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From the *N*-heterocyclic carbene-catalyzed conjugate addition of alcohols to the controlled polymerization of (meth)acrylates.

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Abstract: Among various *N*-heterocyclic carbenes (NHCs) tested, only the 1,3-bis-(*tert*-butyl)imidazol-2-ylidene (NHC^{tbu}) proved to selectively promote the catalytic conjugate addition of alcohols onto (meth)acrylate substrates. This rather rare example of NHC-catalyzed 1,4-addition of alcohols was investigated as a simple means to trigger the polymerization of both methyl methacrylate and methyl acrylate (MMA and MA, respectively). Well-defined α -alkoxy poly(methyl (meth)acrylate) (PM(M)A) chains whose molar masses could be controlled by the initial [(meth)acrylate]₀/[ROH]₀ molar ratio were ultimately obtained in DMF at 25 °C. A hydroxyl-terminated poly(ethylene oxide) (PEO-OH) macro-initiator was also employed to directly access PEO-*b*-PMMA amphiphilic block copolymers. Investigations into the reaction mechanism by DFT calculations revealed the occurrence of two competitive concerted pathways, involving either the activation of the alcohol or that of the monomer by NHC^{tbu}.

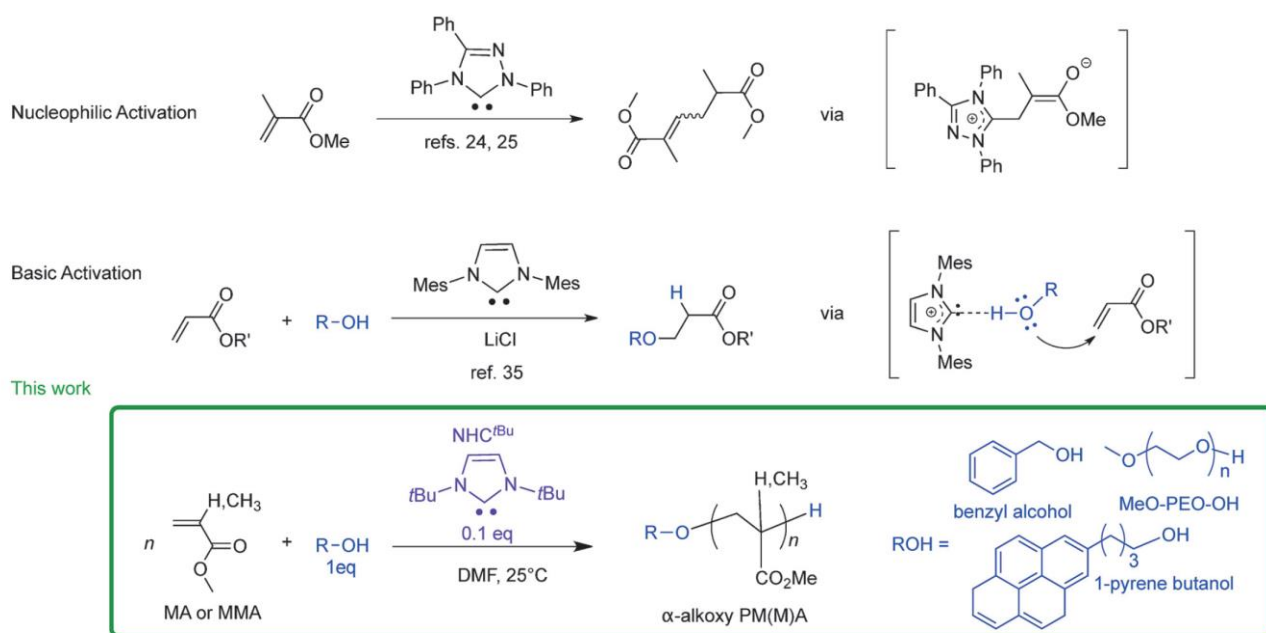
Keywords: Organocatalysis • *N*-Heterocyclic Carbenes • Polymerization • (Meth)acrylates • DFT calculations

Introduction

N-heterocyclic carbenes (NHCs) have received a great deal of attention in the past two decades.^[1-6] Not only can NHCs serve as powerful ligands for transition metals,^[7-9] but they have also emerged as true organic catalysts in molecular chemistry^[10-15] and, more recently, in precision polymer synthesis.^[16-18] The three following activation pathways can be distinguished: i) ambiphilic activation of aldehydes and enals, leading to the inversion of polarity (umpolung) of the carbonyl group, owing to the σ -donor and π -acceptor properties of NHCs;^[19-22] ii) nucleophilic activation of α,β -unsaturated substrates based on the σ -donor properties of NHCs and, iii) Brønsted basic activation of acidic substrates.

Nucleophilic activation (see Scheme 1), which consists in the 1,2 or 1,4-addition of the NHC onto saturated or conjugated esters, respectively, has been widely investigated for various NHC-catalyzed transformations, such as the transesterification reaction, the Morita-Baylis-Hillman reaction,^[23] and the dimerization of methyl methacrylate (MMA)^[24, 25] or the tetramerization of methyl acrylate (MA).^[26] The catalytic step-growth polymerization of bis(meth)acrylate monomers, by iterative dimerization of methacrylate moieties, has been recently applied as a means to achieve unsaturated poly(esters).^[27] Interestingly, various 1:1 or 1:2 reaction adducts between a NHC and a Michael (meth)acrylate acceptor, that is, following a non-catalytic process, have also been reported.^[28-30] Although all of them involve the initial nucleophilic 1,4-addition of the NHC to the (meth)acrylate, different reaction outcomes have been eventually isolated, depending on the nature of the carbene. The direct polymerization of MMA initiated by a specific NHC, namely, 1,3-bis-(*tert*-butyl)imidazol-2-ylidene (NHC^{tBu}) has even been reported, albeit in a non-controlled fashion.^[28, 29, 31, 32]

In contrast to the aforementioned ambiphilic and nucleophilic activation modes, the Brønsted activation by NHCs has been less studied, despite their rather high basicity. Such activation has not only allowed transesterification reactions, but also conjugate additions of protic nucleophiles, such as amines (Aza-Michael),^[33] thiols (Sulfa-Michael) and phosphonic acids (Phospha-Michael),^[34] onto α,β -unsaturated substrates to be performed under mild conditions. The rather unusual selective oxa-Michael addition of alcohols onto various α,β -unsaturated ketones and esters has also been described, in presence of 1,3-bis-(mesityl)imidazol-2-ylidene (NHC^{Mes}) and an equivalent of LiCl (see Scheme 1).^[35] In contrast, with the 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (TPT) as catalyst and acrylonitrile as substrate,^[24, 25, 36] no oxa-Michael type reaction was noted in presence of alcohols. Instead, dimerization of acrylonitrile, which proceeds *via* nucleophilic activation by the NHC, was observed, the alcohol playing in this case the role of a co-catalyst facilitating proton transfer reactions. Very recently, this concept has been applied to the synthesis of saturated poly(esters) by the TPT-catalyzed repetitive oxa-Michael additions from hydroxyl-functionalized acrylates.^[37] Those examples highlight that the oxa-Michael addition of alcohols (*basic activation*) may be favoured over the conjugate addition of the NHC to the substrate (*nucleophilic activation*), depending on the nature of the carbene/substrate combination. However, despite the different ways to activate α,β -unsaturated esters such as (meth)acrylates, their catalytic and direct transformation into poly(meth)acrylates has never been considered. In fact, only the so-called group transfer polymerization (GTP), which is based on the repetition of the Mukaiyama-Michael reaction and requires the specific use of air-sensitive silyl ketene acetal (SKA) initiators, has been implemented to prepare well-defined poly(meth)acrylates.^[38-40] Here we demonstrate, for the first time, that a peculiar NHC, namely, 1,3-bis-(*tert*-butyl)imidazol-2-ylidene (NHC^{tBu}), can be used as organocatalyst enabling the selectively oxa-Michael addition of simple alcohols onto MMA or MA, in absence of any other additives. On this basis, we evidence that the polymerization of both monomers can lead to α -alkoxy poly(meth)acrylate chains, in contrast to other NHCs used so far. These NHC^{tBu}-organocatalyzed, ROH-initiated polymerizations can be controlled at 25 °C in DMF by the initial [monomer]₀/[ROH]₀ molar ratio. Furthermore, this method is suitable for the facile preparation of amphiphilic poly(ethylene oxide)-*b*-poly(methyl methacrylate) block copolymers, using a hydroxyl-containing poly(ethylene oxide) macro-initiators. Density functional theory (DFT) calculations suggest the occurrence of two competitive low-energy pathways, involving either a basic activation of the alcohol or a nucleophilic activation of the monomer, in perfect agreement with experimental observations.



Scheme 1. Catalytic transformation of (meth)acrylate substrates by NHCs.

Results and Discussion

The NHC^{tBu}-catalyzed polymerization of MMA in the presence of benzyl alcohol (BnOH) as initiator was first investigated in DMF at 25 °C. Remarkably, these conditions yielded PMMA's with narrow dispersities (\mathcal{D}) and molar masses controlled by the initial $[MMA]_0/[BnOH]_0$ ratio (Table 1, entries 1-4 and Figure 1a). The ¹H NMR spectrum of a purified PMMA (Figure 2a) confirmed the presence of benzyl groups in α -position of PMMA chains ($\delta = 4.98$ ppm), the calculated molar mass being in accordance with the theoretical value. The presence of the α -benzyloxy end group was further confirmed by the absorbance at 260 nm detected in the UV SEC traces (Figure 2b).

Matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) analysis of an oligomeric PMMA (entry 2), revealed the presence of four different populations (A, B, C and D, Figure 3), with peak-to-peak mass increment of 100 mass units (= mass of one MMA unit) in all cases. Population A is in perfect agreement with the formation of α -benzyloxy PMMA chains (initiation by BnOH), while population B might be the result of a chemical modification of population A by formal release of NaH during ionization. Population C was ascribed to α -1,3-bis-(*tert*-butyl)imidazolium PMMA's generated by direct initiation of the polymerization by NHC^{tBu} (see Scheme S1 in supporting information, SI). Finally, population D could correspond to α -methoxy PMMA's, where the methoxy could arise from the NHC^{tBu}-catalyzed transesterification of MMA with BnOH (see Scheme S1). Since experimental molar masses, as determined both by SEC and NMR, were in good agreement with theoretical values for low molar masses targeted (at low $[MMA]_0/[BnOH]_0$ ratios), the relative proportion of the different populations does not seem to reflect the sample composition. Thus, we assume that the proportion of populations C and D were not representative of the sample composition.

Observation of a linear evolution of molar masses with conversion (Figure S1 in SI) and successful chain extension experiments further established the living character of these polymerizations (Table S1 and Figure S2). At $[MMA]_0/[BnOH]_0$ ratios higher than ~ 25 , however, molar masses somewhat deviated from the expected values (entry 4). Similar observations have been reported by Hedrick, Waymouth *et al.* regarding the NHC-catalyzed ring-opening polymerization of D,L-lactide in presence of alcohol initiators.^[17, 41, 42] This has been attributed to the occurrence of competitive nucleophilic and basic mechanisms (monomer and alcohol activation by NHC, respectively; *vide infra*).

Table 1. Representative NHC^{tBu}-catalyzed polymerizations of MMA and MA in presence of alcohol in DMF at 25 °C.

| entry | Monomer (M) | Initiator (I) | [NHC]/[I]/[M] | Time (h) | Conv. ^a (%) | $\overline{M}_n^{\text{theo b}}$ (g.mol ⁻¹) | $\overline{M}_n^{\text{c}}$ (g.mol ⁻¹) | \overline{D}^{c} |
|-------|-------------|---------------------------|---------------|----------|------------------------|---|--|---------------------------|
| 1 | MMA | PhCH ₂ OH | 0.1/1/5 | 5 | 100 | 600 | 900 | 1.1 |
| 2 | MMA | PhCH ₂ OH | 0.1/1/10 | 5 | 100 | 1,100 | 1,400 | 1.2 |
| 3 | MMA | PhCH ₂ OH | 0.1/1/25 | 24 | 100 | 2,600 | 2,600 | 1.4 |
| 4 | MMA | PhCH ₂ OH | 0.1/1/50 | 24 | 92 | 4,600 | 8,000 | 1.9 |
| 5 | MMA | 1-pyrenebutanol | 0.1/1/10 | 24 | 100 | 1,200 | 1,300 | 1.4 |
| 6 | MMA | MeO-PEO ₃₃ -OH | 1/1/50 | 24 | 100 | 6,100 | 6,200 | 1.3 |
| 7 | MA | PhCH ₂ OH | 0.1/1/12 | 5 | 100 | 1,100 | 700 | 1.2 |
| 8 | MA | PhCH ₂ OH | 0.1/1/24 | 24 | 100 | 2,200 | 1,300 | 1.4 |
| 9 | MA | PhCH ₂ OH | 0.1/1/36 | 24 | 92 | 2,800 | 2,400 | 1.6 |
| 10 | MA | PhCH ₂ OH | 0.1/1/48 | 24h | 82 | 3,300 | 3,900 | 2.0 |

a. Conv.= % monomer conversion determined by ¹H NMR spectroscopy; b. Theoretical molar mass $\overline{M}_n^{\text{theo}} = M_{\text{ROH}} + M_{\text{M}} \times \frac{[\text{M}]_0}{[\text{ROH}]_0} \times \text{conv.}$ with M_{ROH} and M_{M} the molar masses of the initiator and the monomer unit, respectively; c. Characterization of polymers by SEC in THF using polystyrene standards for calibration.

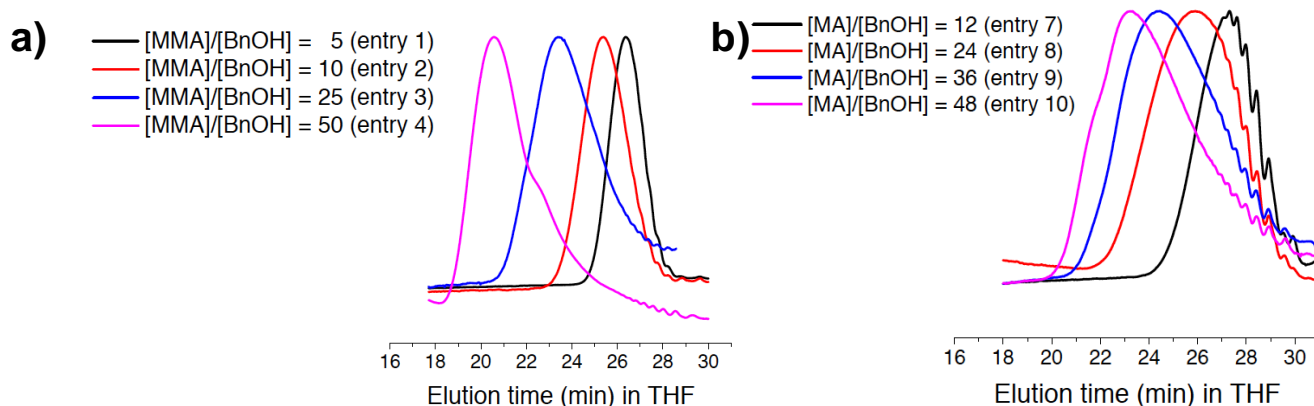


Figure 1. SEC (RI) traces of a) PMMA's and b) PMA's obtained using NHC^{tBu} as catalyst and BnOH as initiator.

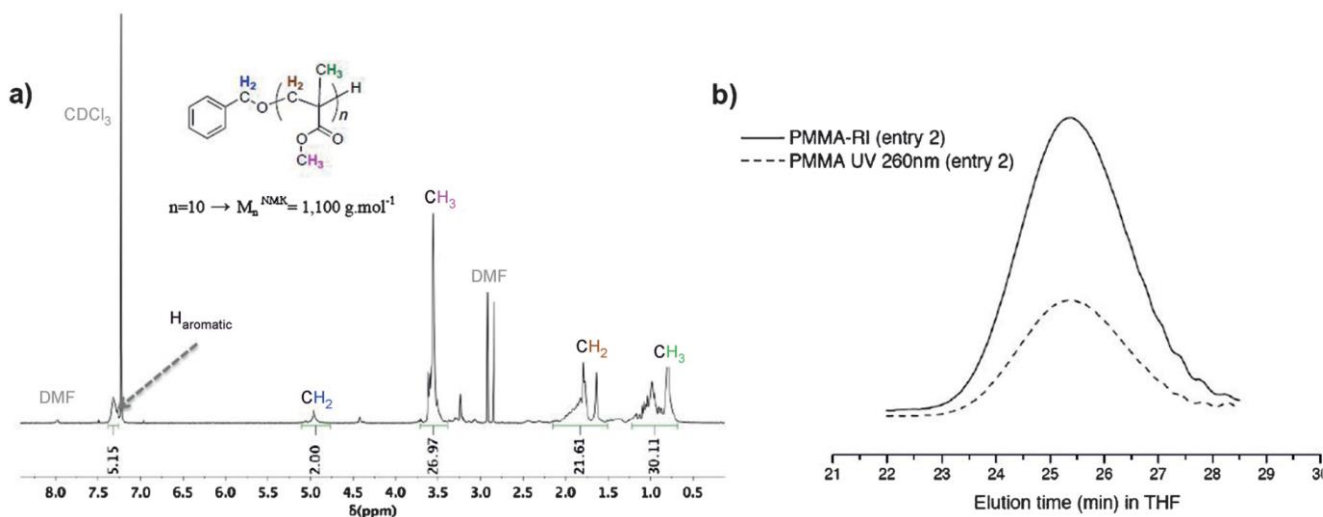


Figure 2. a) ^1H NMR (CDCl_3) and b) SEC traces of a PMMA initiated by BnOH and catalyzed by NHC^{tBu} (Table 1, entry 2).

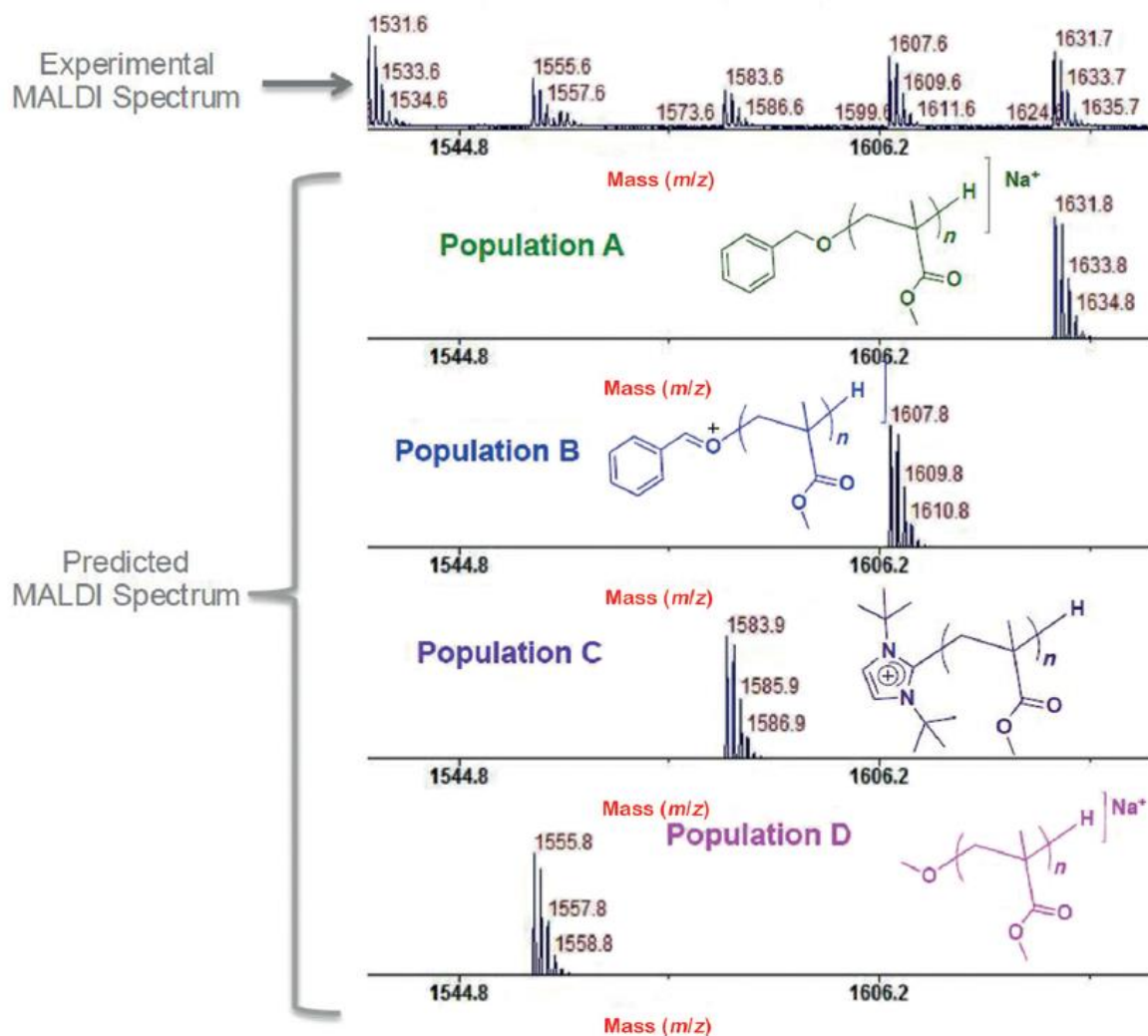


Figure 3. MALDI-ToF spectrum of a PMMA initiated by BnOH and catalyzed by NHC^{tBu} (Table 1, entry 2).

This method was next applied to both 1-pyrenebutanol (entry 5; see Figures S3-4) and hydroxy-poly(ethylene oxide), MeO-PEO₃₃-OH (entry 6) as (macro)initiators. In the latter case, facile synthesis of well-defined amphiphilic PEO-*b*-PMMA block copolymers could thus be achieved (Table 1, entry 6; see also Table S2 and Figure S5). Analysis by diffusion-ordered NMR spectroscopy (DOSY) provided the diffusion coefficient of the obtained block copolymers, which are related to their hydrodynamic radius and molecular weight. In the DOSY NMR spectrum of these MeO-PEO₃₃-PMMA block copolymers (Figure 4 and S6-7) only one diffusion coefficient was observed, evidencing the formation of pure copolymers with an unimodal distribution. Indeed, different diffusion coefficients would be observed with a mixture of homopolymers or with copolymers of various molar masses. As expected, values of the observed diffusion coefficients were found to decrease as the molar mass of the copolymer increased (Table S2) since the diffusion of similar species is related to their size, and that bigger species have a smaller diffusion coefficient. Transmission electron microscopy (TEM) of MeO-PEO₃₃-PMMA₅₀ aqueous solution revealed a nano-organization through spherical aggregates of a diameter in the range 24-32 nm (Figure S8), compatible with the formation of micelles resulting from the self-assembly of the PEO-*b*-PMMA amphiphilic block copolymer.

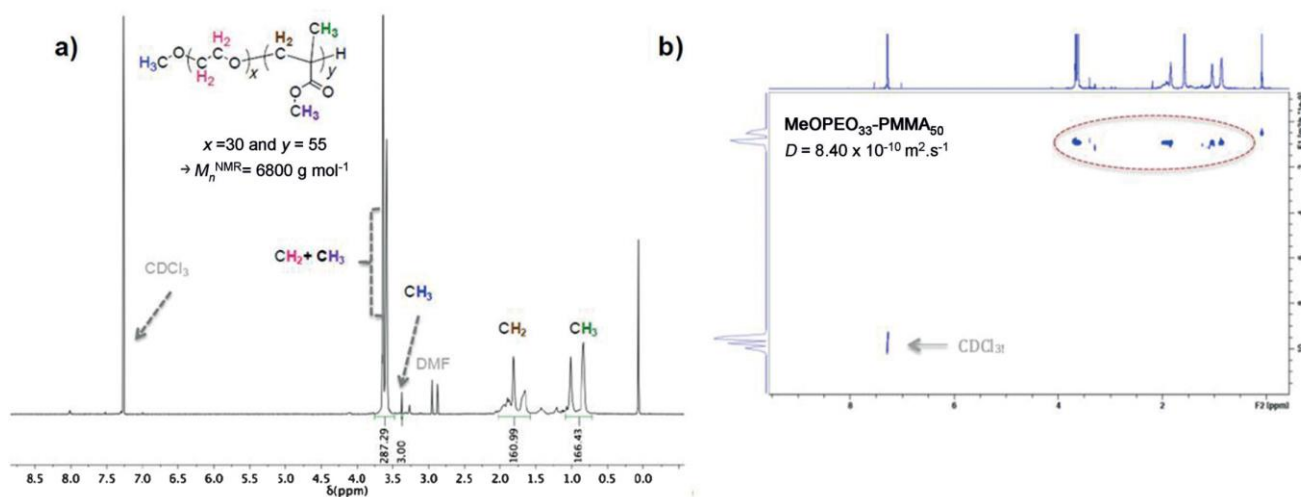


Figure 4. a) ^1H NMR (in CDCl_3) and b) DOSY spectra (in CDCl_3) of $\text{MeOPEO}_{33}\text{-PMMA}_{50}$ (Table 1, entry 6).

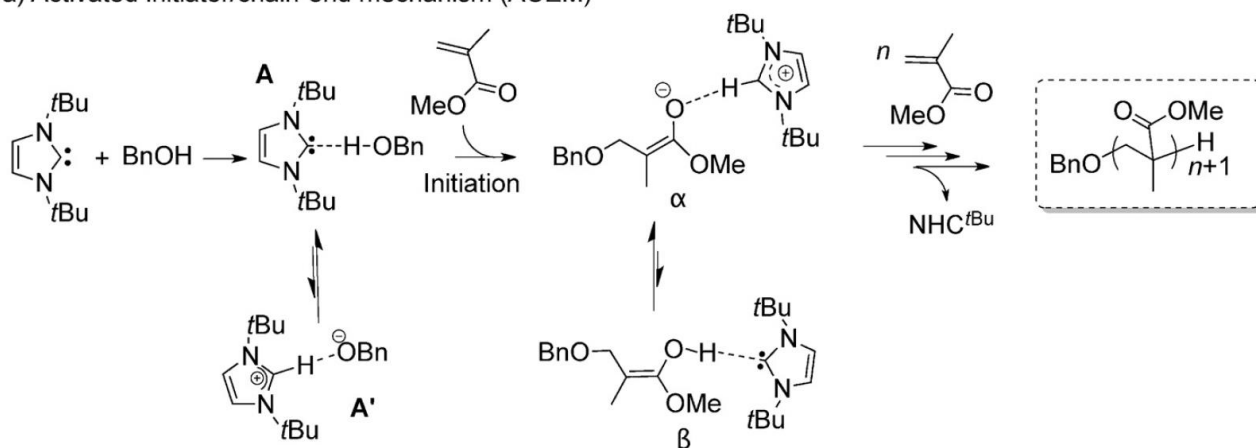
Intriguingly, no polymer was formed when attempting to polymerise MMA with other NHCs than NHC^{fBu} ($\text{pK}_a^{\text{DMSO}} = 22.8$)^[43] in the presence of BnOH . Thus, NHC^{iPr} ($\text{pK}_a^{\text{DMSO}} = 22.3$)^[43] gave the same cyclodimer as that observed in absence of alcohol (Figure S9),^[29] while 1,3-bis-(isopropyl)-4,5-(dimethyl)imidazol-2-ylidene ($\text{NHC}^{\text{iPrMe}}$; $\text{pK}_a^{\text{DMSO}} = 24.7$)^[43] and NHC^{Mes} ($\text{pK}_a^{\text{DMSO}} = 17.0$)^[43] did not give any polymer either, evidencing the remarkable selectivity of NHC^{fBu} .

To highlight the versatility of this NHC^{fBu} -catalyzed polymerization method, MA was next chosen as a monomer substrate. In absence of alcohol initiator, various reaction products arising from (non) catalytic processes have been isolated, depending on the carbene structure.^[26, 30] However, we found that MA (50 eq.) could smoothly be polymerized in DMF at 25 °C, again using BnOH (1 eq.) as initiator and a catalytic amount of NHC^{fBu} (0.1 eq.). Molar masses of the resulting PMA's were again well-controlled by the initial $[\text{MA}]_0/[\text{BnOH}]_0$ ratio (Table 1, entries 7-10; Figure 1b). These results, as a whole, evidence the ability of this carbene for the controlled polymerization of (meth)acrylates, in the presence of a simple alcohol as a chain regulator.

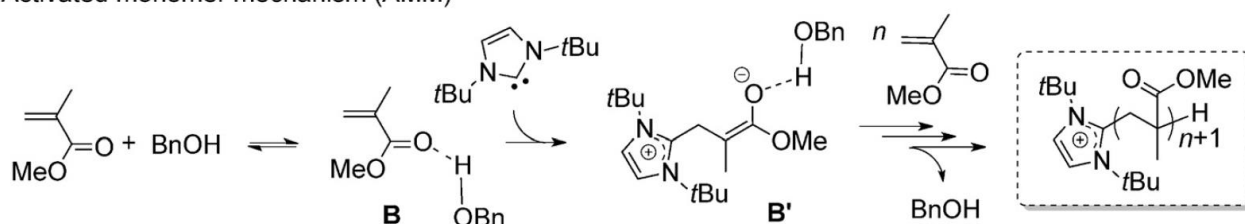
To gain a better insight into the polymerization mechanism of MMA, density functional theory (DFT) calculations were performed at the M06-2X/6-31G** level of theory taking into account solvent effects (DMF) by using a SMD solvation model (for computational details, see SI).

Two mechanisms can eventually be proposed, depending on the role of NHC^{fBu} (Scheme 2 and Figure 5). Due to its rather high basicity, NHC^{fBu} could interact with BnOH (**A** and **A'** in Scheme 2a) and assist the conjugate 1,4-addition of the alcohol onto MMA, thus playing the role of a true catalyst (Scheme 2a).^[35] The resulting imidazolium enolate ion pair, denoted as α , could then propagate the anionic polymerization by selective repeated 1,4-addition reactions onto incoming MMA molecules.^[44] The charged active species (α) might be in equilibrium with a neutral enol-type dormant form (β) that is hydrogen-bonded to the NHC (Scheme 2a). However, a nucleophilic mechanism involving the direct 1,4-conjugate addition of NHC^{fBu} onto a MMA monomer could also be operative (see Schemes 2b and Figure 5). In this case, the role of the alcohol would be to increase the electrophilicity of monomers *via* hydrogen bonding to the C=O group (**B**, Scheme 2b), while the carbene would play the role of a direct initiator. The ensuing zwitterionic imidazolium enolate **B'** would then propagate the polymerization by repeated 1,4-addition reactions of MMA. The mechanism of the zwitterionic polymerization of MMA, directly initiated by NHC^{fBu} (in absence of ROH), has been previously reported (see Figure S13 for comparison of the energy profiles).^[28, 29] Details of DFT calculations, including the geometrical description of the TS, can be found in the SI.

a) Activated initiator/chain-end mechanism (ACEM)



b) Activated monomer mechanism (AMM)



Scheme 2. Proposed general mechanisms for: a) activated initiator/chain-end mechanism and b) activated monomer mechanism for the NHC^{tBu} -catalyzed polymerization of MMA in presence of benzyl alcohol (BnOH).

In the NHC^{tBu} -catalyzed, BnOH-initiated polymerization mechanism (Scheme 2a and Figure 5), initiation consists in the conjugate addition of BnOH onto MMA, assisted by NHC^{tBu} . The carbene was indeed found to strongly interact with BnOH, leading to a BnOH- NHC^{tBu} adduct **A** (ΔH : -11.1 kcal/mol), while an equilibrium between this adduct and the corresponding imidazolium alkoxide **A'**, in favor of **A**, was computed (**A'** is less stable than **A** by 6.9 kcal/mol). Interestingly, and in accordance with previous reports,^[45] deprotonation of BnOH by NHC^{tBu} does not occur under these conditions. Instead, a BnOH- NHC^{tBu} adduct is formed, as attested by the 3.1 ppm downfield shift of the hydroxyl proton of BnOH as observed by ^1H NMR (Figure S10), and by the chemical shift of the C_a carbon of NHC^{tBu} at 196 ppm in ^{13}C NMR ($\delta = 220$ and 134 ppm for C_a and $\text{C}_{a'}$ in the free carbene and in the imidazolium, respectively; Figure S11).

Addition of the activated alcohol **A** onto MMA was next investigated computationally (Figure 5, mechanism in black). This reaction initially proceeded *via* the formation of the imidazolium enolate **1** ($\Delta H = 2.8$ kcal/mol; Figure 5), where the imidazolium cation was hydrogen-bonded to the O atom of the BnO moiety. Transfer of the imidazolium, from the benzyloxy to the enolate chain end (generating α as intermediate) was predicted to be exothermic ($\Delta H = -5.2$ kcal/mol). Overall, both BnOH- NHC^{tBu} adduct **A** and the corresponding benzyloxyenolate featuring an imidazolium counter-cation, α , were found quasi iso-energetic (**A** being less stable than α by 2.4 kcal/mol), and a small energy barrier of 10.8 kcal/mol was computed from **A** to **TS1**. This transformation was calculated to occur *via* a concerted but strongly asynchronous transition state (see **TS1** in Figure S14). Again, note that the active form, α , is in equilibrium with a dormant form β (equilibrium shifted in the direction of α) where the carbene is hydrogen-bound to the enol chain end (Scheme 2a).

The second addition of MMA, which leads to the imidazolium enolate ion pair α' (Figure 5), was found highly exothermic ($\Delta H = -14.7$ kcal/mol), and the corresponding energetic barrier was calculated very low (2.9 kcal/mol). Here again, a concerted but asynchronous TS could be located on the potential energy surface (see **TS'** in Figure S14). The imidazolium cation, that is hydrogen-bonded to the ester group of the first MMA molecule incorporated in α' during initiation, is then transferred to the enolate chain end in α'' ($\Delta H = -4.6$ kcal/mol). As already observed in the initiation step, the active imidazolium enolate ion pair α'' is in equilibrium with a dormant form β'' ($\Delta H = 6.0$ kcal/mol in favor of α''). Overall, this process not only appeared thermodynamically and kinetically favored, but also proved compatible with experimental observations made at 25 °C in DMF.

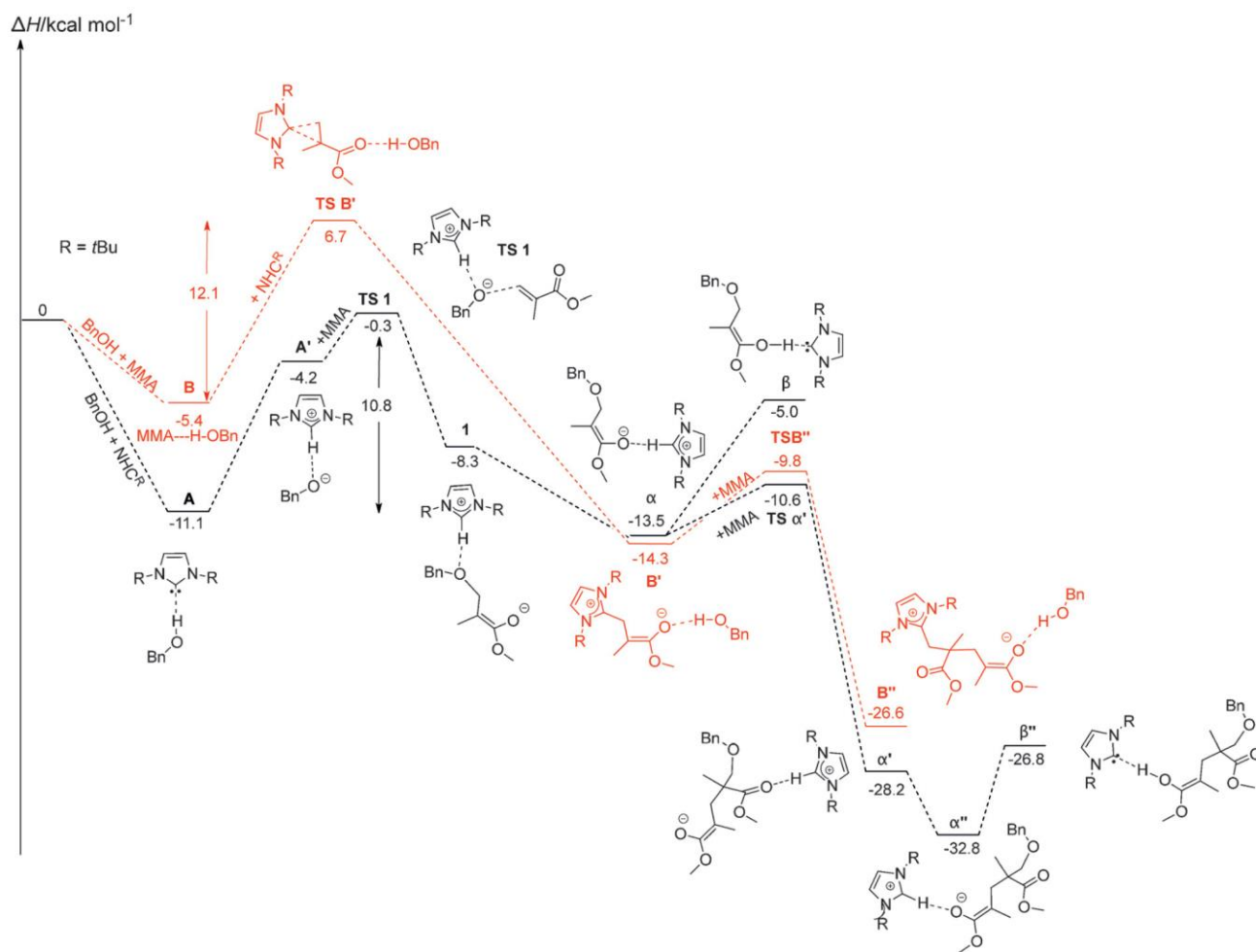


Figure 5. Activated initiator/chain-end (black) and activated monomer mechanism (red) for the NHC^{tBu} -catalyzed polymerization of MMA in presence of benzyl alcohol (BnOH). Structures of the transition states have been omitted for clarity (see SI). All enthalpy values (ΔH and ΔH^\ddagger) are in kcal/mol.

The alternative mechanism involving the direct addition of NHC^{tBu} onto MMA was also investigated computationally (Scheme 2b and Figure 5, mechanism in red). As expected, BnOH stabilizes both MMA (compound **B**) and the imidazolium enolate **B'**, resulting from this conjugate 1,4-addition, the reaction being exothermic by 8.9 kcal/mol. From a kinetic standpoint, the 1,4-addition of NHC^{tBu} onto MMA-ROH proved easier (by 3.5 kcal/mol) than the corresponding reaction in absence of BnOH (12.1 vs. 15.6 kcal/mol, with and without alcohol, respectively (see Figure S13)). The second addition of MMA, forming compound **B''**, was predicted to be exothermic ($\Delta H = -12.3$ kcal/mol) and associated with a low energetic barrier (4.5 kcal/mol). Note that the presence of the alcohol has only a minor influence on the energetic of the propagation step, small differences, between the reaction in presence and absence of BnOH, being calculated for the activation barrier ($\Delta\Delta H = 1.6$ kcal/mol) and

the thermodynamic ($\Delta\Delta H = -2.4$ kcal/mol) of these transformations (Figure S13). Hence, the favorable energetic values computed both for the initiation and propagation steps of the direct NHC^{tBu} -initiated polymerization of MMA, in presence of BnOH, are also compatible with the presence of α -imidazolium PMMA chains, as also observed experimentally on the basis of MALDI-ToF MS analysis (see Figure 3).

Thus, the rather small differences observed computationally in terms of energetic profile for both the first and the second addition of MMA suggest that both concerted mechanisms may occur experimentally. However, the polymerization of MMA initiated by the alcohol prevails, especially at low $[\text{MMA}]_0/[\text{BnOH}]_0$ ratio, allowing polymer chain ends to be efficiently controlled under these conditions.

Conclusions

The 1,3-bis-(*tert*-butyl)imidazol-2-ylidene (NHC^{tBu}) was evidenced to catalyze the oxa-Michael addition of alcohols onto (meth)acrylic substrates, in absence of any other additives. Importantly, this highly efficient and selective reaction allowed initiating and controlling the polymerization of these monomers, affording α -alkoxy PM(M)A's. In contrast to traditional anionic polymerization or group transfer polymerization of (meth)acrylates that require very low temperature or complex/expensive initiators, NHC^{tBu} -catalyzed polymerizations can be performed at 25 °C in DMF, with simple alcohols as controlling agents. This method also allows achieving amphiphilic block copolymers based on PMMA and PEO, from a hydroxyl-containing PEO macro-initiator. Investigation of the polymerization by DFT revealed that both the alcohol and the monomer activation mechanisms could compete, both initiation and propagation steps proceeding by a concerted low-energy pathway. This unprecedented strategy further expands the scope of organocatalyzed polymerization mediated by NHCs. Catalytic selective multiple conjugate additions of various protic initiators onto Michael acceptors is undergoing in our group.

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