


ORIGINAL ARTICLE

Dual catalysis with an *N*-heterocyclic carbene and a Lewis acid: Thermally latent precatalyst for the polymerization of ϵ -caprolactam

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Abstract

So far, the earlier reported strong correlation between basicity of an *N*-heterocyclic carbene (NHC) and its reactivity in poly(ϵ -caprolactam) (PA6) synthesis resulted in a substantial limitation of applicable carbenes. Here, to overcome this issue, 1,3-dimethylimidazolium-2-carboxylate, an easily accessible, air and moisture-stable NHC, was applied as thermally latent initiator. In order to compensate for its low basicity, reactivity was enhanced by the addition of both a Lewis acid and an activator to ease the initial polymerization step. The resulting mixtures of ϵ -caprolactam, the CO₂-protected NHC, a Lewis acid and *N*-acylazepan-2-one constitute homogeneous, thermally fully latent “single-component” blends for the anionic polymerization-based synthesis of PA6. They can be stored both in the liquid and solid state for days and months, respectively, without any loss in activity. The role of the Lewis acid as well as technical implications of the prolonged pot-times are discussed.

KEYWORDS

ϵ -caprolactam, latent, *N*-heterocyclic carbenes, one-component, polyamide 6

1 | INTRODUCTION

Polyamides are manufactured via a step-growth polymerization from diamines and diacids, from lactams hydrolyzed with water, or via a chain growth polymerization (anionic ring-opening polymerization [AROP]) from lactams^{1–6} and possess favorable mechanical and physicochemical properties.^{1–12} Alternatively, cationic polymerizations can be used, too.^{5–6,9} Among those polyamides that are synthesized by AROP, polyamide 6 (PA6) is the most widespread. The monomer is well-available and synthesized via a Beckmann

rearrangement from cyclohexanone. Activators like *N*-acetylazepan-2-one (*N*-acyl- ϵ -caprolactam [CLA-Ac]) or other acylated lactams, adducts of ϵ -CLA and (di-)isocyanates (*N*-substituted carbamoyl lactams) as well as initiators like sodium ϵ -CLA and magnesium bromide- ϵ -CLA (CLA-MgBr) have been described.^{6–8,11,13–16} The viscosity of CLA melts is comparable to the one of water and allows the use of thermoplastic reaction transfer molding (T-RTM) and liquid composite molding (LCM) techniques.^{2–3} Particularly for LCM, a controllable latency is useful to initiate the reaction at a certain state by external stimuli.^{3,17}

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N-heterocyclic carbenes (NHCs) as well as their protected and latent analogues are widely used in polymer chemistry, either as initiators or catalysts, including dual catalytic approaches.^{17–24} Especially, hexahydropyrimidin-2-ylidene-derived carbenes or their derivatives with large aliphatic side groups can serve as thermally latent initiators for the ROP of lactams.^{12,25–26} Their high basicity allows the synthesis of both PA6 and PA6/PA12 copolymers. Thus, the pK_a value of hexahydropyrimidin salts has been determined by different authors to be in the range of 27–29 (in DMSO), mainly depending on the nitrogen substituents.^{27–30} Since CLA and lauryllactam possess a pK_a of approximately 27,⁴ initiation with tetrahydropyrimidin-2-ylidenes is quantitative and fast. However, a major drawback of tetrahydropyrimidine-derived carbenes is related to their synthesis that entails a three-step reaction under inert gas conditions,^{31–34} which severely impedes their technical use. Overall, the necessity to use strongly basic NHCs so far substantially limited the use of NHCs in PA6 synthesis.^{12,25–26}

In contrast, 1,3-dimethylimidazolium-2-carboxylate (5u-Me-CO₂) is synthesized in a convenient one-step procedure from 1-methylimidazol and dimethyl carbonate. Another appealing feature is that 5u-Me-CO₂ is not sensitive to ambient conditions and even tolerates water.^{35–36} One disadvantage, however, is its reduced basicity that leads to a pK_a value of the corresponding imidazolium salt of about 22.^{28–30,37–39} In order to compensate for the reduced basicity and to make 5u-Me-CO₂ applicable to PA6 synthesis, a dual catalyst approach that entails the addition of a Lewis acid in conjunction with a common activator like CLA-Ac has been elaborated and is presented herein.

2 | EXPERIMENTAL

2.1 | General

All polymerizations were executed under a nitrogen atmosphere in an MBraun LABmaster sp glove box connected to an MBraun MB SPS-800 solvent purification system (SPS), which provided *n*-pentane, diethyl ether, dichloromethane, THF, and toluene. Alternatively, standard Schlenk techniques were used. Workup was carried out at ambient conditions with as-received chemicals. Glass ware was dried in an oven at 120°C for at least 1 h prior to use.

2.2 | Chemicals

CLA was received as a gift from Brüggemann GmbH & Co. KG and used without any further purification. CLA

was either stored inside a glove box or under an atmosphere of argon. *N*-Acetylazepan-2-one (CLA-Ac) was purchased from Sigma Aldrich and dried and distilled from CaH₂ and degassed prior to use. CLA-Ac was stored inside the glove box over 0.4 nm molecular sieves. Methanoic acid 98% (Acros Organics), MgCl₂ ≥ 99% (Merck KGaA), LiCl 99% (Grüssing), D₂SO₄ 99.0% (Eurisotop GmbH), and propan-2-one (Friedrich Scharr KG) were used without further purification. SPS solvents were provided by VWR. Then, 0.4 nm molecular sieves were received from Carl Roth GmbH und Co. KG. After drying overnight at 150°C under vacuum, it was stored inside the glove box. 5u-Me-CO₂ was synthesized according to the literature.³⁵

2.3 | Analysis

NMR spectra were measured on a Bruker Avance III 400 (400 MHz for proton and 101 MHz for carbon). Chemical shifts are given relative to the solvent. Solvent shifts were taken from the literature.^{40–41} The MestreNova v12.0 and topspin software were used. Polyamide samples were separated from the precipitation medium by centrifugation. For these purposes, a Hettich Universal 320 centrifuge was used at 4500 rpm for 15–99 min. DSC measurements were carried out on a Perkin Elmer Differential Scanning Calorimeter DSC 4000 (pan size was 50 µl, constant nitrogen flow of 20 ml/min, sample weight 1–10 mg, software: Pyris and on a Q2000 equipped with an autosampler (TA Instruments, pan size 40 µl, sample weight 1–10 mg, software: Advantage). Gel permeation chromatography (GPC), applying *m*-cresol at 70°C, was performed on PSS SDV columns (precolumn 20 µm, 8 × 50 mm; 1000 Å, 20 µm, 8 × 300 mm; 10,000 Å, 20 µm, 8 × 300 mm) at a flow rate of 1 ml/min using PS standards. Relative viscosities were determined using an Ubbelohde viscosimeter with solutions of 0.01 g/ml polymer in 96% H₂SO₄. Values were correlated with the M_n values of PA6 samples obtained from GPC measurements and used to estimate the M_n values of the PA6 samples prepared (see SI).

2.4 | Polymer synthesis—Direct approach

Inside a glove box, all substances (monomer, the carbene precursor, optionally an activator and a Lewis acid) were weighed into an oven-dry 4 or 10 ml screw top vial equipped with a Teflon-coated magnetic stir bar. Then, 0.5–5 g of monomer were used. The vial was closed and then placed into a drill hole of an aluminum block,

which was preheated to the reaction temperature and then placed on the heating plate of magnetic stirrer. After an appropriate time, the reaction was allowed to cool to room temperature outside the aluminum block.

2.5 | Polymer synthesis—Prehomogenization approach

All substances (monomer, carbene precursor, activator, and Lewis acid) were weighed into an oven-dry 4 or 10 ml screw top vial equipped with a Teflon coated magnetic stir bar. The vial was closed and then placed into a drill hole of an aluminum block, preheated to 75–90°C and then placed on the heating plate of magnetic stirrer. Quickly, a clear solution formed. The mixture was either cooled to room temperature or stored in the liquid state for several days or directly used for polymerization.

2.6 | A, Mixture stored as solid

The above-described solution was allowed to cool to room temperature and was stored (up to 6 months) as a solid. For polymerization, eventually with additional monomer, aliquots were placed into a screw top vial equipped with a Teflon coated magnetic stir bar. The vial was closed before it was placed into a drill hole of an aluminum block and put on the heating plate of magnetic stirrer. Eventually, the mixture was preheated to 70–80°C to melt it. Then the reaction was allowed to cool to room temperature outside the aluminum block.

2.7 | B, Direct polymerization of the mixture

In order to polymerize the mixture, the vial was placed into a drill hole of an aluminum block, preheated to the reaction temperature and then placed on the heating plate of magnetic stirrer. Finally, the reaction was allowed to cool to room temperature outside the aluminum block.

2.8 | C, Mixture stored as liquid

The solution was stored at 75°C up to 5 days. In order to polymerize the mixture, the vial was placed into a drill hole of an aluminum block, preheated to reaction temperature, and placed on the heating plate of magnetic stirrer. Finally, the reaction was allowed to cool to room temperature outside the aluminum block.

2.9 | Polymer synthesis—Work up

After the reaction, the polymer was allowed to cool to room temperature. For each gram of monomer, 4–12 ml of methanoic acid, depending on the target molecular weight resulting from the initiator to monomer ratio, were added to the product. The higher the ratio, the more solvent was used and the longer it took to dissolve the polymer, typically 1–3 days. The polymer was precipitated from acetone. For 1 g of monomer 30–150 ml of acetone were used. The polymer was centrifuged for 15–99 min at 4500 rpm. Afterward, the supernatant solution was discarded and the polymer was dried under reduced pressure between room temperature and 70°C for at least 24 h.

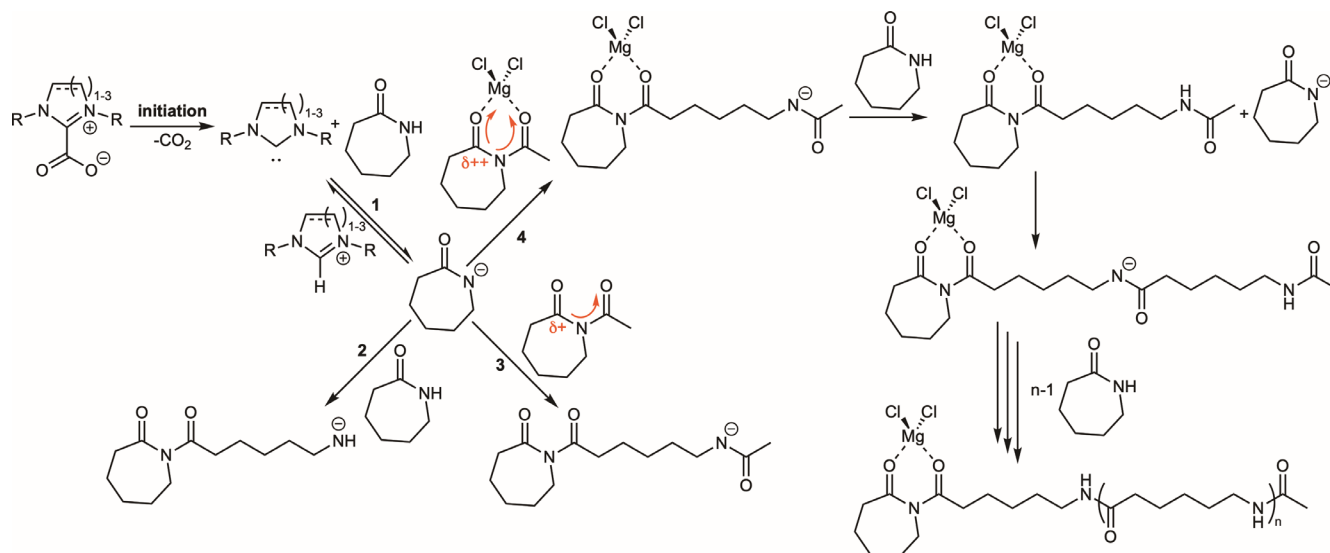
3 | RESULTS AND DISCUSSION

To overcome the initiation period in the AROP of lactams, it is very common to add, or form in situ, activated lactams with an electron-withdrawing moiety at the nitrogen atom to activate the carbonyl for nucleophilic attack by deprotonated lactams and start the chain growth reaction (Scheme 1, Routes 1, 2, and 3).^{5–6} Here, it is important to understand the initiation step as equilibrium reaction because a later redeprotonation of the imidazolium salt, formed through the deprotonation of the lactam, is in view of its pK_a highly likely.

Another possibility to accelerate the reaction is to increase the amount of initiator (base). Neglecting chain transfer reactions, the ratio of monomer to initiator directly influences the molecular weight of the resulting PA6; thus, higher concentrations of initiator lead to accelerated reaction but also to decreased molecular weights. Here, as an alternative, Lewis acids based on different cations were added (Scheme 1, Route 4).

3.1 | Activation by Lewis acids

First experiments applying 5u-Me-CO₂, as sole initiator and in conjunction with Lewis acids like LiCl and MgCl₂ (Table 1, Entries 1–3) lead to an increased polymer yield in case a Lewis acid was added. Control experiments were executed for all activators (Table 1, Entries 4–6). A further increase in LiCl concentration leads to an, expected, small increase in yield (Table 1, Entries 7–9). By contrast, the addition of larger amounts of MgCl₂ suppressed the reaction (Table 1, Entries 10–12), so did a combination of CLA-Ac and 5u-Me-CO₂ (Table 1, Entry 13). We tentatively assign this suppression of the polymerization by an excess of MgCl₂ in contrast to LiCl by a



SCHEME 1 Initiation reaction and anionic ring-opening polymerization (AROP) of ϵ -caprolactam, eased by an electron-deficient activator (red arrows) [Color figure can be viewed at wileyonlinelibrary.com]

complex formation between the NHC and the Lewis acid.³¹

We already reported on the synthesis of polyurethanes, on the AROP of ϵ -CLA and on poly(oxazolidinone)^{31,32,42,43} using a “dual catalysis” approach. Additionally, dual catalysis in the ROP of propylene oxide, lactones, and carbamates, especially related to PA6 formation, deserves to be mentioned.^{21,44–46} In such an approach, the catalytic system consists of both an NHC acting as nucleophile or base and a Lewis acid that activates the monomer, thereby rendering it more electrophilic.⁴⁷ Here, the combination of a Lewis acid and CLA-Ac in conjunction with 5u-Me-CO₂ resulted in 74% yield in case of LiCl (Table 1, Entry 14). However, in case MgCl₂ was used, quantitative yields were achieved (Table 1, Entry 15), despite the low basicity of 5u-Me-CO₂. The more effective activation of CLA-Ac by MgCl₂ most probably results from the divalent character of magnesium and a better accessibility of higher orbitals compared to Li. To clarify on the improved yield in case both the activator and MgCl₂ were used in conjunction with 5u-Me-CO₂, a CLA-Ac solution in CH₂Cl₂ was mixed with a THF solution of MgCl₂. The clear solution that formed was evaporated to dryness and a colorless solid formed. Its ¹³C NMR spectrum (carbonyl area) is shown in Figure 1 (red) in comparison to the spectrum of pure CLA-Ac (black). The activator's carbonyl signals are downfield shifted by 3.4 and 4.0 ppm, respectively, suggesting a reduced electron density and thus a higher electrophilicity. Note, the formed complex is coordinated by half an equivalent of THF (see SI) and thus, the

electrophilic character might even be increased under reaction conditions under which the THF might well be removed from the complex. Unfortunately, all attempts to remove the THF or isolate the solvent-free CLA-Ac-MgCl₂ complex failed. Nonetheless, the ¹³C shift of proposed structure of the MgCl₂-activated *N*-acyllactam explains the increased reactivity also with regard to the active chain end during the polymerization. Similar effects of Lewis acids, including CLA-MgBr as initiator, have been mentioned earlier.^{5,13,48}

3.2 | Latent homogeneous single-component materials

In view of the most favorable results with MgCl₂, mixtures of CLA, CLA-Ac, MgCl₂, and 5u-Me-CO₂ (500:1:1:1) were prepared, stirred and heated to 75°C (above the melting point of CLA) until a colorless homogeneous solution had formed (1–2 h). After cooling to room temperature, the solidified material was stored inside the glove box and polymerized in portions after 1, 3, and 9 days at 200°C within 1 h (Table 1, Entries 16–18). The double-checked experiments provided exceptional yields >96% at an initiator loading of 0.2 mol%. A validation of these results using a mixture of CLA, CLA-Ac, MgCl₂, and 5u-Me-CO₂ that had been stored for 3 months gave the same results (Table 1, Entry 19). Molecular weights of 60,000 and 240,000 g/mol were found for loadings of 100 ($M_{n,theo} = 11,000$ g/mol) and 500 ($M_{n,theo} = 57,000$ g/mol) equivalents of CLA,

TABLE 1 Polymerizations and control experiments run at 200°C for 1 h applying different activators

Entry	5u-Me-CO ₂ (eq.)	LiCl (eq.)	MgCl ₂ (eq.)	CLA-Ac ^a (eq.)	CLA (eq.)	Yield (%)
1	1	—	—	—	100	17
2	1	1	—	—	100	33
3	1	—	1	—	100	37
4	—	1	—	—	100	<1
5	—	—	1	—	100	<1
6	—	—	—	1	100	<1
7	1	3	—	—	100	52
8	1	5	—	—	100	58
9	1	10	—	—	100	60
10	1	—	3	—	100	<5
11	1	—	5	—	100	<5
12	1	—	10	—	100	6
13	1	—	—	1	100	<1
14	1	1	—	1	100	72
15 ^b	1	—	1	1	100	>96
16 ^{c,d}	1	—	1	1	500	>96
17 ^e	1	—	1	1	500	>96
18 ^f	1	—	1	1	500	>96
19 ^g	1	—	1	1	500	>96
20 ^h	1	—	1	1	1000	>96

Note: Unless otherwise noted, the mixtures were weight in a glass vial before heating but not mixed or homogenized (direct approach).

Abbreviations: CLA-Ac, *N*-acyl- ϵ -caprolactam; GPC, gel permeation chromatography.

^a*N*-acetylazepan-2-one.

^b $M_n = 60,000$ kg/mol, $D_M = 1.9$; determined by cresol-GPC.

^cOne day after homogenization.

^d $M_n = 240,000$ kg/mol, $D_M = 2.1$; determined by cresol-GPC.

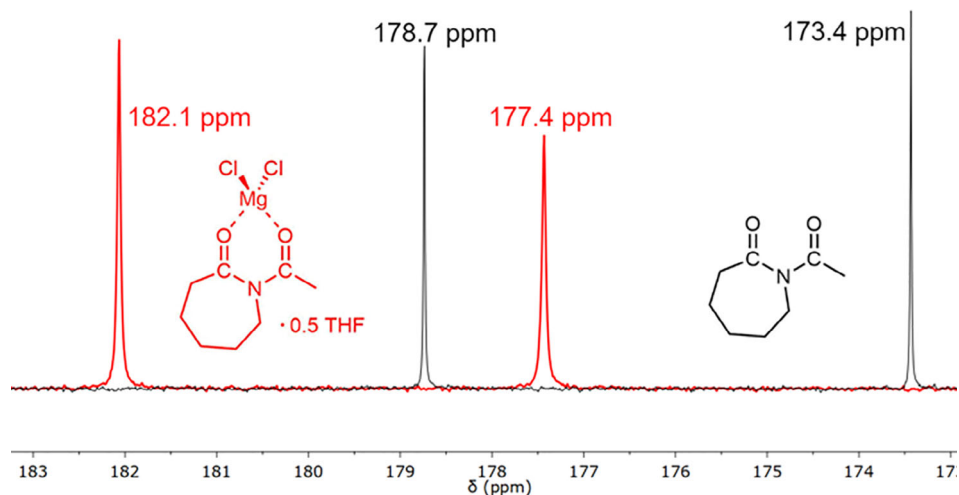
^eThree days after homogenization.

^fNine days after homogenization.

^gThree month after homogenization.

^hPrehomogenized at 75°C.

FIGURE 1 Overlay over the ¹³C NMR spectra of *N*-acyl- ϵ -caprolactam (CLA-Ac; black) and CLA-Ac-MgCl₂ 0.5 THF (red) in CD₃CN



respectively, all relative to one equivalent of MgCl_2 , 5u-Me- CO_2 , and CLA-Ac. These values point, apart from GPC errors resulting from calibration versus PS, toward an incomplete initiation with respect to the deprotonation of the monomer by the carbene. Notably, yields >96% were still obtained at high monomer loadings up to 1000 equivalents of CLA together with one equivalent each of CLA-Ac, MgCl_2 , and 5u-Me- CO_2 (Table 1, Entry 20).

3.3 | Solidification times

The decarboxylation of the CO_2 -protected NHC strongly depends on the polarity of the surrounding medium.³⁶ Thus, the more polar the medium, the lower the decarboxylation rate is. Also, the $C_{\text{carbene}}\text{-CO}_2$ binding energy decreases with decreasing pK_a .^{36,39} In addition, increased temperatures promote carbene liberation. Table 2 provides an overview over the solidification times, that is, the times needed for a polymerization to result in a solidified reaction mixture using different initiator to monomer ratios and polymerization temperatures. Increased monomer loadings as well as lower polymerization temperatures result in prolonged solidification times. Table 2, Entry 4 underlines the stability and latency of 5u-Me- CO_2 . In this experiment, the mixture was stored for 5 days at 75°C prior to polymerization. Again, the catalyst showed virtually no loss of activity. This is of particular relevance for technical applications and for processing, since this high stability and thermal latency of the polymerization mixture allows for substantially prolonged pot times.

Relative viscosities were determined in H_2SO_4 with the aid of an Ubbelohde viscosimeter. Number-average molecular weights were determined therefrom with the aid of literature values (see SI).^{49–50} Increasing molecular

weights correlate well with increasing monomer to initiator ratios. Although the values found by this method are in good accordance with the stoichiometry, they still represent estimated values and should not be used as exact but, instead, as qualitative measures.

3.4 | Polymerizations under ambient conditions

PA6 cast chemistry in industry is not necessarily conducted under strict inert gas conditions, although lactams, especially CLA, rapidly take up humidity. A prehomogenized mixture of CLA, CLA-Ac, MgCl_2 , 5u-Me- CO_2 , produced at 80°C (Table 2, Entry 5) was divided into three portions in closed vials. These were heated to 75°C, the vials were opened to ambient atmosphere and then heated to reaction temperature (see also SI). Prolonged solidification times as compared to Table 2, Entry 1, were observed and are attributed to the up-take of humidity. However, quantitative yields (>96%) were still obtained in all three cases, which is in stark contrast to PA6 synthesis catalyzed by the moisture-sensitive 1,3-dialkyltetrahydropyrimidin-2-ylidenes.^{12,25–26}

3.5 | CLA-isocyanate adduct as activator

Aside from CLA-Ac, CLA isocyanate adducts are commonly used as activators in polyamide synthesis.⁶ Indeed, adducts of two equivalents of CLA and one equivalent 1,6-hexanediisocyanate (HDI- CLA_2) or 4,4'-di(isocyanatophenyl)methane (MDI- CLA_2) are commercially available. Prehomogenized mixtures of CLA, MgCl_2 , 5u-Me- CO_2 , and HDI- CLA_2 or MDI- CLA_2 (300:1:1:1) were produced (75°C, 2 h) and polymerized at 200°C. Solidification times of 7 min (HDI- CLA_2) and

Entry	Temp. → ↓CLA ^a	160°C	180°C	200°C
1	100 ^b	6 (32,000)	3 (37,000)	2 (32,000)
2	200 ^b	7 (160,000)	4 (190,000)	3 (130,000)
3	400 ^b	10 (310,000)	6 (230,000)	5 (420,000)
4	200 ^c	7	4	4
5	100 ^d	10	8	5

TABLE 2 Solidification times in minutes for polymerizations with different catalysts loading at different temperatures and conditions (estimated M_n , g/mol, from relative viscosities)

Abbreviation: CLA-Ac, *N*-acyl- ϵ -caprolactam.

^aEquivalents of CLA with respect to 1 eq. of CLA-Ac, MgCl_2 , and 5u-Me- CO_2 , respectively.

^bMixtures were prehomogenized at 75°C for 1–2 h.

^cThe mixture was kept 5 days at 75°C.

^dMixtures were molten at 75°C before exposure to ambient atmosphere during the reaction. Viscosities were determined in H_2SO_4 .

6 min (MDI-CLA₂) were observed. Notably, the resulting polymers were insoluble in methanoic acid (also in case a huge excess was used); only swelling of the polymer was observed even after several days, suggesting the formation of high-molecular-weight PA6. Again, after extraction of the polymer with acetone and drying under reduced pressure, quantitative yields were found.

4 | CONCLUSIONS

The applicability of 5u-Me-CO₂ as precursor for 1,3-dimethylimidazol-2-ylidene, an NHC with comparably low basicity in the polymerization of CLA with the aid of an activator and a Lewis acid has been demonstrated. The role of the Lewis acid toward improved reactivity has been clarified by NMR spectroscopy. The general utility of these single-component materials for technical applications is underlined by both the full thermal latency and the short solidification times. The latency of the NHC precursor was demonstrated; the corresponding homogeneous “single-component” materials are stable in the solid state for months as well as in the liquid state for days. Use in LCM and T-RTM applications will be reported in due course.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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