerization, pellets of LL (500–2000 mg) were combined with the desired amount of initiator (5–15 mg) and transferred into a Schlenk vessel, which was sealed, removed from the glovebox, and submerged in a preheated oil bath. After the required reaction time, the polymerization was quenched by rapid cooling. The solid polymeric mass was then dissolved in hot *m*-cresol and precipitated from acetone. After the product was washed three to four times with acetone, an off-white polymer was isolated and dried *in vacuo*. All yields given in this work are isolated yields as calculated from the mass of polymer and mass of monomer.

For kinetic experiments, a master batch was created by mixing monomer and initiator using 5–15 g of LL. Both were finely homogenized using mortar and pestle to give a white powder. From this master batch, smaller portions (0.75 g) were taken to conduct polymerizations of varying reaction times. To ensure identical conditions, for each experiment, the same type of vessel and stirrer was used, as well as the same stirring rate.

Copolymerization of LL and ϵ -CLA. For copolymerization, initiator, pellets of LL, and flakes of ϵ -CLA were combined in a Schlenk vessel. This was sealed, removed from the glovebox and submerged in a preheated oil bath. Again the reaction was stopped by

rapid cooling. Dissolving in hot *m*-cresol was possible and work-up proceeded as described above for the homopolymerizations.

To identify the copolymer composition, the polymer yield was calculated. After that, the residual monomer ratio of LL and ϵ -CLA in the washing solution (*m*-cresol enriched acetone) was investigated using GC–MS analysis. The found ratios were compared to a calibration curve using samples containing 25, 50, 67, and 75 mol % of LL. Knowledge of the residual amounts of monomer then allowed for calculating the copolymer composition.

RESULTS AND DISCUSSION

Synthesis of Initiators. To provide a fast and simple nomenclature, the protected NHCs used in this work are named according to the sequence “ring size-substituent-protecting group”. So, **5s-tBu-CO₂** is representing 1,3-di(*tert*-butyl)-imidazolinium-2-carboxylate. “5s” refers to a saturated five-membered ring and thus differentiates imidazolinium- from imidazolium derivatives. Free carbenes like 1,3-di(cyclohexyl)-imidazol-2-ylidene would be abbreviated as **5-Cy**.

The synthetic routes (Scheme 2) that were used to prepare the target compounds (Scheme 1) are well-known in the literature and combine a simple synthesis with a minimal amount of steps while maintaining a high flexibility with regard to *N*-substituents and ring size.^{19,20,28}

Readily available primary amines served as starting material for amidines, which were reacted with dihaloalkanes to yield the cyclic NHC-precursors (**6-Mes-CO₂**, **6-Dipp-CO₂**, **6-Hep-CO₂**, **6-Cy-CO₂**, **6-OMe-CO₂**, **7-Mes-CO₂**, and **7-Dipp-CO₂**). Alternatively, commercially accessible diamines were used for cyclization (**5s-tBu-CO₂**, **6-iPr-CO₂**). With exception of the generation of the free carbenes and concomitant reaction with either CO₂ or the metal salt, no protective atmosphere was necessary. In all cases the initiators were synthesized in a maximum of three steps. In case the NHC-precursors were commercial products, only one step delivered the desired compounds (e.g., **5s-Mes-MCl₂** (M = Mg, Zn, Sn)). Though the methods shown in Scheme 2 generally delivered a broad range of protected NHCs, it was not possible to prepare the CO₂-adduct of compound **1** this way. Though **1** can easily be prepared in high yields, upon addition of a base (potassium hexamethyldisilazide or KHMDS) to a suspension of **1** in THF, decomposition was observed. Similar behavior has been described for comparable benzannulated diazepinium-derived compounds.²⁹

NHC-carboxylates and NHC-metal complexes were obtained as amorphous powders or crystalline materials. After prolonged storage (up to two years) under nitrogen atmosphere at room temperature, NMR analysis showed no visible signs of decomposition or decarboxylation/deprotection.

Homopolymerization of LL. Polymerization experiments were effortlessly possible by mixing initiator and LL (commercial grade monomer, see also the Experimental Section) and subjection of this mixture to heating under nitrogen. Because of the high melting point of LL (152 °C) and the experience from ϵ -CLA homopolymerization,²¹ a reaction temperature of at least 180 °C seemed reasonable. Under these conditions, a monomeric, stirrable melt was formed. In case polymer formed, a rapid solidification after few minutes was observed. When no polymerization took place, the reaction mass stayed liquid and the residues were soluble in acetone after cooling. Table 1 lists the polymerization results with every single initiator.

It is immediately obvious that the structure of the initiator is decisive for the outcome of the polymerization. Quantitative

Table 1. Bulk Polymerizations of LL Using Protected NHCs at *T* = 180 °C^a

no.	NHC	NHC:LL	yield ^b [%]	<i>M_n</i> (PDI) ^c [g/mol]
1	—	pure LL	—	—
2	6-Cy-CO ₂	1:100	100	7100 (2.6)
3	6-Cy-CO ₂	1:300	100	13900 (2.4)
4	6-Cy-CO ₂	1:500	77	13200 (2.4)
5	6-Hep-CO ₂	1:100	93	6700 (2.3)
6	6-iPr-CO ₂	1:100	82	8500 (2.9)
7	6-Mes-CO ₂	1:100	<1	—
8	6-Dipp-CO ₂	1:100	<1	—
9	6-OMe-CO ₂	1:100	<1	—
10	5s-tBu-CO ₂	1:100	96	7000 (2.6)
11	5-tBu-CO ₂	1:100	71	7600 (2.8)
12	5-Cy-CO ₂	1:100	23	11600 (3.1)
13	5-iPr-CO ₂	1:100	<5	—
14	7-Mes-CO ₂	1:100	<1	—
15	7-Dipp-CO ₂	1:100	<1	—
16	5s-Mes-MgCl ₂	1:100	<1	—
17	5s-Mes-ZnCl ₂	1:100	<1	—
18	5s-Mes-SnCl ₂	1:100	<1	—

^aHeating time = 45 min. ^bIsolated yield. ^cGPC (*m*-cresol) relative to PS standards.

yields even at low initiator loadings sharply contrast with reactions delivering absolutely no PA 12. The distinctly best results were obtained using **6-Cy-CO₂**, and generally *N*-alkyl bearing initiators performed well. As was shown for the NHC-mediated synthesis of PA 6,²¹ the activity of the protected NHC can clearly be related to the basicity of the corresponding free carbene. The correlation of ring size and basicity for NHCs is 7 \approx 6 \gg 5s > 5, reflecting the fact that basic properties mainly depend on the N–C–N angle.³⁰ Furthermore, *N*-aryl- instead of *N*-alkyl substitution considerably diminishes the p*K_a* values, which span a range of roughly 21 (**5s-Mes**: 21.3) to 28 (**6-iPr**: 28.2) in H₂O at 25 °C.³¹ Accordingly, for the NHCs presented here, an order of basicity of **6-Cy** \approx **6-Hep** \approx **6-iPr** \gg **5s-tBu** > **5-tBu** > **5-Cy** \approx **5-iPr** \gg **5s-Mes** can be expected. For the inactivity of **7-Mes-CO₂** and **7-Dipp-CO₂**, see below. This is nicely reflected by the polymerization yields in Table 1. Under identical conditions **6-Cy-CO₂** allows quantitative isolation of polymer; very high yields can also be achieved by the action of **6-Hep-CO₂**, **6-iPr-CO₂** and **5s-tBu-CO₂**. **5-tBu-CO₂** already delivers somewhat worse results (entry 11) and **5-Cy-CO₂** seems to represent a case where a limiting minimal basic strength is reached and only 23% of PA 12 can be isolated. At a p*K_a* value lower than that (approximately 24 in H₂O at 25 °C),³¹ the initiators lose their activity and practically no product is formed. A mild exception is the high activity of **5s-tBu-CO₂**, which performs somewhat better than expected. Interestingly, no PA 12 was formed when *N*-aryl bearing initiators were used, irrespective of the ring size. This explains the inactivity of both **7-Mes-CO₂** and **7-Dipp-CO₂** and was even found true for the more electron-rich **6-OMe-CO₂** (entry 9). Also the NHC-metal complexes **5s-Mes-MgCl₂**, **5s-Mes-Zn-Cl₂**, and **5s-Mes-SnCl₂** did not deliver PA 12 (entries 16–18). All these data together suggest that (i) steric factors play a role, too, and (ii) the polymerization process is not susceptible to Lewis acid activation or at least not susceptible enough to overcome the relatively weak basicity of the NHC in action (**5s-Mes**). The same metal complexes performed very well in the polymerization of ϵ -caprolactone,²⁰ though in the presence of

benzylic alcohol, but there a *nucleophilic* pathway (attack by the NHC on the carbonyl and ring-opening) is accessible for this kind of NHC. In contrast to that, the observations discussed above and the rheology measurements (see below) support the assumption of strictly *basic* activity of the free NHCs in lactam polymerization (deprotonation of the lactam). In the absence of NHCs control reactions did not deliver any PA 12 (entry 1).

The molecular weights given in Table 1 are relatively uniform when a ratio of 1:100 (NHC:LL) is applied, ranging from 6700 to 8500 g/mol in all examples with the exception of **5-Cy-CO₂**. There, the molecular weight is higher (11 600 g/mol, entry 12) although the conversion is low, which can be related to ineffective initiation due to the relatively low basicity of the free NHC. Impressively, the use of **6-Cy-CO₂** allows raising the ratio of initiator to monomer to 1:300 (Table 1, entry 3), and still quantitative yields are achieved. The tripling of the ratio roughly is accompanied by a doubling of the molecular weight, which emphasizes the nonliving character of anionic lactam polymerization (compare entries 2 and 3; see also discussion below). Finally, at an initiator loading of 0.2 mol % the conversion of monomer arrives at 77% after 45 min (entry 4).

Compared to the homopolymerization of ϵ -CLA,²¹ the polymerization of LL results in better yields and considerably lower molecular weights. Keeping the different melting points in mind (180 °C, PA 12; 225 °C, PA 6), it seems reasonable to assume that chain mobility is an important factor. A reaction temperature below the melting point of the polymer can cause precipitation of the polyamide from the melt of its own monomer and thus “bury” the growing chains, the more so since polyamides can display high degrees of crystallinity.²⁵ Consequently, in the case of LL polymerization, a more complete conversion alongside a higher concentration of growing chains can be expected in the melt, which would result in lower molecular weights. In addition to this, anionic ROP of lactams is usually accompanied by side reactions and far from being a living process.³² Because of that molecular weights cannot be calculated in the same way as it can be done for truly living anionic polymerizations. Furthermore, discrepancies in molecular weight can be induced by residual water content of the monomer (see below).

To gain further insight into the polymerization process, the conversion of monomer over time was studied (Figure 2). The resulting mass of solidified PA 12 during reaction and its limited solubility do not allow removing samples for

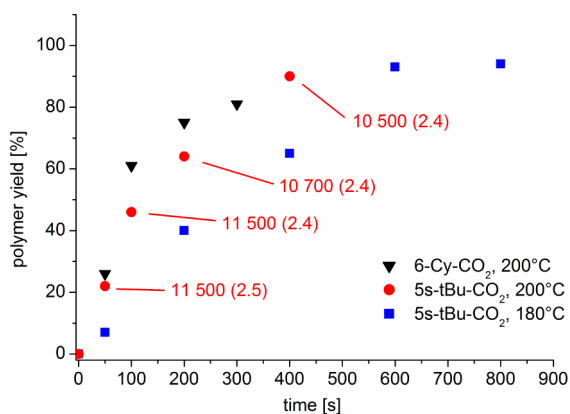


Figure 2. Polymer yield vs reaction time and M_n (PDI) for one set of experiments. [NHC]:[LL] = 1:100. Formation of homogeneous, stirred melt = t_0 .

investigation by NMR or GC-MS, so each point given in Figure 2 represents an independent polymerization. These were taken from one batch of mixed initiator and monomer and processed under identical conditions, except for varying reaction times (see also Experimental). At 180 °C, **5s-tBu-CO₂** reaches isolated polymer yields of >90% after 600 s. An increase of the polymerization temperature to 200 °C results in the same isolated yields after only 400 s. **6-Cy-CO₂** promotes an even faster reaction, especially in the early stages of the polymerization. It is not uncommon to polymerize lactams anionically via batch or extrusion techniques at temperatures of 250–270 °C.²⁷ This underlines that the reaction conditions applied so far are relatively mild and a further increase in the polymerization rates at higher temperatures can well be expected. An equally interesting point is the correlation of conversion and molecular weight during polymerization. To this end, the polyamides received after different reaction times were subjected to GPC analysis (see also Figure 2 for one set of examples). Importantly, the growing monomer conversion is not accompanied by according chain growth but by a certain decrease of molecular weight. This behavior is most probably effected by “chain multiplication”, a side reaction that is caused by the lactam anion attacking the amide bonds of the polymer.³³ This process gains importance as the concentration of polymer increases and leads to a degradation of the polyamide parallel to further incorporation of monomer, with the overall result of slowly decreasing molecular weight. Though there is a paucity on reaction kinetics and especially reaction kinetics coupled with molecular weight analysis in the literature, it has been described that in anionic ROP of lactams high molecular weights are built up very fast to degrade thereafter, which contrasts the hydrolytic lactam polymerization.³⁴ We observed this effect in all investigated polymerizations (see Supporting Information for further examples), which again strongly supports the proposed basic action of the NHC.

Recording of the polymerization rheology (Figure 3) allows a complementary view on the reaction process. In a rheometer

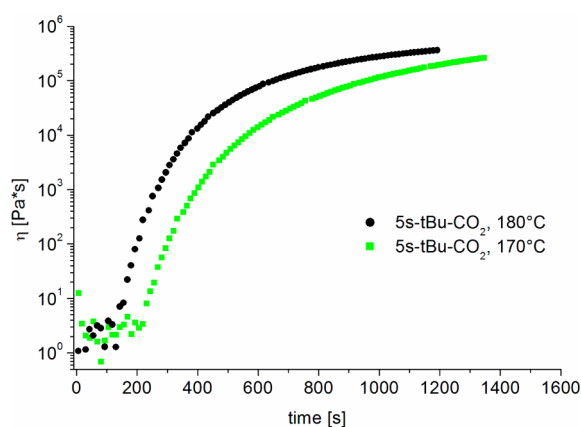


Figure 3. In-situ rheological measurement of LL homopolymerization. [NHC]:[LL] = 1:100.

equipped with plate geometry and preheated plates the homogenized mixtures of LL and initiator were inserted and the increase in viscosity (up to 10^6 Pa·s) over time was measured. An induction period with unchanged viscosity (monomeric melt) is followed by a rapid increase of viscosity. Induction times like these are typically encountered in anionic

ROP of lactams,²⁶ because the first polymerization step consists of the ring-opening of nonactivated lactam (see Scheme 1). Industrially, a preactivated monomer (“activators”, see also introduction) is added to suppress these induction times. As can be seen from Figure 3, in the case of **5s-tBu-CO₂** and an initiator loading of 1 mol %, the polymerization starts after about 160 s at 180 °C. At 170 °C, the induction period is somewhat longer (200 s). The growing viscosities reflect formation of polymeric material, but this can only indirectly be compared to monomer consumption, as viscosity itself depends on temperature, molecular weight, molecular weight distribution and crystallinity. However, the accelerating effect of increased temperature observed in the kinetic experiments (Figure 2) is mirrored by the results from rheology. Comparing the curves at 170 and 180 °C (Figure 3), the former displays a considerably lower viscosity after the same reaction time than the latter (10^3 vs 10^4 Pa·s after 400 s). This allows safely assuming a lower degree of conversion, the more so since the lower temperature should increase the viscosity. From an engineering point of view and for future extrusion experiments, a correlation of kinetics and rheology is of course highly desirable.^{27,35}

In the solid state, NHC–carboxylates are known to be stable up to high temperatures,^{14a} and consequently, we observed no diminishing activity of the monomer/initiator mixtures over a period of 1 month. The samples were hereby stored at room temperature under exclusion of water. However, exposition of the powdered mixtures to atmosphere for 1 h resulted in complete quenching of any polymerization activity. This may be attributed to the uptake of water, either by the finely powdered monomer or by the initiator itself. The reactivity of NHC–CO₂ adducts toward water ranges from inertness³⁶ over formation of hydrogen carbonates¹³ to decomposition,^{14a} depending on structure and conditions. Generally, this observed sensitivity toward atmospheric humidity is in accordance with the assumption of an anionic polymerization mechanism.

Copolymerization of LL and ϵ -CLA. Having established that the NHC-mediated homopolymerization of LL and ϵ -CLA²¹ is possible, the copolymerization of both monomers and the composition of the resulting copolymer was investigated. To this end, the same reaction conditions (bulk, 180 °C) and the best initiator (**6-Cy-CO₂**) were used as described above. Flakes of ϵ -CLA and pellets of LL were combined with the required amount of initiator (molar ratio of [NHC]:[LL]:[ϵ -CLA] = 1:50:50, which corresponds to a LL-content of 64% by weight). Several batches were reacted this way and stopped after different polymerization times. The precipitation and washing solutions were collected, concentrated and analyzed by GC–MS to calculate the ratios of residual monomer. This allowed to determine the composition of the PA 6/12 copolymer (see also Experimental). Figure 4 depicts the results for this series of experiments.

As expected, isolated yields increased over time from 17% after 140 s to 96% after 45 min. More interesting, a clear preference for the incorporation of ϵ -CLA at the beginning of the polymerization is apparent. In the early stages of the reaction, only 25% of the polymer constitute of LL. Only at higher conversions, where the monomeric melt is enriched with LL, it is consumed more frequently. In other words, a copolymer with a considerable gradient is formed. Strong support for the accuracy of these data is provided by thermal analysis. A growing amount of incorporated LL is mirrored by a

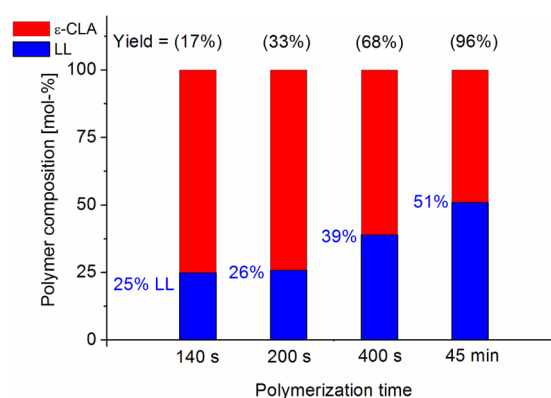


Figure 4. Bulk copolymerization of LL and ϵ -CLA using **6-Cy-CO₂**. [NHC]:[LL]:[ϵ -CLA] = 1:50:50 at $T = 180$ °C. With growing conversion the incorporation of LL increases.

decrease in the melting point of the corresponding copolymer (Table 2), which is lower than that of either homopolymer. The effect is quite strong and in good agreement with results from the literature, where PA 6/12 of varying constitution was prepared.²³ There, a minimum melting point was found at a molar ratio of 50% LL in the copolymer, which fits the data given in Table 2 (see Supporting Information for examples of DSC analyses). The melting points listed in Table 2 refer to polyamide that was stored under ambient conditions prior to DSC measurements, which means that the melting points are roughly 10 °C lower than expected from dry polyamide due to uptake of atmospheric water. It should be noted that after prolonged reaction times, again “chain multiplication” was observed, the molecular weight decreased from 13 200 g/mol after a polymerization time of 140 s to 9400 g/mol after 400 s (Table 2). The effect is somewhat stronger than in LL homopolymerization (see above) and accordingly seems to continue. Thus, after 45 min of polymerization, it was not possible to observe a peak via GPC analysis of the corresponding sample. This is most presumably due to both the formation of lower molecular weights and a very broad molecular weight distribution, as judged from GPC analysis. It should be emphasized that the decrease in molecular weight is not responsible for the lowering of the melting point (compare entries 1, 4, and 5 in Table 2). However, it can be expected that the nonliving polymerization process in combination with chain multiplication will entail a “scrambling” of the gradient, particularly in case longer reaction times are applied.

Judging from the polymerization mechanism (Scheme 1), the most important factors for copolymer composition should be (a) the pK_a -value of the lactams, (b) ring tension and heat of polymerization of the respective lactams, and (c) effect of the counterion (protonated NHC). For both LL and ϵ -CLA, a pK_a -value of 27.2 (DMSO, 25 °C) is reported.³⁷ So there should be no preference in the formation of “activated monomer” (deprotonated lactam) for either monomer. The higher ring tension and concomitant higher heat of polymerization of ϵ -CLA,³³ however, are obviously decisive for the outcome of the copolymerization and cause the preference for ϵ -CLA incorporation at the onset of the polymerization. For conventionally activated and catalyzed copolymerizations of ϵ -CLA and LL a similar tendency has been observed.³⁸ There, the distribution of the monomeric units within the copolymer, whether in a more random or a more “blocky” way, is influenced by the nature of the catalysts.³⁹ Whether the same is

Table 2. Bulk Copolymerizations of LL and ϵ -CLA Using 6-Cy-CO₂ at $T = 180\text{ }^{\circ}\text{C}$

NHC:LL: ϵ -CLA	t	mol % LL ^a /yield ^b [%]	T_m [$^{\circ}\text{C}$]	M_n (PDI) ^c [g/mol]
1:50:50	140 s	25/17	171	13200 (2.4)
1:50:50	200 s	26/33	163	9900 (2.4)
1:50:50	400 s	39/68	138	9400 (2.1)
1:50:50	45 min	51/96	120	n.d.
1:150:150	45 min	47/86	120	13200 (2.5)
1:100:0	45 min	100/100	169	7100 (2.6)

^aThe mol % of LL in the copolymer, calculated by GC–MS analysis of residual monomer content. ^bIsolated overall yield of polymer. ^cGPC (*m*-cresol) relative to PS standards.

true for NHC-mediated anionic copolymerizations has still to be investigated, but a truly innocent role of the protonated NHC as counterion seems doubtful. Size as counterion and formation of ion pairs can well be expected to influence the copolymerization preferences.

Decreasing the initiator loading (entry 5, Table 2) to 1:150:150 still allows isolating the PA 6/12 copolymer in good yields of 86%. In accordance to the high conversion, a high degree of LL incorporation and a low melting point is found. It is interesting to note that LL homopolymerization with an applied ratio of NHC:LL of 1:300 still produces quantitative yields (see above), while the copolymerization shows somewhat reduced activity. Since chain mobility should not be a problem here (low melting point of the copolymer) it seems most probable that residual water content in the commercial ϵ -CLA is responsible for the loss of activity.

CONCLUSION

It has been demonstrated that protected NHCs are well suited for the application as thermally latent initiators in the additive-free bulk polymerization of laurolactam. Mixtures of initiator and monomer are storable for weeks without any loss of activity and allow effortless polymerization by simple heating. After thermal activation, polymerizations were shown to proceed swiftly and moderately controlled. Success in the production of the polyamide is dependent on the structure of the initiating NHC, where 1,3-di(cyclohexyl)-tetrahydropyrimidinium-2-carboxylate (6-Cy-CO₂) turned out to be the most efficient pre-initiator in this study. With this protected NHC, quantitative yields of PA 12 are accessible in relatively short polymerization times with acceptable molecular weight distribution. The correlation of NHC-basicity and NHC-activity in polymerization, the sensitivity toward atmospheric humidity, the occurrence of “chain multiplication” and the observation of induction times all support the presence of lactam anions and thus a basic action of the NHC.

Finally, the copolymerization of LL and ϵ -CLA was investigated. It was found that a gradient copolymer is formed, with ϵ -CLA being incorporated preferentially at the onset of the polymerization. The considerable discrimination between both monomers by the polymerization system in spite of their very similar physical properties promises the possibility of producing more “blocky” polyamides in simple bulk polymerization by appropriate choice of monomers and reaction conditions. Work on these topics seems certainly worthwhile and is currently carried out in our group.

Overall, the simple and cheap preparation of the protected NHCs and the application of an easy-to-handle one-component system certainly make this process an interesting choice for large scale extrusion polymerization, especially since the NHC–

CO₂/monomer mixtures constitute a completely metal-free approach to polyamides.

ASSOCIATED CONTENT

Supporting Information

¹³C NMR of compound 1, further details on molecular weight development during polymerization, a figure showing chain multiplication, and DSC graphs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*(M.R.B.) E-Mail: michael.buchmeiser@ipoc.uni-stuttgart.de.

Funding

Notes

Financial support by Evonik Industries and the University of Stuttgart is gratefully acknowledged.

ACKNOWLEDGMENTS

B.Sc. Laura Widmann is gratefully acknowledged for support in synthesis. Manfred Simmet (IKT Stuttgart) and Dr. Rainer Gutmann (ITCF Denkendorf) are thanked for help with polymer characterization. Finally, L. Brüggemann KG (Heilbronn, Germany) is acknowledged for a gift of ϵ -caprolactam.

REFERENCES

- (a) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606–5655. (b) Marion, N.; Díez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988–3000. (c) Nair, V.; Vellalath, S.; Babu, B. P. *Chem. Soc. Rev.* **2008**, *37*, 2691–2698.
- (2) Maji, B.; Breugst, M.; Mayr, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 6915–6919.
- (3) (a) Biju, A. T.; Padmanaban, M.; Wurz, N. E.; Glorius, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 8412–8415. (b) Vora, H. U.; Wheeler, P.; Rovis, T. *Adv. Synth. Catal.* **2012**, *354*, 1617–1639. (c) Grossmann, A.; Enders, D. *Angew. Chem., Int. Ed.* **2012**, *51*, 314–325.
- (4) Ryan, S. J.; Candish, L.; Lupton, D. W. *Chem. Soc. Rev.* **2013**, *42*, 4906–4917.
- (5) Magill, A. M.; Cavell, K. J.; Yates, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 8717–8724.
- (6) Benhamou, L.; Chardon, E.; Lavigne, G.; Bellemin-Lapponnaz, S.; César, V. *Chem. Rev.* **2011**, *111*, 2705–2733.
- (7) (a) Fèvre, M.; Pinaud, J.; Gnanou, Y.; Vignolle, J.; Taton, D. *Chem. Soc. Rev.* **2013**, *42*, 2142–2172. (b) Dove, A. P. *ACS Macro Lett.* **2012**, *1*, 1409–1412.
- (8) (a) Zhang, Y.; Chen, E. Y.-X. *Angew. Chem.* **2012**, *124*, 2515–2519. (b) Scholten, M. D.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2008**, *41*, 7399–7404.
- (9) (a) Raynaud, J.; Absalon, C.; Gnanou, Y.; Taton, D. *J. Am. Chem. Soc.* **2009**, *131*, 3201–3209. (b) Raynaud, J.; Ottou, W. N.; Gnanou, Y.; Taton, D. *Chem. Commun.* **2010**, *46*, 3203–3205.
- (10) (a) Kamber, N. E.; Jeong, W.; Gonzalez, S.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2009**, *42*, 1634–1639. (b) Shin, E.

- J.; Jeong, W.; Brown, H. A.; Koo, B. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2011**, *44*, 2773–2779.
- (11) Nyce, G. W.; Glauser, T.; Connor, E. F.; Möck, A.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 3046–3056.
- (12) Rodriguez, M.; Marrot, S.; Kato, T.; Stérin, S.; Fleury, E.; Baceiredo, A. *J. Organomet. Chem.* **2007**, *692*, 705–708.
- (13) (a) Fèvre, M.; Pinaud, J.; Leteneur, A.; Gnanou, Y.; Vignolle, J.; Taton, D.; Miqueu, K.; Sotiropoulos, J.-M. *J. Am. Chem. Soc.* **2012**, *134*, 6776–6784. (b) Fèvre, M.; Coupillaud, P.; Miqueu, K.; Sotiropoulos, J.-M.; Vignolle, J.; Taton, D. *J. Org. Chem.* **2012**, *77*, 10135–10144.
- (14) (a) van Ausdall, B. R.; Glass, J. L.; Wiggins, K. M.; Aarif, A. M.; Louie, J. J. *J. Org. Chem.* **2009**, *74*, 7935–7942. (b) Fèvre, M.; Vignolle, J.; Taton, D. *Polym. Chem.* **2013**, *4*, 1995–2003. (c) Hans, M.; Wouters, J.; Demonceau, A.; Delaude, L. *Eur. J. Org. Chem.* **2011**, *2011*, 7083–7091. (d) Delaude, L.; Demonceau, A.; Wouters, J. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1882–1891.
- (15) (a) Bantu, B.; Pawar, G. M.; Decker, U.; Wurst, K.; Schmidt, A. M.; Buchmeiser, M. R. *Chem.—Eur. J.* **2009**, *15*, 3103–3109. (b) Bantu, B.; Pawar, G. M.; Wurst, K.; Decker, U.; Schmidt, A. M.; Buchmeiser, M. R. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1970–1976.
- (16) Norris, B. C.; Sheppard, D. G.; Henkelman, G.; Bielawski, C. W. *J. Org. Chem.* **2011**, *76*, 301–304.
- (17) (a) Coulembier, O.; Dove, A. P.; Pratt, R. C.; Sentman, A. C.; Culkin, D. A.; Mespouille, L.; Dubois, P.; Waymouth, R. M.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4964–4968. (b) Coulembier, O.; Lohmeijer, B. G. G.; Dove, A. P.; Pratt, R. C.; Mespouille, L.; Culkin, D. A.; Benight, S. J.; Dubois, P.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 5617–5628.
- (18) Arduengo, A. J., III; Calabrese, J. C.; Davidson, F.; Rasika Dias, H. V.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J.; Tamm, M.; Schmutzler, R. *Helv. Chim. Acta.* **1999**, *82*, 2348–2364.
- (19) Naumann, S.; Schmidt, F. G.; Schowner, R.; Frey, W.; Buchmeiser, M. R. *Polym. Chem.* **2013**, *4*, 2731–2740.
- (20) Naumann, S.; Schmidt, F. G.; Frey, W.; Buchmeiser, M. R. *Polym. Chem.* **2013**, *4*, 4172–4181.
- (21) Naumann, S.; Epple, S.; Bonten, C.; Buchmeiser, M. R. *ACS Macro Lett.* **2013**, *2*, 609–612.
- (22) (a) Memeger, W.; Campbell, G. C.; Davidson, F. *Macromolecules* **1996**, *29*, 6475–6480. (b) Yang, H.; Zhao, J.; Yan, M.; Pispas, S.; Zhang, G. *Polym. Chem.* **2011**, *2*, 2888–2892.
- (23) Garner, D. P.; Fasulo, P. D. *J. Appl. Polym. Sci.* **1988**, *36*, 495–509.
- (24) Udiipi, K.; Davé, R. S.; Kruse, R. L.; Stebbins, L. R. *Polymer* **1997**, *38*, 927–938.
- (25) Marchildon, K. *Macromol. React. Eng.* **2011**, *5*, 22–54.
- (26) Odian, G. G. *Principles of polymerization*; Wiley: Hoboken, NJ, **2004**.
- (27) (a) Luisier, A.; Bourban, P.-E.; Månson, J.-A. E. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3406–3415. (b) Luisier, A.; Bourban, P.-E.; Månson, J.-A. *Composites Part A: Appl. Sci. and Manuf.* **2003**, *34*, 583–595.
- (28) Iglesias, M.; Beetstra, D. J.; Knight, J. C.; Ooi, L.-L.; Stasch, A.; Coles, S.; Male, L.; Hursthouse, M. B.; Kingsley, J. C.; Dervisi, A.; Fallis, I. A. *Organometallics* **2008**, *27*, 3279–3289.
- (29) (a) Kolychev, E. L.; Portnyagin, I. A.; Shuntikov, V. V.; Khrustalev, V. N.; Nechaev, M. S. *J. Organomet. Chem.* **2009**, *694*, 2454–2462. (b) Scarborough, C. C.; Popp, B. V.; Guzei, I. A.; Stahl, S. J. *J. Organomet. Chem.* **2005**, *690*, 6143–6155.
- (30) (a) Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940–6952. (b) Nelson, D. J.; Nolan, S. P. *Chem. Soc. Rev.* **2013**, *42*, 6723–6753.
- (31) Higgins, E. M.; Sherwood, J. A.; Lindsay, A. G.; Armstrong, J.; Massey, R. S.; Alder, R. W.; O'Donoghue, A. C. *Chem. Commun.* **2011**, *47*, 1559–1561.
- (32) (a) Kušková, M.; Roda, J.; Králíček, J. *Makromol. Chem.* **1978**, *179*, 337–344. (b) Roda, J.; Králíček, J.; Karel, Š. *Eur. Polym. J.* **1976**, *12*, 729–732. (c) Šebenda, J.; Kouřil, V. *Eur. Pol. J.* **1971**, *7*, 1637–1648. (d) Tani, H.; Konomi, T. *J. Polym. Sci., Part A: 1* **1966**, *4*, 301–
318. (e) Costa, G.; Pedemonte, E.; Russo, S.; Savà, E. *Polymer* **1979**, *20*, 713–718.
- (33) Sekiguchi, H. in: Ivin, K. J.; Saegusa, T. *Ring-opening polymerization*; Elsevier Applied Science: London, 1984, 809–918.
- (34) (a) Vieweg, R.; Müller, A. *Kunststoff-Handbuch Band VI: Polyamide*; Hanser: Munich, 1966; (b) Griehl, W. *Faserforsch. Textiltech.* **1956**, *7*, 207.
- (35) Davé, R. S.; Kruse, R. L.; Udiipi, K.; Williams, D. E. *Polymer* **1997**, *38*, 949–954.
- (36) Smiglak, M.; Holbrey, J. D.; Griffin, S. T.; Reichert, W. M.; Swatloski, R. P.; Katritzky, A. R.; Yang, H.; Zhang, D.; Kirichenko, K.; Rogers, R. D. *Green Chem.* **2007**, *9*, 90–98.
- (37) Hashimoto, K. *Progr. Polym. Sci.* **2000**, *25*, 1411–1462.
- (38) (a) Frunze, T.; Kotelnikov, V.; Kurashev, V.; Ivanova, S.; Komarova, L.; Korshak, V. *Polym. Sci. USSR* **1976**, *18*, 348–353. (b) Kricheldorf, H. R.; Hull, W. E. *J. Polym. Sci., Polym. Chem.* **1978**, *16*, 2253–2264.
- (39) For an overview see: Dubois, P.; Coulembier, O.; Raquez, J.-M. *Handbook of ring-opening polymerization*; Wiley-VCH: Weinheim, Germany, **2009**, Chapter 7.8.