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Polymerization of *ε*-Caprolactam by Latent Precatalysts Based on Protected N-Heterocyclic Carbenes

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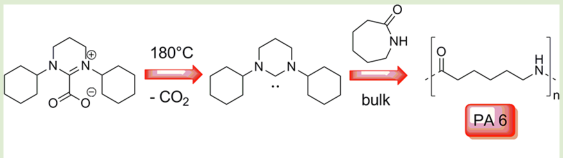
Supporting Information

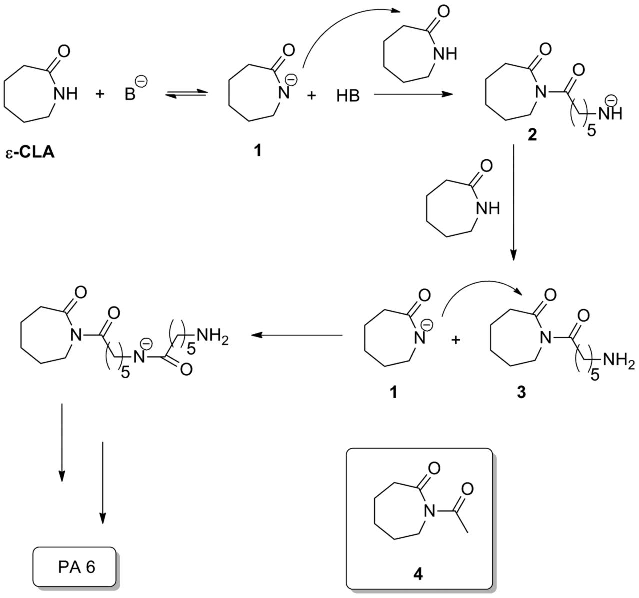
ABSTRACT: The cyclic amide *ε*-caprolactam (*ε*-CLA) is efficiently polymerized by thermally latent C-2-protected N-heterocyclic carbenes (NHCs) to give the corresponding polyamide (PA 6). Carbon dioxide- and metal salt-protected NHCs were used as precatalysts, out of which the free carbenes were generated thermally. This way, a premixing of the corresponding initiator with *ε*-CLA was possible to yield a storable and directly polymerizable mixture. The screening of a variety of differently constituted carbenes showed the importance of basicity of the active species, thereby revealing *N*-alkyl-bearing tetrahydropyrimidinium-based carbenes as the most active ones. Rapid production of PA 6 in high yields was possible in bulk polymerization at 180 °C, the best activity displayed by 1,3-dicyclohexyltetrahydropyrimidinium-2-carboxylate (**6-Cy-CO$_2$**). In situ rheology during polymerization showed the characteristics typical for the anionic polymerization of *ε*-CLA.



one-component, metal-free and storable latent polymerization system

Polyamides are among the most important polymeric materials and have gained a strong position in areas as diverse as textiles, high-performance fibers, or construction materials.[1] Apart from polycondensation,[1] the polymerization techniques include the ring-opening polymerization (ROP) of lactams, which applies to the commercially important product poly(*ε*-caprolactam) (PA 6).[2] Though solubility issues present difficulties when reaction kinetics are investigated, the generally accepted mechanism of the anionic ROP of *ε*-caprolactam involves the formation of "activated monomers" (**1**) which react with monomeric *ε*-CLA to form a primary amine-anion (**2**) which in turn regenerates a deprotonated lactam (Scheme 1).[3] The key step is the formation of an acylated lactam (**3**), which is activated compared to the nonacylated lactam by its markedly more electron-deficient character. It is thus more easily opened, and the polymerization proceeds rapidly. The first acylation is usually accompanied by a pronounced induction time. Industrially, the addition of preactivated monomer (e.g., *N*-acyl lactam (**4**)) is used to suppress these induction times and provide faster reactions.[4] To initiate the anionic ROP, strong bases like alkaline metals, hydrides, or Grignard reagents have been used.[3,5] Handling of these compounds on a larger scale can prove difficult. Consequently, no stable one-component system containing both the initiator and *ε*-CLA has yet been reported. However, the realization of room-temperature-stable, latent resin systems based on one-component systems for reaction transfer molding applications, e.g., for the synthesis of fiber−matrix composites, is highly desirable.

Scheme 1. Mechanism for the Anionic ROP of *ε*-CLA and Chemical Structure of the Frequently Used Activator *N*-Acyl Lactam



One class of organocatalysts that is of growing importance in polymer chemistry is N-heterocyclic carbenes (NHCs).[6] NHCs possess inherent nucleophilic and basic properties, and factors like steric encumbrance or electronic characteristics can be designed due to a wealth of versatile preparation strategies.[7] Free carbenes have been used to polymerize lactones,[8]

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acrylates,[9] siloxanes,[10] or epoxides.[11] Furthermore, it was shown that CO_2-, isothiocyanate-, or metal salt-adducts of NHCs can act as thermally latent precatalysts, opening the possibility to control the onset of polymerization by application of heat.[9b,12] Despite all these advantages of carbene organocatalysis, there is indeed only one single publication describing the interaction of carbenes with lactams. In a patent filed by DuPont in 2006, imidazolium- and imidazolinium-based *free* carbenes were added to ε-CLA, and the mixture was subjected to heating.[13] The best results were obtained by using 1,3-di-1-adamantyl-imidazol-2-ylidene applying a temperature of 200 °C for 60 min. This resulted in a yield of 84%, but a very high catalyst loading was necessary, restricting the ratios of NHC to monomer to only 1:30. Other carbenes delivered much lower yields. In view of these findings, the commercial importance of polyamides, and the lack of scientific investigations, a more in-depth examination seemed prudent. To this end, the thermally labile carbene progenitors depicted in Figure 1 were prepared via a simple synthetic route (see also Supporting Information).[9b,12a,b,14]

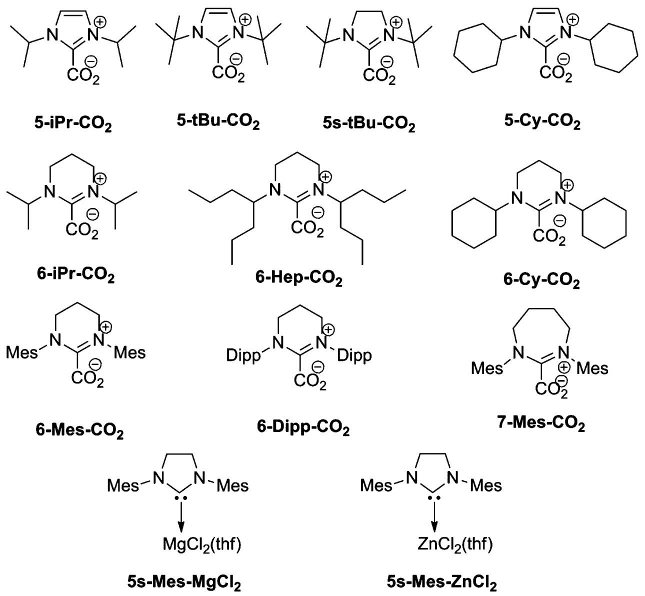


Figure 1. Protected NHCs used in this work and nomenclature according to: ring size-substituent-protecting group. Mes = 2,4,6-trimethylphenyl. Dipp = 2,6-diisopropyl-phenyl.

Table 1. Bulk Polymerizations of ε-CLA Using Protected NHCs at T = 180°C[a]

#	NHC	NHC: ε-CLA	yield[b] [%]	M_η [g/mol][c]
1	-	-	-	-
2	**6-iPr-CO_2**	1:110	69	140 000
3	**6-iPr-CO_2**	1:300	35	250 000
4	**6-Hep-CO_2**	1:120	78	240 000
5	**6-Cy-CO_2**	1:160	85	280 000
6	**6-Cy-CO_2**	1:300	76	420 000
7	**6-Mes-CO_2**	1:140	<1	-
8	**6-Dipp-CO_2**	1:140	<1	-
9	**5s-tBu-CO_2**	1:140	62	180 000
10	**5-tBu-CO_2**	1:140	41	170 000
11	**5-Cy-CO_2**	1:140	<5	-
12	**5-iPr-CO_2**	1:140	<5	-
13	**7-Mes-CO_2**	1:140	<1	-
14	**5s-Mes-$MgCl_2$**	1:140	<1	-
15	**5s-Mes-$ZnCl_2$**	1:140	<1	-

[a] Heating time = 45 minutes. [b] Isolated yield. [c] Determined by viscosimetric measurements.

The initiators, which are usually obtained as powders, were mixed with ε-CLA (commercial grade, see Supporting Information) and heated under nitrogen for a certain reaction time, after which the sample was cooled to room temperature and quenched by addition of formic acid. If polymerization took place, the monomeric melt was observed to solidify rapidly. Selected results are listed in Table 1.

It is obvious that the chemical structure strongly influences the outcome of the polymerizations. Depending on the ring size and the substituents, the resulting yields range from 85% consumption of monomer to complete inactivity. Control reactions lacking a carbene precursor did not deliver any poly(ε-caprolactam) (entry 1). Alkyl-substituted tetrahydropyrimidinium-derived compounds (**6-iPr-CO_2**, **6-Cy-CO_2**, **6-Hep-CO_2**, entries 2–6) perform well, followed by **5s-tBu-CO_2** and its unsaturated counterpart **5-tBu-CO_2** (entries 9 and 10). The initiators **5-Cy-CO_2** and **5-iPr-CO_2** delivered practically no PA 6 (entries 11 and 12). Considering the pK_a-value of ε-CLA (27.2 in DMSO at 25 °C)[5] and the mechanism shown in Scheme 1, these observations can indeed be explained by the requirement that a suitable initiator for anionic ROP of ε-CLA should display, namely, strong basicity. Thus, the activity of the different NHC-carboxylates used correlates with the pK_a-values of the corresponding free carbenes. It is well-known that six- and seven-membered NHCs are much more basic than the more common imidazolium- or imidazolinium-derived carbenes.[15] For the free carbene **6-iPr**, a value of 28.2 has been determined, compared to 25.2 for **5-tBu** and 21.3 for **5s-Mes** (in water, 25 °C).[16] Generally, imidazole- and imidazolin-2-ylidenes do not differ greatly, but *N*-aryl- instead of *N*-alkyl-substitution significantly lowers the pK_a-values. Accordingly, for the carbenes generated by the precatalysts presented in this work, an order of basicity of **6-Cy** ≈ **6-Hep** ≈ **6-iPr** ≫ **5s-tBu** > **5-tBu** > **5-Cy** ≈ **5-iPr** ≫ **5s-Mes** can be assumed. This is mirrored by the yields listed in Table 1 and also the solidification of the polymerization mass, which happens at a much earlier stage of the polymerization in the case that strongly basic carbenes are used (see also Supporting Information). The limiting basic properties necessary to induce polymerization seem to be reached when **5-Cy-CO_2** is used and almost no polymer is formed. Polymerizations at 140 and 160 °C using *N*-alkyl-bearing tetrahydropyrimidinium-2-carboxylates did result in the formation of polymer; however, yields were found to be lower, and solidification was observed to occur at a later point than in polymerizations carried out at 180 °C. It can be assumed that the lower viscosities at higher temperatures allow for higher mobility of the growing chains in the polymerization mass and consequently lead to higher conversions. **6-Cy-CO_2** produces yields that are superior to all others (entries 5, 6) though it is the progenitor for a carbene that should be only marginally more basic than **6-iPr**. Together with the fact that aryl-substituted carbenes did not yield any PA 6, irrespective of their ring size, this points to the influence of other aspects aside from basicity. It should be kept in mind that the reaction conditions at 180 °C are harsh compared to what is usually applied in carbene chemistry. Thus, stability of the active species and its propensity toward side reactions at these elevated temperatures must also be considered as important factors.

Metal-protected NHCs did not deliver polyamide (entries 14 and 15). Clearly, coordination of the Lewis acidic metal ions to the amide moiety (and thus acidification of the N−H bond) is not sufficient to counterbalance the relative low basicity of the parent carbene (**5s-Mes**). This contrasts sharply with recent findings concerning the polymerization of ε-caprolactone, where the presence of metal ions has a strong effect on polymerization rate and carbene activity.[17]

The molecular weights given in Table 1 are high, suggesting that either initiation was incomplete or a broad molecular weight distribution (MWD) exists ($M_{n(theor.)}$ for PA 6_{100} = 11 300 g/mol). These considerations do not exactly apply, as the anionic ROP of ε-CLA is no truly "living" process.[2,3] Chain transfer reactions, the inhomogeneity of the system (caused by the precipitation of PA 6 from the monomeric melt), and the limited solubility of the polymer have restricted the discussion of reaction kinetics and molecular weight distribution in the literature.[18] Especially when no activator is used, the MWD broadens, and the expected degree of polymerization cannot simply be calculated from initiator/monomer ratios.[19] However, when ratios are raised from 1:110 to 1:300 or from 1:160 to 1:300 (entries 2/3 and 5/6) the molecular weight increases accordingly, so a certain degree of control seems possible. Complete decarboxylation of the initiator can be assumed since most described applications of NHC−CO_2-adducts are conducted at much lower temperatures than 180 °C.[9b,12,20]

Following the increasing viscosity during the polymerization process offers the possibility to observe both the onset and progress of the reaction and therefore indirectly reflects monomer consumption. Using a rheometer with plate geometry under nitrogen atmosphere, the monomer/initiator mixtures were heated to reaction temperature, and the rheological data were recorded (see also Supporting Information). Viscosities of up to 10^6 Pa·s could be measured, which allowed studying the polymerization till the final polymer was formed (Figure 2). Interestingly, an induction time was observed, where the viscosity of the melt did not change. As discussed above, these induction times are typical for the anionic ROP of lactams in case no activator is used. After the induction period the viscosity builds up rapidly. When the mixture was held in the melt (90 °C) for several minutes prior to rheological measurement, the induction times shortened. This suggests that decarboxylation and formation of the acylated lactam take place, but polymerization does not start under these conditions. Indeed, in no case was formation of PA 6 at $T < 100$ °C observed, which is comparable to reports where Grignard reagents were used to initiate polymerization.[21] It is certainly tempting to evade addition of activators by simple elimination of the induction times via preheating, the more since preheating is routinely done (and necessary) in industrial techniques like reactive extrusion or reaction-injection-molding. However, investigations into this are not yet concluded, and more detailed experiments will elucidate the effect of preheating.

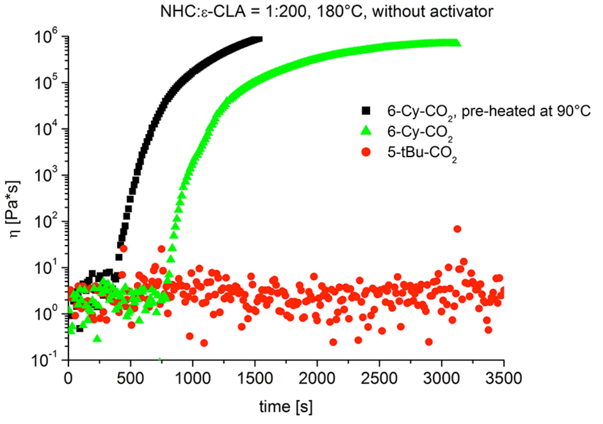
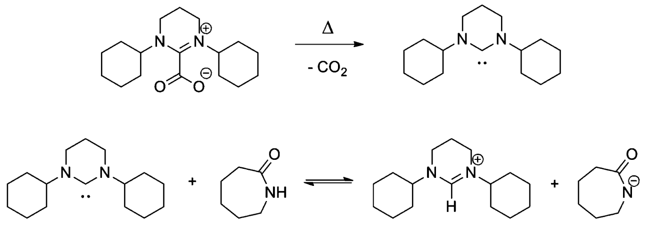


Figure 2. In situ rheological measurement of polymerizations using different protected NHCs.

Both the strong dependence on basicity of the initiator and the presence of induction times support the existence of a classical anionic polymerization mechanism as is proposed in Scheme 2. Importantly, the same behavior, including the strong dependence on basicity, has been observed with phosphazene-based initiators,[22] which have also been used to polymerize β-lactam.[23]

Scheme 2. Proposed Mode of Interaction Between NHC-Carboxylates of Strongly Basic Carbenes and ε-CLA



At room temperature, the protected NHC and ε-CLA coexist without interaction. Notably, we did not observe diminishing activity of the initiator/monomer mixtures over a period of 4 weeks. This is in accordance with reports on the solid-state decarboxylation of NHC−CO_2-adducts, which were found to require relatively high temperatures.[24] This suggests that prolonged storability is possible, in the case that moisture-free conditions are provided. Thus, pure NHC-carboxylates did not show signs of decomposition after months or even years of storage under nitrogen at room temperature. When heat is applied, the NHC is deprotected, and it then deprotonates the monomer. "Activated monomer" is formed, the protonated NHC acting as a counterion. Monomer consumption then commences as shown in Scheme 1. Recently, the existence of two separate reaction pathways for the carbene-mediated polymerization of methyl methacrylate was described, compromising a nucleophilic and a basic mechanism.[9b] The results presented in this work are in accordance with these findings.

Overall, NHC-(organo)catalysis has proved its worth in the field of polyamide synthesis. Preparation of a one-component system that is stable and storable at room temperature, solely consisting of the monomer and the initiator, is possible. Since ε-CLA destined for anionic polymerization is usually sold packed airtight due to the hygroscopic nature of the monomer, a premixing with NHC-carboxylates is uncomplicated and technically feasible. If, in addition to this, the occurrence of induction times could be reduced or eliminated, the described process can be attractive for reaction injection molding processes, e.g., for those used for the manufacturing of fiber−matrix composites for lightweight structures. Finally, in view of these findings, high-temperature applications of NHCs in general can be considered realizable.

ASSOCIATED CONTENT

Supporting Information

Experimental details on synthesis, rheology experiments, and characterization methods. Graph for correlation of solidification and yield. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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