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Protected *N*-heterocyclic carbenes as latent organocatalysts for the low-temperature curing of anhydride-hardened epoxy resins

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ABSTRACT

Epoxy resins based on commonly used epoxy compounds, various anhydrides and CO_2-protected *N*-heterocyclic carbenes (NHCs), which combine the favorable properties of fast curing at low reaction temperatures, pot life in the range of hours to days and full homogeneity in the form of low-viscosity liquids, are presented. These characteristics are achieved by careful tuning of the components. 1,3-Dimethylimidazolium-2-carboxylate (**5u-Me-CO_2**) as a thermally latent organocatalyst offers facile one-step preparation and robustness towards atmospheric conditions as well as the high reactivity required once the polymerization is "switched on" by heating. A systematic screening of several epoxy compounds and 14 different anhydrides is conducted to identify the monomers that are suited best for rapid monomer consumption and thus for low curing temperatures. From these experiments, more than 15 different systems were found where a homogeneous liquid can be formed in the absence of further additives (no solvent or reactive thinner). Several of these one-component mixtures were investigated more detailed by in-situ DSC and rheology measurements. In general, the combination of aliphatic epoxides and low-melting or liquid anhydrides delivers the fastest polymerization under the mildest conditions, while maintaining a very low initial viscosity ($<$ 100 mPa·s at room temperature), thereby offering access to sprayable precursor systems. Full curing within minutes, as evidenced by DSC experiments, is achieved at T = 100–120 °C, depending on the composition of the resins.

1. Introduction

Arguably, *N*-heterocyclic carbenes (NHCs) constitute the most versatile and successful class of organocatalysts established in recent time [1–4]. Their key beneficial properties include structural variability, high nucleophilicity and Brønsted-basicity as well as the intriguing chemistry of the carbene reactive center itself, which has enabled challenging chemical transformations like *Umpolung* reactions or the addition to double bonds, among many other examples [5–10]. Polymer chemistry has profited solidly from these advances in organic chemistry: NHC-triggered organopolymerization [11–13] can nowadays be applied to prepare polymers via ring-opening polymerization (lactones [14–18], lactams [19,20], epoxides [21–23], cyclosiloxanes [24–27] and others), by conjugate addition [28,29] (including a wide range of acrylic monomers) but also by condensation reactions [30–33]. In many cases, NHCs provide these services with additional benefits, such as increased polymerization rates, excellent control of end-groups or advantageous polymer architectures such as cyclic structures [11–13,34].

However, the transition from laboratory use to commercial, large-scale applications has so far been hampered by some inherent problems that come with the use of NHCs. The main difficulties can be identified as (a) sensitivity to protic compounds/impurities

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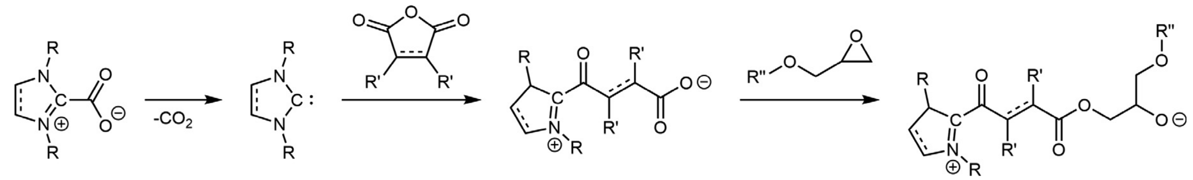


Fig. 1. Proposed initiation step for curing of anhydride-hardened epoxy resins by thermal deprotection of the catalyst and alternating, anionic copolymerization of the monomers [35].

(water), (b) limited storability and (c) synthetic requirements, which can be prohibitive for use in polymer industry.

The rapid epoxy curing system presented in this work is intended to minimize the above mentioned disadvantages while capitalizing on the benefits that can be derived from using NHCs. Our group has recently published the curing of anhydride-hardened epoxy resins initiated by CO_2- or metal-protected NHCs [35] (Fig. 1), a process that has also been shown to be compatible with vacuum-assisted resin infusion (VARI), thereby offering access to well-performing fiber-reinforced composite materials [36]. Reaction with carbon dioxide transforms the free NHC into a compound that is readily stored; its reactivity is blocked, but can be restored by heating, thus rendering the whole system latent with a one-time thermal "switch" to start polymerization [37,38]. It was furthermore shown that mixtures of an epoxy compound, anhydride and protected NHC can be fully homogeneous, stable under atmospheric conditions and do not require special storage conditions or purification of the monomers [35]. DSC experiments further revealed that pot times up to four weeks were possible, whereby this property was dominated by the protecting group and the chemical structure of the NHC. Since reactivity depends on both decarboxylation and inherent reactivity of the free NHC, the overall observed polymerization rates result from a superposition of these effects. In general, steric pressure facilitates the loss of CO_2, but might also hinder interaction of the free NHC with the monomer. Inversely, NHCs with small *N*-substituents have repeatedly shown to engage monomers more readily [14–18], but adducts with carbon dioxide are also more stable [37,38]. While the relative contribution of both effects remains elusive and will be different for every NHC, it was found that even over longer storage time the curing profile did not change, irrespective of the chemical structure of the NHC [35], which indicates that degradation of the protected NHC to carboxylic acid [39] or azolium hydrogen carbonate [40,41] did not occur to a significant degree. As a consequence of the high reactivity of NHCs, when released by warming, they are superior to commonly used accelerators for warm-curing epoxy resins, which allows for low catalyst loadings, fast polymerization kinetics and generally relatively mild curing temperatures. Mechanistically, initial reaction of the NHC with the anhydride was proposed (Fig. 1), on account of the relative slowness of NHC-addition to epoxides [21–23]. The anionic copolymerization of epoxides and anhydrides typically proceeds strictly alternating [42], a more complete polymerization scheme can be found in the SI (Fig. S2). Finally, it should be considered that after addition and ring-opening of the anhydride an acylazolium species forms (Fig. 1), reminiscent of the well-understood polymerization of lactones [14–18]. Hence the positively charged imidazolium moiety could be displaced from the carbonyl carbon by nucleophilic substitution, which would set the NHC free anew and render the whole process catalytic in nature. However, this analogy is not yet corroborated and still requires further investigation.

The results discussed in the following represent an extension of this system to a wide array of different epoxy compounds (Fig. 2, four examples) and anhydrides (14 examples), with the specific aim to generate compositions that are homogeneous with low viscosity (and preferentially *sprayable*) and that can be cured at low temperatures ($T < 120$ °C), while still maintaining useful pot times (hours to days). A range of different catalysts is investigated with emphasis on 1,3-dimethylimidazolium-2-carboxylate, **5u-Me-CO₂**, a pre-catalyst that can be synthesized in a single step from cheap starting materials and which is insensitive to atmospheric conditions [43]. We envision a low-viscosity, latent, low-T-curing epoxy resin to be advantageous for a significant number of applications, including composite preparation, restoration/repair works and the formulation of advanced adhesives. The development of powerful, yet latent, monomer or catalyst systems remains one of the hotspots of epoxy resin research [44]; notable recent innovations include application of masked amines (as hydrolysis-labile imines [45] or thermally labile carbamates [46]) for amine-hardened resins, while for warm-curing epoxide/anhydride composition the employment of photosensitive amidines [47], quaternary ammonium salts [48] and aminimides [49] has been reported. The fact that imidazoles are used as cheap and efficient accelerators in non-latent setups has inspired research efforts regarding "blocked" imidazoles [50–52].

2. Results and discussion

A range of different CO_2-protected NHCs (Fig. 3) was synthesized and tested for reactivity in a reference system consisting of bisphenol-A diglycidyl ether (BADGE, **E1**) and hexahydrophthalic anhydride (HHPA, **A1**). Reactivity was established by conducting differential scanning calorimetry (DSC) measurements on non-cured mixtures of the anhydride, the epoxy compound and latent catalyst. While onset and maximum of the observed exothermic curing process can be used to analyze curing kinetics, the integral delivers the released amount of heat and thus a measure for completeness of the reaction when compared to standard systems (see Fig. 4 for typical examples) [35,53]. ΔH values were found to be in agreement with literature data [54], strongly suggesting that full curing was achieved under these conditions. This was also underlined by DSC control heating cycles, which found no post-curing peaks; T_g was also found to be in the range typical for fully cured **E1**/**A1** resins (see Table S7, where a listing of several T_g values is given for different curing systems investigated in this work).

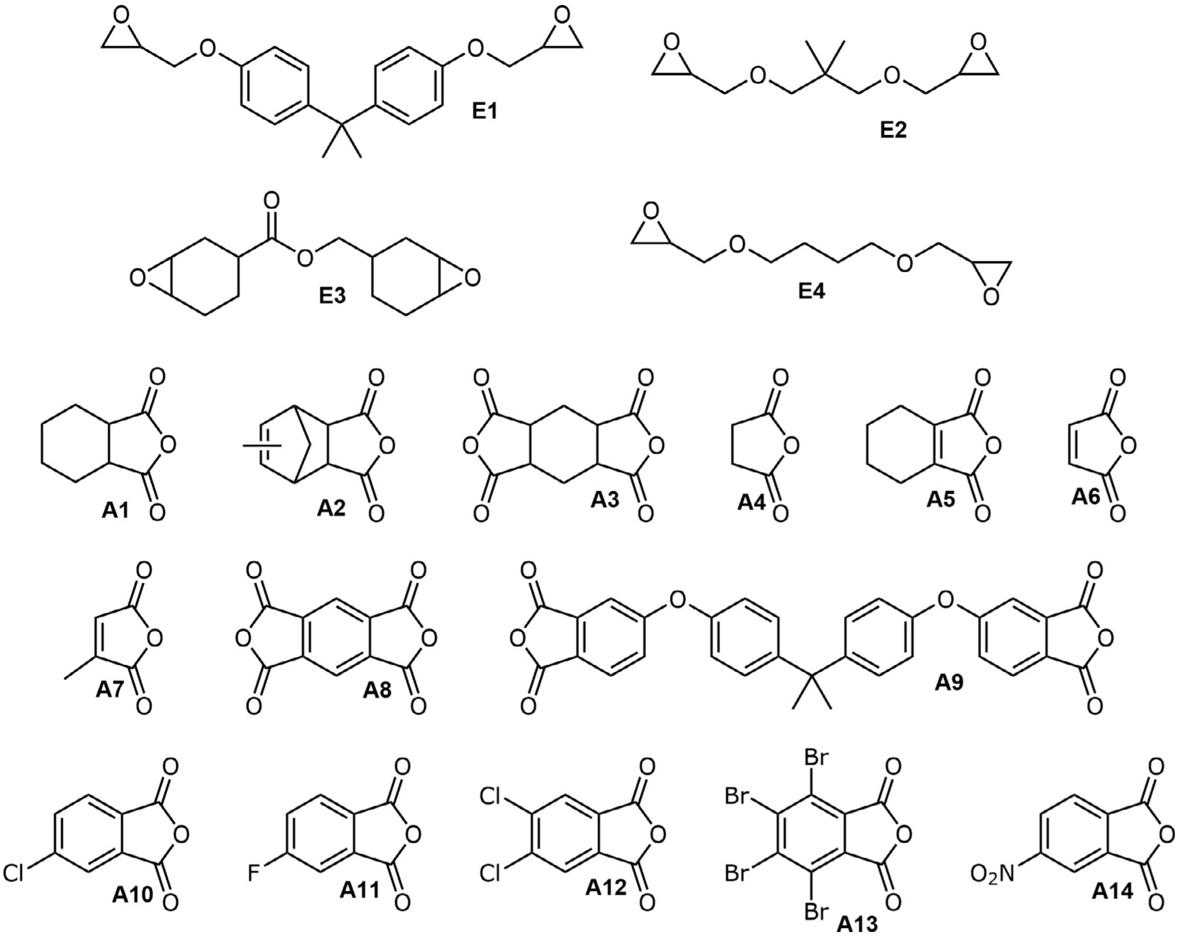
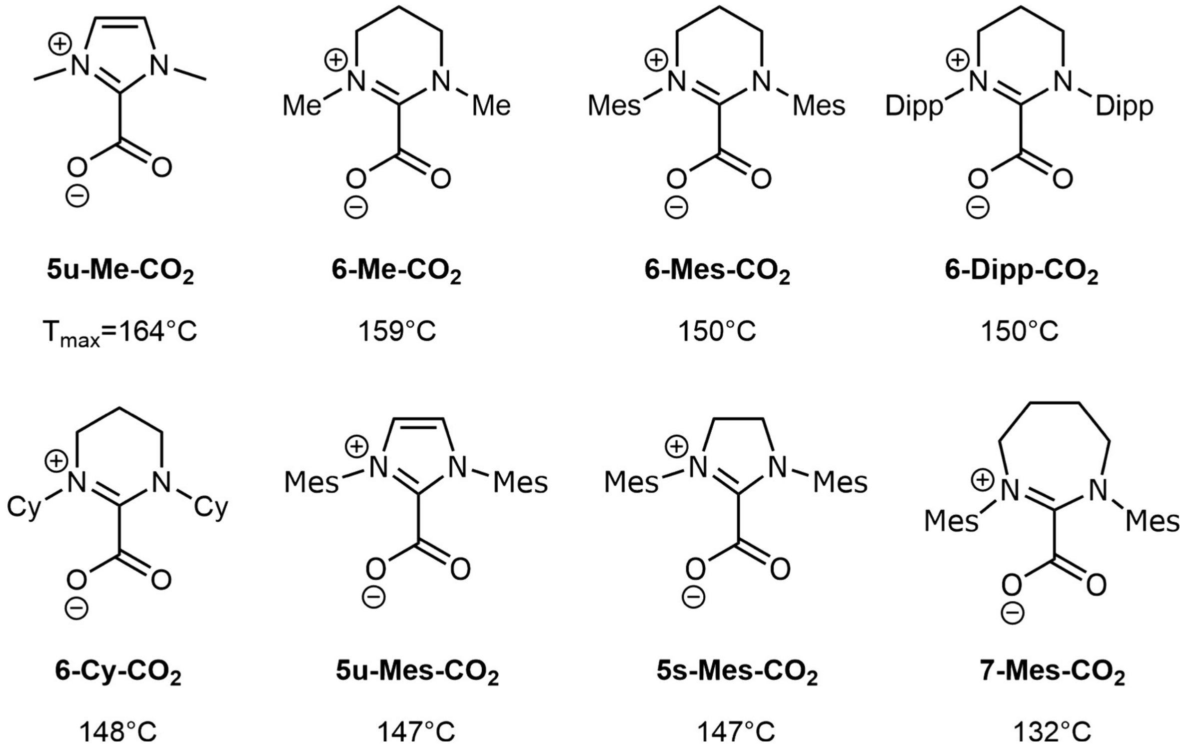


Fig. 2. Epoxy and anhydride compounds investigated in this study.

At a constant heating rate of 5 K/min, the peak maximum (T_{max}) was selected as the most suitable marker to judge the relative reactivity of the different catalysts. When the corresponding values are compared for the different protected NHCs (Fig. 3), it is obvious that differences in reactivity exist ($\Delta T_{max} \approx 30$ K) in accordance with our previous study [35]. The highest reactivity was found for **7-Mes-CO$_2$** ($T_{max} = 132$ °C), while systems based on **5u-Me-CO$_2$** show a corresponding value of 164 °C. The higher T_{max} in the case of **5u-Me-CO$_2$** attests to the lower activity of this pre-catalyst in relative terms, which can be explained by the steric conditions surrounding the C-CO$_2$ bond. Thus, the large mesityl substituents present in **7-Mes-CO$_2$** force the CO$_2$-moiety out of the N-C-N plane, thereby reducing conjugation; the increased steric pressure clearly facilitates dissociation of carbon dioxide and subsequent polymerization initiated by the NHC. **5u-Me-CO$_2$** in contrast offers minimal steric obstruction and decarboxylation is delayed. Indeed, in the absence of substrate, this compound experiences decomposition of the entire structure prior to decarboxylation [37,38]. All other investigated latent catalysts perform in an intermediate range between these two protected NHCs. Overall, differences are subtle, which in turn justifies the application of **5u-Me-CO$_2$** over the use of the somewhat more active, yet also synthetically more demanding pre-catalysts. A typical synthetic sequence for the preparation of a CO$_2$-protected NHC involves the deprotonation of a precursor salt and reaction with CO$_2$ under dry conditions [28,29]. Contrasting that, Rogers and co-workers have shown that **5u-Me-CO$_2$** can be prepared *in a single step* using dimethyl carbonate and 1-methylimidazole (Fig. 5) [43]. No additional deprotonation steps or dry reaction conditions are necessary, while a simple washing is sufficient to receive analytically pure product. We have performed this method on a 500 g scale, modifying the washing process slightly (see Experimental Section, SI). **5u-Me-CO$_2$** can be stored under ambient conditions for weeks; other protected NHCs sometimes require storage under nitrogen as they are hygroscopic which leads to decomposition or the formation of hydrogen carbonates [40,41].

Simple synthesis and cheap starting materials allowed for the use of a higher catalyst loading of **5u-Me-CO$_2$** to lower T_{max} and speed up the polymerization process: when 8 mol-% (relative to **E1**) were applied, T_{max} decreased to 125 °C, while at 15 mol-% this value lowered to 120 °C (Table 1). The same effect occurred in case the sterically more hindered compounds **6-Cy-CO$_2$** and **6-Mes-CO$_2$** were used, there T_{max} decreased to 111 and 110 °C, respectively. Notably, with the latter two pre-catalysts, suspensions formed at higher catalyst loadings, most probably because these protected NHCs are less polar than **5u-Me-CO$_2$**.

Although mixtures containing the protected NHC, **E1** and **A1** displayed favorable properties such as homogeneity and fast curing at T = 160 °C within eight minutes, compositions displayed room temperature viscosities of 500 mPa·s [35] and curing kinetics that



5u-Me-CO_2 T_{max}=164°C

6-Me-CO_2 159°C

6-Mes-CO_2 150°C

6-Dipp-CO_2 150°C

6-Cy-CO_2 148°C

5u-Mes-CO_2 147°C

5s-Mes-CO_2 147°C

7-Mes-CO_2 132°C

Fig. 3. Protected NHCs employed for thermal latent curing of the epoxy resins with corresponding T_{max} for each composition (molar ratio **E1**:**A1**:NHC-CO_2 100:200:1; heat rate 5 K/min, 20 to 250 °C) obtained from DSC. (Me = methyl; Mes = 2,4,6-trimethylphenyl; Dipp = 2,6-diisopropylphenyl; Cy = cyclohexyl).

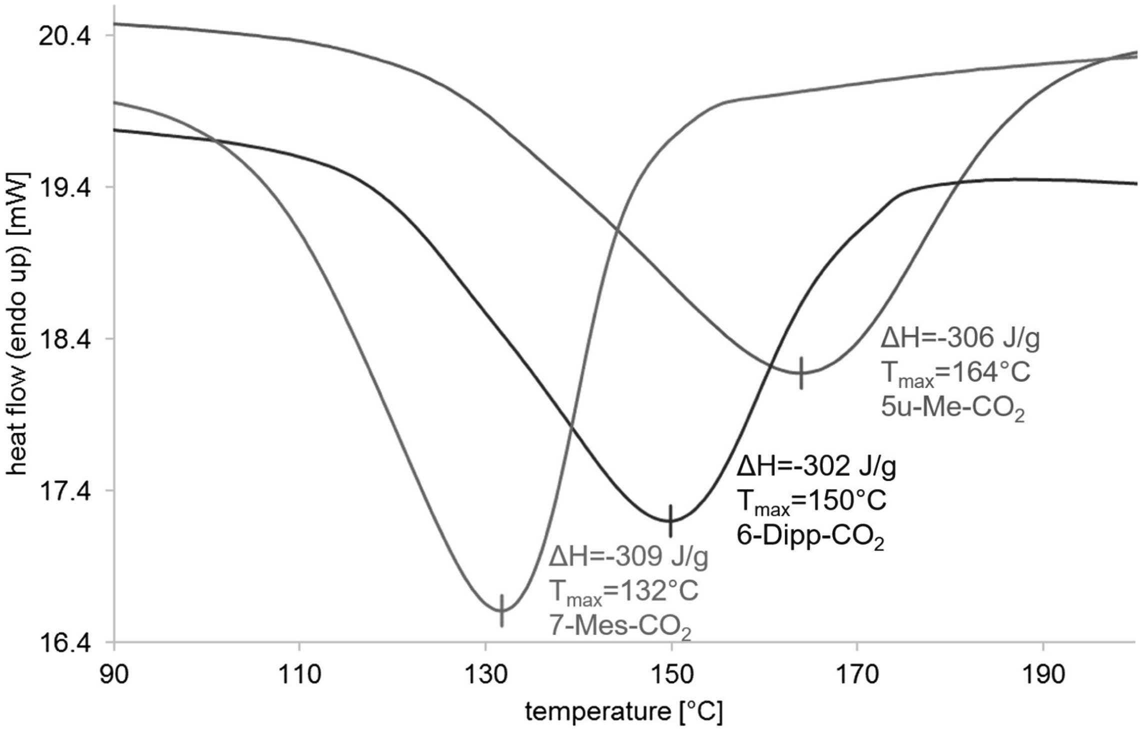


Fig. 4. Typical curing behavior of **E1**/**A1** in the presence of different NHC-CO_2 pre-catalysts, ramping the temperature with 5 K/min from 20 to 250 °C (**E1**:**A1**:NHC-CO_2 100:200:1).

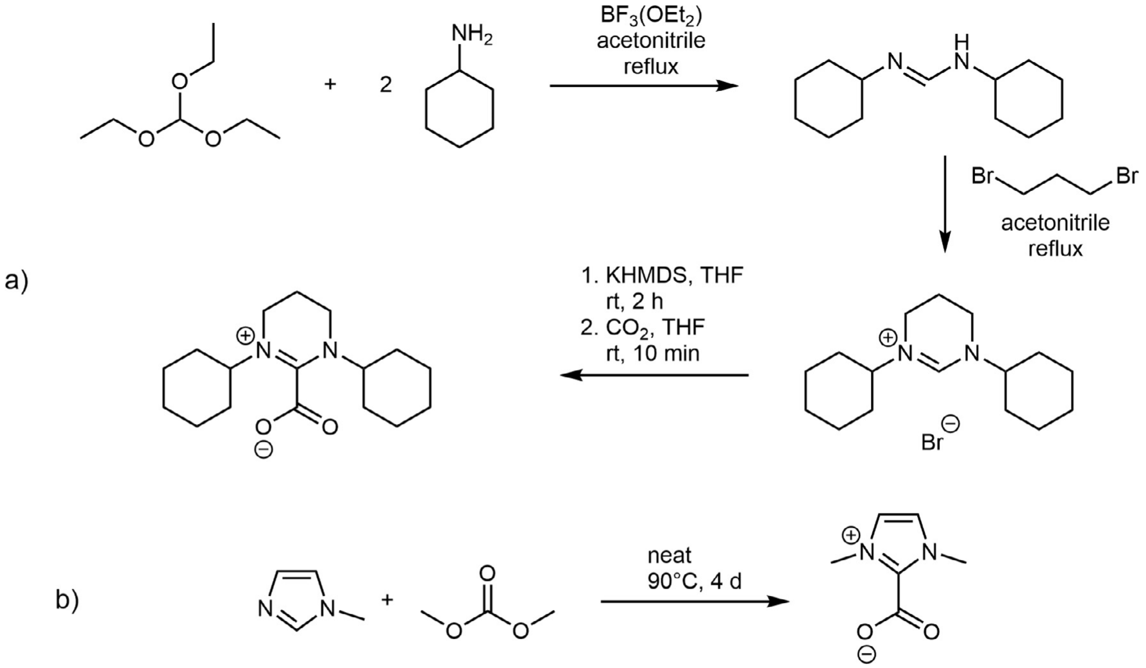


Fig. 5. (a) Typical inert gas synthetic route for CO_2 adducts of NHCs. (b) one-pot synthesis for **5u-Me-CO₂**.

both possessed potential for further optimization. In order to identify alternative epoxides and anhydrides that could serve for these purposes, an extensive range of different compounds was investigated (Fig. 2), always using **5u-Me-CO_2** as latent pre-catalyst in a molar ratio of epoxide compound/anhydride/NHC = 100:200:8, which typically corresponded to ≈2 wt.% protected NHC in these compositions (for the dianhydrides **A3**, **A8** and **A9** this ratio was consequently changed to 100:100:8). A condensed overview over these results, again using $T_{\max}$ as a convenient marker for the speed of the curing process, is shown in Table 2. Generally, three main strategies were followed to further tailor the properties of the compositions. Those were (a) the introduction of electron withdrawing groups on the anhydride component to facilitate ring-opening (**A8**, **A10**-**A14**), (b) employment of more flexible epoxides (like aliphatic **E2**, **E4**) or (c) the use of liquid/low melting anhydrides (**A1**, **A2**, **A7**, **A9**). While (b) and (c) were primarily intended to decrease the viscosity of the resulting mixtures, curing kinetics were also expected to profit from faster diffusion, especially in the early stages of the polymerization. Indeed, this approach was more successful than the application of activating group-bearing anhydrides (-F, -Cl, -NO_2) with regard to the preparation of homogeneous, stable mixtures. While the activated anhydrides repeatedly allowed for very low $T_{\max}$ values (< 100 °C) and therefore rapid polymerization kinetics (less than 3 min at 160 °C for the **E2**/**A6**/**5u-Me-CO_2** system), it was not possible to form fully homogeneous compositions under the reaction conditions applied here (that is, without solvent or reactive thinner), because the anhydride fraction did not dissolve fully. In many cases, significant reaction was observed already at room temperature shortly after preparation of the one-component mixture (Table 2, entries marked n.d.); this was most pronounced for the highly activated anhydride **A14** bearing a nitro-group. These examples also underline the influence of the epoxy compound, clearly showing that **E2** and **E3** yielded lower $T_{\max}$ values than **E1** or **E4**, when combined with the activated anhydrides (**A10**-**A14**). However, it remains of high interest to see that compositions based on these anhydrides provide very rapid curing at low temperatures. Difficulties concerning homogeneity might be circumvented by addition of reactive thinner or by application of the one-component system as a paste. It should be noted that the overall polarity of the polymerization system will influence the stability of NHC-CO_2-adducts [55,56].

Fully homogeneous mixtures were successfully realized using **E1**-**E4** with **A1**, **A2**, and **A7** (citraconic anhydride), but also by **E1**/**A5** (cyclohexene anhydride), **E4**/**A5**, **E1**/**A6** (maleic anhydride), **E3**/**A6**, and **E4**/**A6** (Table 2). Relative to the reference system using

Table 1
Impact of catalyst concentration on T_{max} for different protected NHCs. *inhomogeneous mixtures (catalyst does not fully dissolve).

$T_{\max}$ [°C]						
Eq.	**5u-Me-CO_2**	wt.%	**6-Cy-CO_2**	wt.%	**6-Mes-CO_2**	wt.%
1	163	0.2	148	0.5	143	0.6
8	125	1.7	120	3.6	117*	4.5
15	120	3.2	111*	6.8	110*	8.4

Molar ratio **E1**:**A1**:NHC = 100:200:1–15; heat rate 5 K/min, 20 to 250 °C.

Table 2

T_{max} [°C] of different epoxy/anhydride mixtures, applying **5u-Me-CO$_2$** as latent catalyst. *labels suspensions at room temperature (anhydride not fully dissolved). n.d. = not determined; viscosity increase already observed at room temperature shortly after mixing.

Anhydride	Epoxy			
	E1	**E2**	**E3**	**E4**
A1	125	133	133	131
A2	146	145	149	146
A3	146*	101*	98*	165*
A4	124*	108*	117*	132*
A5	131	135*	131*	132
A6	152	116*	115	142
A7	125	126	113	125
A8	110*	91*	n.d.	96*
A9	130*	n.d.	135*	108*
A10	134*	120*	117*	122*
A11	126*	117*	n.d.	121*
A12	129*	101*	93*	104*
A13	114*	91*	95*	114*
A14	105*	n.d.	n.d.	n.d.

All resins with a molar ratio of epoxide compound/anhydride/NHC = 100:200:8 or 100:100:8 (**A3**, **A8**, **A9**). T_{max} determined from DSC (heating rate 5 K/min, 20–250 °C).

HHPA (**A1**), it becomes obvious that application of bicyclic **A2** results in a somewhat slower curing process (T_{max} = 145–149 °C), while the room temperature-liquid **A7** (m.p. 6–10 °C) allows for accelerated monomer consumption (T_{max} = 113–126 °C). Interestingly, maleic anhydride seems especially sensitive to changes in the epoxy co-monomer with significant differences occurring for **E1** (152 °C) and cyclohexene oxide-bearing **E3** (115 °C).

To retrieve more information about the latency times of the one-component mixtures and gain a deeper understanding of the viscosity-conversion relations as well as curing kinetics, the rheology of several selected systems was investigated in combination with detailed DSC experiments. Specifically, compositions based on maleic anhydride (**E2**/**A6** and **E3**/**A6**) using epoxide/anhydride/**5u-Me-CO$_2$** = 100:200:8 (molar ratio), as well as a more complex mixture based on the reference system containing additionally reactive thinner and the activated monomer **A10** (**E1**/glycidylphenylether/**A1**:**A10**:**5u-Me-CO$_2$** = 50:100:100:100:8, molar ratio) were chosen. The latter composition was fully homogeneous in spite of containing **A10**, and allowed for evaluating the influence of this activated anhydride when used in conjunction with **A1**. Each system was tested by a set of isothermal and dynamic DSC experiments and rheology measurements at different, constant temperatures. Two examples will be discussed in the following, the corresponding data for all other systems can be found in the Supporting information (Figs. S3-18 and Tables S1-6).

For the composition **E2**/**A6**, viscosity development strongly depended on temperature (Fig. 6). At room temperature (25 °C), a viscosity of 43 mPa·s is found, which expectedly did not change over the observed time span of 30 min. Likewise, at 45 °C a lower viscosity of 21 mPa·s was found, again with no significant rise over time, attesting to the latent nature of the catalyst. Importantly, in

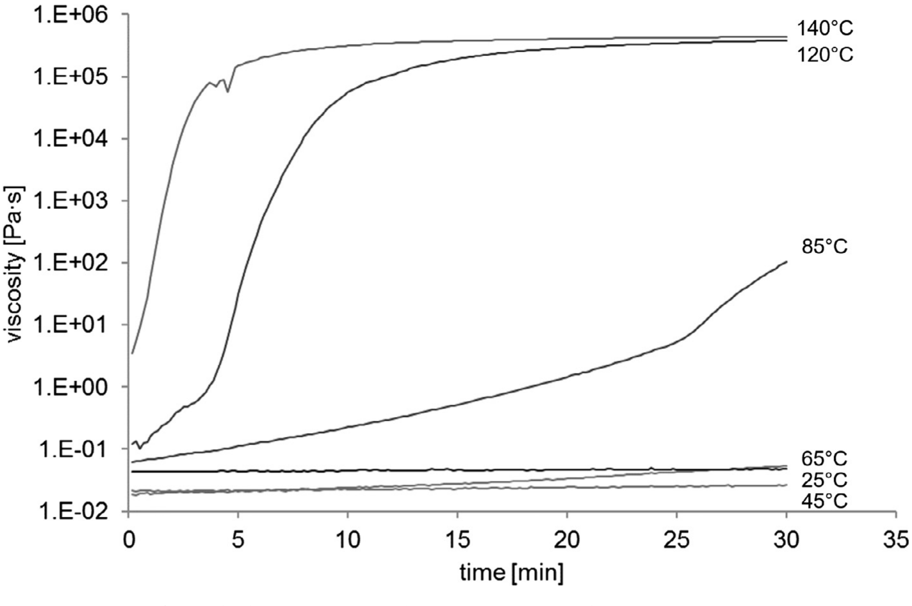


Fig. 6. Rheology measurement of **E2**/**A6**/**5u-Me-CO$_2$** at different temperatures.

Table 3
Released energy during DSC post-curing experiments of the system **E2/A6/5u-Me-CO_2**[a].

Curing temperature [°C][b]	Released energy [J/g][c]
100	−0.2
90	−14.8
80	−107.0

[a] Conditions: 20 K/min, 25–250 °C;

[b] Temperature at which the sample was cured previously in isothermal experiments (t = 20 min).

[c] Integration range 63.0–244.5 °C.

both cases the liquid mass has a low enough viscosity to be sprayable (which can be accomplished with mixtures having a viscosity < 500 mPa·s, although this depends on the technical setup). At 65 °C, viscosity slowly increased over time, yet still remained well below the limit of sprayability; a pot time of at least 30 min is thereby still given. At 85 °C, a more rapid polymerization was found, which within minutes lead to a state where free flow was not possible anymore. Correspondingly, when the sample was heated to higher temperature, the reaction swiftly reached completion within ten minutes at 140 °C. It should be noted that these are very short curing times at mild curing temperatures compared to conventional setups [57] (for example, **E1**/**A1** using 1-cyanoethyl-2-ethyl-4-methylimidazole as accelerator at 75–105 °C with curing periods between up to 6000 min [58]; bisphenol-S-diglycidyl ether/phthalic anhydride/tetrahydrophthalic anhydride in the presence of *N*,*N*-dimethylbenzylamine requires 150 °C for 2 h, followed by 180 °C for 2 h [59]; glycidylphenyl ether/**A1** catalyzed by 1–methylimidazole/dimethylbenzylamine is heated at 100–140 °C for 3–5 h [60]). These findings are underpinned by DSC measurements: isothermal experiments at 120–160 °C (20 min) demonstrated that already in the short time needed to heat samples up to the desired temperature significant curing proceeds, attesting to the high reactivity of the composition (Fig. S3). DSC control cycles (Table 3, up to 250 °C, 20 K/min) of these samples showed that post-curing only occurred for resins heated to less than 100 °C in the previous isothermal experiments, indicating that full curing is achieved at 100 °C and underlining the exceptionally high activity of these one-component mixtures.

Moving to **E1**/glycidylphenylether/**A1**/**A10**/**5u-Me-CO_2**, interesting similarities can be observed. At room temperature, a viscosity of 111 mPa·s was found; this compares favorably to mixtures of bulk **E1**/**A1** (500 mPa·s) [35] and to the heterogeneous nature of bulk **E1**/**A10**. At 45 and 65 °C, 47 and 32 mPa·s, respectively, were found in the initial stages. Especially in the latter case an incremental increase in viscosity was detected (Fig. 7), but which still remained low, indicating that polymerization had not progressed much. Consequently, even at 65 °C a pot time of at least 30 min is given. Within the observed time range full curing was achieved at both 140 °C and 120 °C, as evident from the rheology data. Again this is supported by the DSC findings, where post-curing is very limited for samples pre-cured at 100 °C and non-existent for those pre-cured at 120 °C (Table 4). This example shows that the curing parameters for a well-established system such as **E1**/**A1** can be successfully tuned towards faster reaction at lower temperatures by application of a highly reactive NHC-based catalyst and suitable, more reactive co-monomers.

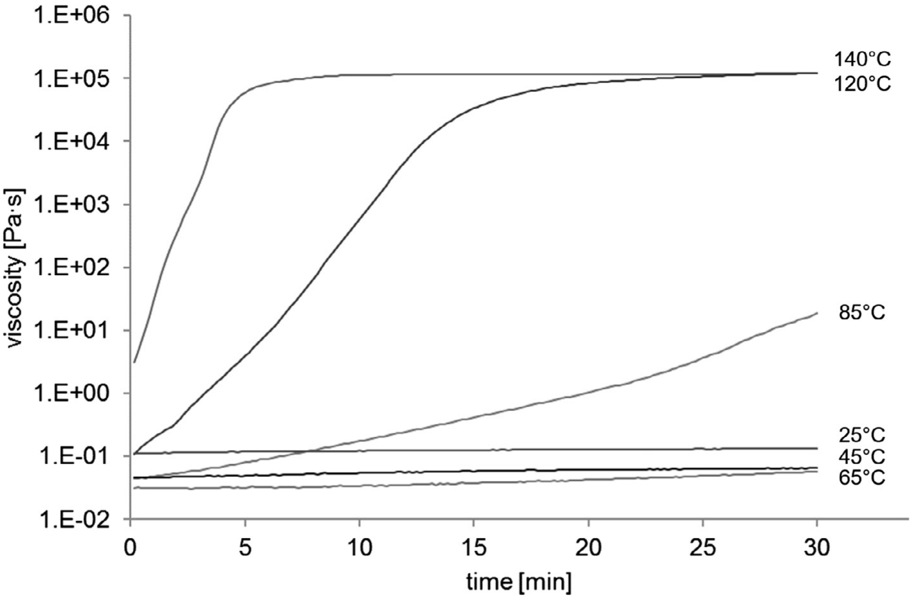


Fig. 7. Rheology measurement of **E1**/glycidylphenylether/**A1**/**A10**/**5u-Me-CO_2** at different temperatures.

Table 4
Released energy during DSC post-curing experiments of system **E1**/glycidylphenylether/**A1**/**A10**/**5u-Me-CO$_2$**.[a]

Curing temperature [°C][b]	Released energy [J/g][c]
100	−43.8
90	−97.2
80	−196.8

[a] Conditions: 20 K/min, 25–250 °C;
[b] Temperature at which the sample was cured previously in isothermal experiments (t = 20 min).
[c] Integration range 63.0–244.5 °C.

The lowest viscosity at room temperature was found for **E2**/**A7** with only 25 mPa·s, while for **E3**/**A6** 60 mPa·s was determined (SI). Both systems show very similar tendencies when compared to the previously discussed examples, however, the **E3**/**A6** system already showed a noticeable increase in viscosity at 45 °C (Fig. S16).

3. Conclusion

The curing properties of latent one-component epoxy/anhydride compositions using thermally triggerable CO$_2$-protected NHCs have been optimized with regards to low viscosity and fast curing kinetics at low-temperature conditions. This has been achieved by application of a well accessible and remarkably robust protected NHC (**5u-Me-CO$_2$**), which is prepared in a single step from commodity chemicals. The systematic investigation of several commonly used epoxy compounds in combination with an exhaustive range of anhydride components has allowed identifying compositions that can be fully cured at $T < 120$ °C or even at 100 °C and less, as evidenced by in-situ DSC and rheology measurements. Additionally, these mixtures provide useful pot times of hours to days, depending on temperature and catalyst loading. A judicious choice of co-monomers also ensures that fully homogeneous, low-viscosity and even technically sprayable one-component mixtures are obtained, potentially widening the range of applications. The advantages of an easily handled NHC precursor in combination with the catalytic power of the free NHC thus result in readily applicable systems that make best use of NHC organocatalysis, while minimizing the liabilities that frequently hinder large scale application of this type of catalyst. Further investigations regarding optimization of the resins presented here are currently conducted in our group, focusing also on the mechanical properties of these low-T cured materials.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2017.05.032.

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