Organocatalyzed Polymerization

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Harnessing the Potential of N-Heterocyclic Carbenes for the Rejuvenation of Group-Transfer Polymerization of (Meth)Acrylics**

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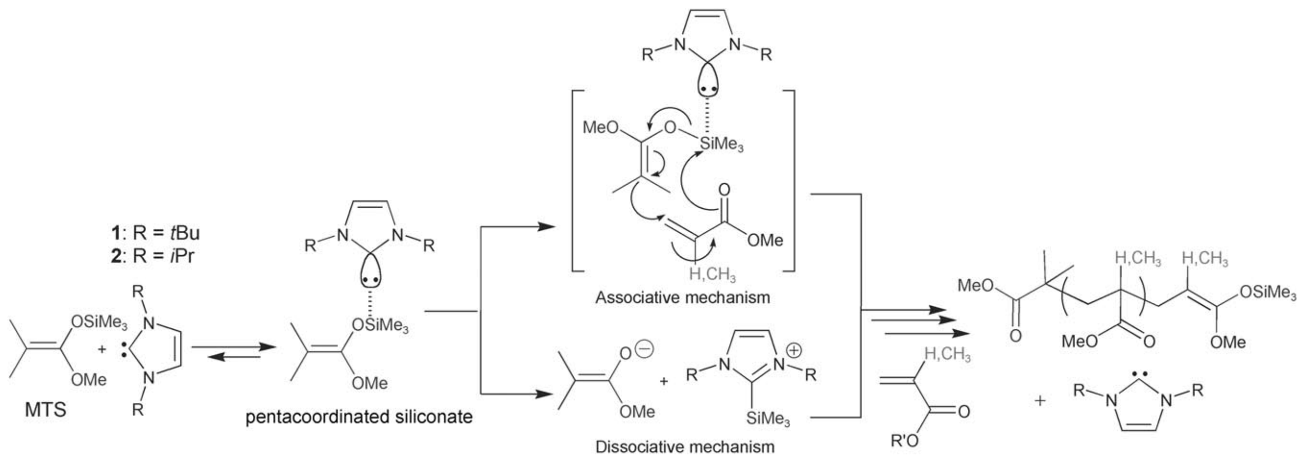
At the time of its disclosure in 1983 by Webster et al., group-transfer polymerization (GTP) was greeted as a major breakthrough in polymer chemistry, for it describes the living polymerization of (meth)acrylic monomers at ambient temperature.[1] GTP is initiated and propagates by the conjugate addition of silyl ketene acetals to incoming (meth)acrylic monomers and the concomitant transfer of the trimethylsilyl group to chain end (Scheme 1),[1,2] through repeated Mukaiyama–Michael-type reactions.[3] A catalyst is required for GTP to proceed: anions such as HF_2^-, F^- or CN^- perform best for methacrylic monomers in polar solvents, whereas Lewis acids, such as AlR_2Cl or $ZnCl_2$, and apolar media are most suitable for acrylic monomers.[1–4] The absence of a unique catalytic system that could be used for the two classes of monomers soon appeared as a weakness of GTP, synthesis of *all*-(meth)acrylate block copolymers by GTP being not practical. As a matter of fact, industrial outcomes of this discovery mainly concern the production of star-shaped poly(methacrylate)s for automotive applications.[2,5]

Herein, we demonstrate that N-heterocyclic carbenes (NHCs) can efficiently catalyze the GTP of both methacrylic and acrylic monomers in regular polar or apolar organic media.[6] Since the reports by Bertrand et al.[7] and Arduengo et al.[8] describing the first stable carbenes, their utilization as synthetic tools in organic chemistry has outreached all expectations.[9] Apart from their role as efficient ligands for transition-metal-based organometallic complexes,[10] they have emerged as powerful organic catalysts.[9] The immense catalytic potential of NHCs can be explained by their structural diversity and their rates and selectivities, which compare well with the most active and selective metal-based or enzymatic catalysts.[7–10] Most NHC-catalyzed reactions consist in the activation of carbonyl moieties, a chemistry that Waymouth, Hedrick et al. have elegantly applied to NHC-catalyzed ring-opening polymerization (ROP) of cyclic esters.[11] NHCs can also activate other electrophilic groups, such as trialkylsilyl for the cyanosilylation, or the trifluoromethylsilylation of ketones and/or aldehydes.[12] Capitalizing on this finding, Baceiredo et al. showed that NHCs catalyze the ROP of cyclosiloxanes[13] and be encapsulated in a silicone-based polymer for a facile air manipulation.[14]



Scheme 1. Associative versus dissociative mechanisms for NHC-mediated GTP.

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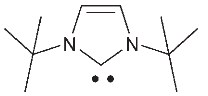
Herein we show that silyl ketene acetals can be activated by NHCs to trigger the living polymerization of both methacrylic and acrylic monomers.



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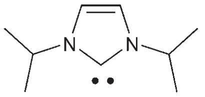

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Carbene-catalyzed GTP of methyl methacrylate (MMA), initiated with 1-methoxy-2-methyl-1-trimethylsiloxypropene (MTS), was first investigated at room temperature in the presence of NHC **1** or **2** (1 to 5% molar relative to MTS), and THF as solvent. These two NHCs were selected for their ease of preparation as free molecules, with no need to generate them in situ. Poly(MMA) samples synthesized in this way were obtained in quantitative yields after a few hours of reaction, with molar masses corresponding closely to the ratio [MMA]/[MTS], and dispersity indexes *D* lower than 1.3 (Table 1, entries 1 to 5). Figure 1a shows the size-exclusion chromatography (SEC) traces of five different PMMA samples, including that of a sample with a molar mass as high as 100000 g mol^{-1} (Table 1, entry 4) which has not been achieved using regular anionic catalysts for GTP.[1,2] These results indicate that NHC-catalyzed GTP of MMA is living, and confirm that bare NHCs **1** and **2** activate the Si–O bond, in an identical fashion to Lewis bases in catalyzed Mukaiyama aldol-type reactions.[3,12]

Table 1: GTP of MMA and tBA in the presence of NHC **1** or **2**.

Entry	Monomer	NHC	Solvent	[NHC]/[I]/[M]	*t* [h]	th. M_n[a] [g mol^{-1}]	exp. M_n[b] [g mol^{-1}]	D
				Homopolymers				
1		**1**	THF	0.05/1/20	8	2000	2600	1.27
2		**1**	THF	0.05/1/90	8	9000	9900	1.10
3		**1**	THF	0.05/1/200	8	20000	18500	1.11
4	MMA	**1**	THF	0.05/1/1000	8	100000	110000	1.3
5		**2**	THF	0.05/1/200	8	20000	22500	1.08
6		**2**	THF	0.05/1/100	8	10000	10800	1.09
7		**2**	toluene	0.05/1/100	16	10000	10900	1.3
8		**2**	THF	0.01/1/40	1	5120	5800	1.15
9		**2**	THF	0.01/1/80	1	10240	12800	1.15
10		**2**	THF	0.01/1/150	1	19200	21000	1.2
11		**2**	THF	0.01/1/300	1	38400	33000	1.25
12	*t*BuA	**1**	THF	0.01/1/40	1	5120	4800	1.3
13		**2**	toluene	0.01/1/50	8	6400	4900	1.4
14		**2**	toluene	0.01/1/100	8	12800	12600	1.3
15		**2**	toluene	0.01/1/200	8	25600	22200	1.19
16		**1**	toluene	0.01/1/100	8	12800	11500	1.6
				Tri- and Diblock Copolymers				
17	MMA 1st		THF	0.01/1/30	16	3000	2900	1.25
18	tBA 2nd	**2**	THF	0.01/1/30	24[c]	6840	6500	1.35
19	MMA 3rd		THF	0.01/1/60	48[c]	12840	12600	1.4
20	MMA 1st	**2**	toluene	0.05/1/100	16	10000	10900	1.3
21	tBA 2nd		toluene	0.05/1/80	24[c]	20240	21900	1.3

[a] Theoretical molar masses: th. $M_n = ([\text{Monomer}]/[\text{I}])$. conv. $M_{MU} + M_I$, where M_{MU} and M_I are the molar masses of the monomer unit and the (macro)initiator: MTS or polymer precursor for entries 18, 19, and 21, respectively, and conv. is the monomer conversion determined by gravimetry. [b] Experimental molar masses obtained by SEC in THF using polystyrene standards for calibration. [c] Cumulated time of the experiment.

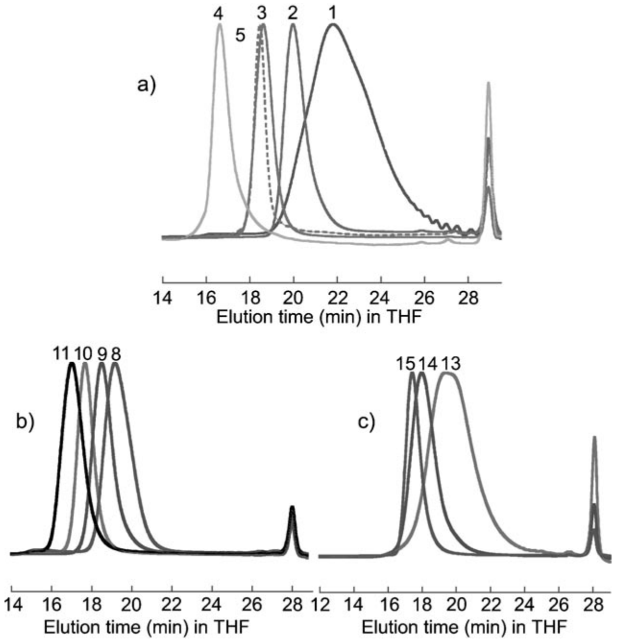
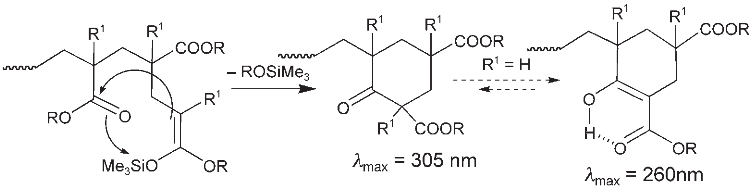


Figure 1. SEC traces of a) poly(MMA)s obtained in THF, b) poly(tBA)s obtained in THF, and c) poly(tBA)s obtained in toluene (see Table 1 for numbering) The dashed line in (a) corresponds to 5.

The more nucleophilic NHC **2** leads to poly(MMA) with a lower dispersity (Table 1, entries 5 and 6), which is probably due to a higher silicophilicity compared to **1**, thus inducing a higher rate of exchange of the $SiMe_3$ moieties. To what extent this interaction/activation develops—whether it brings about the formation of pentacoordinated silicon-based intermediates or generates true imidazolium enolates—is of importance, as it affects the mechanism of propagation of living ends. There has indeed been heated debate in the literature about the actual mechanism of GTP: Depending upon the nature of catalyst and the overall experimental conditions, either the dissociative or the associative mechanism prevails.[1–2,4,16–18] Proponents of the dissociative mechanism demonstrated that strong anions, such as HF_2^-, generate enolate-type ionic species when reacted with silyl ketene acetals, whereas those advocating for associative mechanism showed that weak bases give rise to pentacoordinated silicon intermediates (Scheme 1). Herein, MTS and NHC **1** were mixed in a 1/1 molar ratio and characterized by ^{13}C and ^{29}Si NMR spectroscopy: no enolate-type species could be detected, in contrast to the observation made for HF_2^--catalyzed GTP,[19] which suggests that NHC-assisted GTP proceeds by an associative mechanism, and pentacoordinated silicon intermediates are the active species.

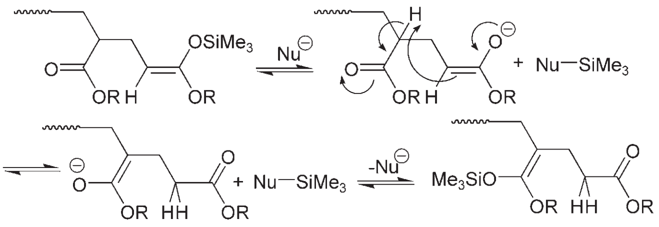
To assess the applicability of carbene-induced GTP in solvents of varying polarity, MMA was then polymerized in toluene in the presence of **2** using MTS (Table 1, entry 7). Under these conditions, poly(MMA)s of expected molar mass, and with a slightly broader dispersity than that exhibited by the THF-derived sample (Table 1, entry 6), were obtained. The rate constant of propagation (k_p) for MMA is smaller in toluene than in THF,[18] thus the reaction took longer to reach completion in this solvent. The tail observed in the low molar mass region of the SEC trace of the latter sample was further investigated, as it might well mirror the occurrence of termination reactions during propagation. The anionic polymerization of MMA is indeed prone to a backbiting reaction: the attack of the antepenultimate carbonyl group by the terminal silyl ketene acetal, forming cyclic β-keto esters, which can be detected by UV spectroscopy at 305 nm (Scheme 2).



Scheme 2. Back-biting reaction (R^1 = H or Me).

Analysis by SEC with an UV detector at 305 nm did not show any absorption which would indicate the presence of such cyclic β-keto ester end-groups. This reflects the living character of the carbene-assisted GTP of MMA in toluene, and represents a major step forward, as no anionic system had allowed the polymerization under living conditions for this monomer at room temperature in an apolar solvent.[20] The slightly broadened distribution of molar masses merely mirrors the slow exchange of carbene between the silyl ketene acetal-ended growing chains compared to the faster rate of propagation. In addition, PMMAs produced in toluene exhibited a slightly higher syndiotacticity (70 %) than samples obtained in THF (63 %).[21]

The success at controlling the GTP of MMA with NHCs as catalysts prompted us to address the polymerization of acrylates under similar conditions, and challenge the widely held view that nucleophile-catalyzed GTP of acrylates is generally uncontrolled, which the exception of the very peculiar case of the system based on HgI_2/Me_3SiI.[22,23] Lewis base catalysed GTP of acrylates is indeed prone to termination reactions that occur through internal isomerization (Scheme 3), which is seldom discussed in the literature. The consequence is the broadening of the molar mass distribution owing to a loss of living chain ends. In addition, growing polyacrylate chains, like their polymethacrylate homologues, are also liable to back-biting reactions which cause the formation of enolized cyclic β-keto ester endgroups observed at 260 nm by UV spectroscopy (Scheme 2).[23]



Scheme 3. C–O isomerization during GTP of acrylates.

If carried out in THF in the presence of NHC (**1** or **2**), the GTP of *tert*-butyl acrylate (tBA) was complete within less than one hour and afforded poly(tBA) samples with excellent control of molar mass (Table 1, entries 8 to 11, and Figure 1 b) and sharp distributions.

The absence of any tail in the low molar mass domain, and the totally flat signal released by the UV detector set at 260 nm, attest to the truly living character of the NHC-assisted GTP of tBA: the samples produced under these conditions were thus free of cyclic β-keto ester endgroups that are due to backbiting and unaffected by the internal isomerization mentioned above. Similar results were obtained with toluene as solvent, although longer reaction times were required (Table 1, entries 13 to 15, and Figure 1 b) owing to a slower rate of propagation. As in the case of MMA, using the less nucleophilic NHC **1** gave poly(tBA)s with a broader dispersity, both in THF and toluene (Table 1, entries 12 and 16). These findings demonstrate the uniqueness of NHCs in their capacity as nucleophilic catalysts to control the GTP of alkyl acrylates in either polar or apolar media.

Our next target was the synthesis of block copolymers by sequential GTP of the two monomers. To this end, MMA was polymerized in THF, followed by polymerization of tBA. The poly(MMA)-*b*-poly(tBA) diblock obtained then served as precursor for the synthesis of a poly(MMA)-*b*-poly(tBA)-*b*-poly(MMA) triblock copolymer (Table 1, entries 17 to 19, Figure 2). In both chain-extension cases, the SEC traces exhibit a clear shift towards the high molar mass domain, indicative of an efficient crossover. Furthermore, copolymer-

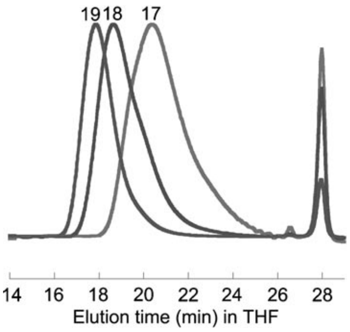


Figure 2. SEC analysis of the poly(MMA)-*b*-poly(*t*BuA)-*b*-poly(MMA) block copolymer (see Table 1 for numbering).

ization could be achieved indifferently starting from living poly(MMA)- or living poly(tBA) chain ends. A poly(MMA)-*b*-poly(tBA) diblock copolymer could also be readily derived in toluene by sequential GTP (Table 1, entries 20 and 21), which opens up access to *all*-(meth)acrylic block copolymers with microstructures that can only be obtained in apolar media.

In summary, we have established that carbenes are silicophilic enough to readily activate silyl ketene acetals and bring about the living GTP of (meth)acrylic monomers at room temperature in polar or apolar medium. Poly((meth)acrylate)s of dispersities <1.3 and molar masses matching the [monomer]/[silylketene acetal] ratio can be derived in quantitative yields. NHCs **1** and **2**, however, seem to be less silicophilic catalysts than regular anionic ones, such as bifluorides that strongly binds to Si–O. We are currently uncovering the mechanism of these NHC-induced GTPs and the implication to the stereochemistry of the polymerization process and the properties of the corresponding materials.

Experimental Section

All the experiments were performed under an inert atmosphere using standard Schlenk techniques. Dry, oxygen-free solvents and monomers were employed. THF was distilled over Na/benzophenone and toluene over polystyryllithium prior to use. Monomers (MMA and tBA) were purified by distillation over CaH_2. NHCs were prepared by slightly modifying already reported procedures:[15] the di-*tert*-butylimidazolium salt was deprotonated with *n*BuLi and the diisopropylimidazolium salt with NaH and a catalytic amount of *t*BuOK. NHCs **1** and **2** were purified by sublimation and by distillation under vacuum, respectively. Solutions of these catalysts were kept in a glove-box under an argon atmosphere. Size-exclusion chromatography was performed using a three-column set of TSK gel TOSOH (G4000, G3000, G2000) calibrated using polystyrene (PS) standards, with THF as eluent and trichlorobenzene as a flow marker. In a typical polymerization, the appropriate amount of NHC and MTS were introduced by syringe in a vacuumed flame-dried Schlenk in a glove-box; for example, 1 mL of a 5×10^{-3} M solution of **2** and 100 μL of MTS (5×10^{-4} mol). After removal of the Schlenk tube from the glove box, 20 mL of THF (or toluene) were added under vacuum. After homogenization, 5.3 mL (5×10^{-2} mol) of MMA or 5.8 mL of *t*BuA (4×10^{-2} mol) were introduced dropwise over 15 min and 1 min, respectively. Molecular characteristics of the polymers are provided in Table 1.

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