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ARTICLE

Group Transfer Polymerization of (Meth)acrylic Monomers Catalyzed by *N*-Heterocyclic Carbenes and Synthesis of All Acrylic Block Copolymers: Evidence for an Associative Mechanism

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ABSTRACT: *N*-Heterocyclic carbenes (NHCs), namely, 1,3-bis-(diisopropyl)imidazol-2-ylidene (**1**) and 1,3-bis(di-*tert*-butyl)imidazol-2-ylidene (**2**) were employed as neutral organocatalysts to bring about the group transfer polymerization (GTP) of both methacrylic and acrylic monomers, including methyl methacrylate (MMA), *tert*-butylacrylate (*t*BA), and *n*-butylacrylate (nBA). This could be achieved at room temperature using 1-methoxy-2-methyl-1-trimethylsiloxypropene (MTS) as initiator in polar or apolar medium. In this way, polymethacrylates and polyacrylates with molar masses in the range 10 000−300 000 g·mol^{-1}, corresponding to the initial [monomer]/[MTS] ratio and with polydispersities lower than 1.2, were obtained in quantitative yields. The kinetics of GTP of MMA catalyzed by **1** or **2** was further investigated. Though the first-order kinetic plot $\ln[M]_0/[M]$ versus time deviated from linearity at high monomer conversion, no inhibition period was noted at low monomer conversion. Moreover, the polymerization rate dramatically increased as the concentration of initiator increased, with first-order dependence in initiator. When mixed in 1/1 molar ratio, MTS and NHC **1** did not reveal the formation of enolate-type species by ^{29}Si or ^{13}C NMR spectroscopy. Based on these observations, we propose that NHCs activate the silyl ketene acetal initiator and further propagate GTP *via* an associative mechanism. The fact that $\ln[M]_0/[M]$ does not evolve linearly with time in the terminal phase of the polymerization can be understood by a reduced diffusion of the catalyst to the trimethylsilyl end groups. The proposed associative mechanism can also account for the successful control of NHC-catalyzed GTP of acrylates during which termination reactions such as backbiting or internal isomerization could be drastically minimized. Next, was described the synthesis of all acrylic block copolymers based on polyacrylates and polymethacrylates (e.g., PMMA-*b*-PnBA-*b*-PMMA), utilizing the same NHC as catalyst in sequential GTP. It is again argued that such block copolymer formation is favored by an associative mechanism forming highly unstable activated silicon intermediates.

Introduction

Very recently, both our group[1,2] and that of Hedrick and Waymouth et al.[3] demonstrated that *N*-heterocyclic carbenes (NHCs) can advantageously serve to activate silylketene acetals as initiators and propagate (meth)acrylic monomers through a mechanism referred to as group transfer polymerization, known as GTP. This polymerization method was developed in the mid-1980s by researchers at DuPont;[4−7] it enables the polymerization of acrylics and methacrylics at ambient temperatures and above with excellent control over molar masses and polydispersities. GTP is also a synthetic method of choice to complex architectures, including star-like or homogeneous gels based on polymethacrylates.[8−10] GTP of methacrylic monomers involves the addition of the silyl ketene acetal initiator to an incoming monomer molecule and the concomitant transfer of the trimethylsilyl group to chain end (Scheme 1),[2−5] through repeated Mukaiyama-Michael-type reactions.[4,6,11] A catalyst is thus required for GTP to proceed. Anions such as bifluoride (HF_2^-), fluoride (F^-), difluoride (F_2^{2-}), cyanide (CN^-), azide,[5,7] oxyanions, or bioxyanions[12] perform best for methacrylic monomers in polar solvents such as tetrahydrofuran (THF). Such anionic catalysts are used at very low concentration (1−5 mol % relative to the initiator) and are associated with bulky metal-free countercations, such as $[(CH_3)_3N]_3S^+$ or $(n\text{-}C_4H_9)_4N^+$ in order to prevent the growing enolates from undergoing intramolecular termination by backbiting. In contrast, Lewis acids such as AlR_2Cl or $ZnCl_2$ and apolar media (e.g., toluene) are most suitable for acrylic monomers. In the latter case, the resort to large amounts of Lewis acid (approximately 10 mol % relative to the monomer concentration) suggested the prevalence of the so-called activated monomer mechanism.[13] The lack of a unique catalyst that could be used for both classes of monomers soon appeared as a weakness of GTP; the synthesis of large size all-(meth)acrylate di- and triblock copolymers by sequential GTP made of both methacrylic and acrylic monomer units is indeed not straightforward. Thus, GTP did not meet all of the initial expectations, and the industrial outcome of this discovery was limited to the production of star-shaped poly(methacrylate)s for pigment dispersing applications in automotive paints or block copolymeric dispersing agents for jet printer ink.

In the past decade, NHCs have been promoted as highly efficient organic catalysts for miscellaneous reactions of molecular chemistry.[14−18] Their potential in organocatalyzed polymerization reactions has also been exploited mostly for chain growth processes, which include ring-opening polymerization (ROP) of cyclic esters,[19−21] cyclosiloxanes[22] and ethylene oxide[23,24] and GTP of (meth)acrylic monomers.[1−3] In particular, the efficiency of NHCs at catalyzing GTP is due to their

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silicophilicity and their ability to activate silyl ketene acetal groups, an experimental fact that is well-documented in molecular chemistry.[22,25−28] A question of importance then concerns the extent of interaction between $SiMe_3$ groups and NHCs: Do they form activated siliconate intermediates and favor chain propagation by an associative mechanism or do they generate true imidazolium enolates that propagate by a dissociative mechanism? Whether one or the other mechanism prevails has dramatic implications on the stereochemistry of the polymerization and on the tacticity of the corresponding poly(meth)acrylates.[29] There has been a heated debate in the 1980−1990s about the genuine mechanism of GTP.[4,6,7,29−32] Strong anions such as HF_2^- have been demonstrated to generate ionic enolates when reacted with silyl ketene acetals,[32] whereas weak bases such as benzoates give rise to pentacoordinated silicon intermediates (Scheme 1).[12] Muller produced a comprehensive literature based on kinetic modeling to account for the mechanism of GTP induced by different catalysts.[31]

In our previous work, we postulated that NHCs **1** and **2** (Figure 1) would be prone to an associative mechanism in GTP of methyl methacrylate (MMA).[2] In a subsequent study, Hedrick, Waymouth et al. argued in favor of a dissociative mechanism in the light of kinetic data generated while investigating the GTP of MMA catalyzed by NHC **3** (Figure 1).[3] In this contribution, we bring experimental facts in favor of the associative mechanism on the basis of a thorough investigation into the kinetics of GTP catalyzed by **1** or **2**. In particular, we observed that the kinetics of polymerization is first-order dependent on methyl trimethylsilyl-ketene acetal (MTS) as initiator. We also investigated model reactions involving initiator and NHC in a 1/1 molar ratio to gain an insight into the possible active species responsible for NHC-catalyzed GTP. Finally, *n*-butylacrylate and *tert*-butyl acrylate were polymerized by NHC-catalyzed GTP and "all acrylic" block copolymers made of polymethacrylate and polyacrylate were synthesized. These results are discussed in the light of the existence of the two possible mechanisms.

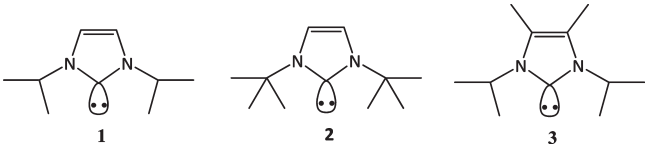


Figure 1. *N*-Heterocyclic Carbenes **1** and **2** previously used by us[2] and in the present work and NHC **3** used by Hedrick, Waymouth et al.[3]

Experimental Section

Materials. Methyl methacrylate (MMA) (Aldrich, ≥99%) was distilled from CaH_2 into a buret. Methyl trimethylsilyl-dimethylketene acetal (MTS) (Aldrich, ≥ 95%) was distilled from CaH_2 and stored in a buret. The other monomers, i.e., *n*-butylacrylate (nBA) (Aldrich, ≥ 99%) and *tert*-butyl acrylate (*t*BA) (Aldrich, ≥ 98%), were distilled from CaH_2 and stored in burets at low temperature. Tetrahydrofuran (THF) was purified by distillation from Na/benzophenone and toluene was distilled from polystyryllithium (PS-Li) prior to use. Tris-(dimethylamino)sulfonium bifluorotrimethylsiliconate (TAS-F_2SiMe_3) was purchased from Aldrich (technical grade) and used as received. NHCs **1** and **2** were prepared by slightly modifying already reported procedures:[33] the diisopropylimidazolium salt (purity ≥97%, assessed by NMR) was deprotonated with NaH and a catalytic amount of tBuOK and the di-*tert*-butylimidazolium salt (purity ≥98%, assessed by NMR) with nBu-Li. NHC **1** was purified by distillation under vacuum whereas NHC **2** was obtained pure by sublimation under vacuum. Solutions of these catalysts were kept in a glovebox under an argon atmosphere.

Instrumentation. ^1H NMR (400 MHz) spectra were recorded on Bruker AC-400 spectrometer in appropriate deuterated solvents. Molar masses were determined by size exclusion chromatography (SEC) that was performed using a three-column set of TSK gel TOSOH (G4000, G3000, G2000 with pore sizes of 20, 75, and 200 Å respectively, connected in series) calibrated with polystyrene standards with THF as eluent (1 mL/min) and trichlorobenzene as a flow marker at 25 °C, using both refractometric and UV detectors (Varian).

Equimolar Model (1:1) Experiments. One to one experiments were conducted in NMR Young tubes to ensure inert atmosphere along the whole measurement. The NMR Young tubes were filled inside the argon atmosphere of the glovebox. NHCs were used pure and directly weighed in the tube and the

Scheme 1. Putative Mechanisms for *N*-Heterocyclic Carbene-Catalyzed Group Transfer Polymerization

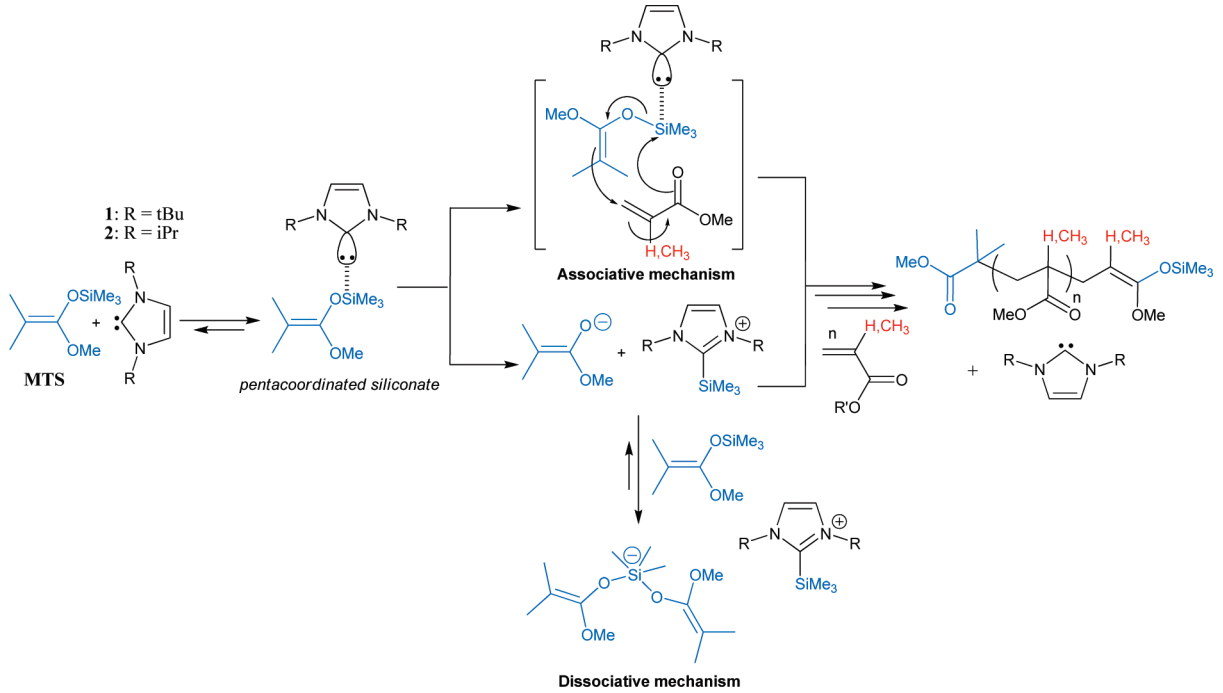


Table 1. Group Transfer Polymerization of Methyl Methacrylate (MMA) Catalyzed by *N*-Heterocyclic Carbene (NHC) 1

expt	solvent	[MMA] (M)	[NHC1] (mM)	[MTS] (mM)	time (h)	convn (%)	$M_{n,th}$[a]	$M_{n,exp}$[b]	PDI[b] (M_w/M_n)
1	THF	2	0.3	5	5	95	38000	36000	1.09
2	THF	2	0.3	13	5	100	15400	14000	1.07
3	THF	2	0.3	27	5	100	7400	6700	1.1
4	THF	1	0.3	2	5	90	45000	55000	1.19
5	THF	1.5	0.3	0.5	10	95	285000	330000	1.3
6	THF	2	0.3		24	10	67000	450000	1.6
7	toluene	2	0.3	5	8.3	92	36800	31000	1.3

[a] Theoretical molar masses ($M_{n,th}$) = ([monomer]/[I]) × convn × MMU + MI, where MMU and MI are the molar masses of the monomer unit and the initiator: Methyl (trimethylsilyl)dimethylketene acetal = MTS, and convn is the monomer conversion determined by gravimetry and/or NMR. [b] Experimental molar masses ($M_{n,exp}$) and polydispersities obtained by size exclusion chromatography (SEC) in tetrahydrofuran (THF) using polystyrene standards for calibration and adjustment with a correction factor obtained using a laser light scattering detector.

appropriate amount of MTS was introduced *via* precision syringes to give 1:1 molar ratios. THF-d_8 was distilled over Na and added *via* a syringe. In a typical experiment, 75 mg of NHC **1** (5×10^{-4} mol) were introduced in a preliminarily flame-dried NMR Young tube, followed by 100 μL of MTS (5×10^{-4} mol) and ~0.4 mL of THF-d_8.

GTP of Methyl Methacrylate. All polymerization were carried out under a dry and inert (argon) atmosphere using Schlenk equipments. In a typical polymerization (entry 2, Table 1), 0.1 mL of a 10^{-1} M solution of NHC **1** (10^{-5} mol or 1.52 mg giving a final concentration of 3×10^{-4} M) and 100 μL of MTS (5×10^{-4} mol giving a final concentration of 13 mM) were introduced via a syringe in a flame-dried special Schlenk apparatus equipped with a withdrawal vial on the side of the main flask, kept in a glovebox under an argon atmosphere. The Schlenk flask was removed from the glovebox prior to the polymerization and 30 mL of dry THF were added under vacuum. After homogenization, 8 mL (7.5×10^{-2} mol) of MMA were introduced at room temperature (thermostatted bath at 25 °C). The addition proceeded discontinuously dropwise over a period of 5 min. After first droplets were added, the color turned pink and then red-orange. At precise time intervals, aliquots were withdrawn using the vacuum flame-dried vial. A droplet of degassed MeOH was then introduced; the reaction mixture in the vial turned colorless instantaneously and the aliquot was removed from the withdrawal vial attached to the flask. The exact volume was provided by transferring it to a small tarred container with a precise syringe. Monomer conversions were determined by ^{1}H NMR spectroscopy as illustrated in Figure 2, by monitoring the disappearance of the vinylic protons of the monomer at 6.05 and 5.5 ppm and the appearance of the peaks at 1.21, 1.02, and 0.84 ppm due to the resonance of the lateral methyl groups of the monomer units. Monomer conversion was double-checked by gravity. Molecular characteristics of all NHC-derived PMMAs are provided in Table 1.

GTP of *n*-Butylacrylate and of *tert*-Butylacrylate. The polymerization procedure is similar to that described above for the synthesis of PMMA, without withdrawal for kinetic purposes. In a typical polymerization (entry 8, Table 2), 50 μL of a 10^{-1} M solution of NHC **2** (0.5×10^{-5} mol or 0.9 mg giving a final concentration of 1.5×10^{-2} M) and 100 μL of MTS (5×10^{-4} mol giving a final concentration of 1.4×10^{-4} M) were introduced via a syringe in a vacuumed flame-dried Schlenk kept in a glovebox under an argon atmosphere. After the Schlenk flask was removed from the glovebox, 30 mL of dry THF were added under vacuum. Then 6 mL (4.2×10^{-2} mol) of nBA were added dropwise at room temperature and the reaction mixture was left for vigorous stirring for a couple of hours. A droplet of degassed MeOH was introduced after completion of the polymerization. Molecular characteristics of all NHC-derived PnBAs and PtBAs are provided in Table 2.

Synthesis of Block Copolymers by Sequential GTP. In a typical polymerization experiment (entry 15, Table 3), 30 μL of a 10^{-1} M solution of NHC **2** (0.3×10^{-5} mol or 0.54 mg, that is, a final concentration of 1×10^{-4} M) and 50 μL of MTS (2.5 10^{-4} mol corresponding to a concentration of 7×10^{-3} M) were

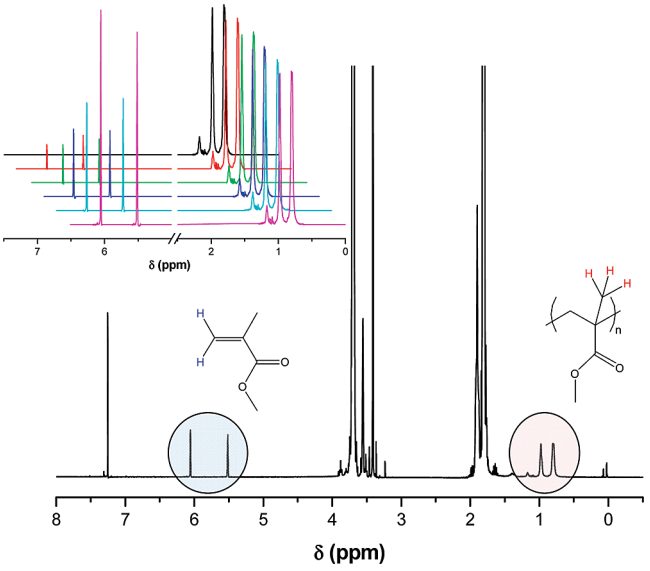


Figure 2. Monitoring of monomer conversion by ^{1}H NMR spectroscopy during group transfer polymerization of methyl methacrylate catalyzed by the *N*-heterocyclic carbene **1** (see also Figure 1 and Experimental Section).

introduced via a syringe in a vacuumed flame-dried Schlenk kept in a glovebox under an argon atmosphere. After removing the Schlenk from the glovebox prior to the polymerization, 30 mL of dry THF were added under vacuum, then 5 mL (4.7×10^{-2} mol) of MMA were introduced at room temperature dropwise. An aliquot was withdrawn after one night of reaction and deactivated by a droplet of degassed MeOH, which was introduced and analyzed to check the completion of the reaction. Onto the living PMMA were slowly added 30 mL of dry THF and 17 mL (0.12 mol) of nBA. An aliquot was withdrawn after one night of reaction for characterization purposes. Onto the living PMMA-*b*-PnBA was slowly added 5 mL (4.7×10^{-2} mol) of MMA. After 24 h of additional reaction, a droplet of degassed MeOH was introduced to terminate the reaction. Molecular characteristics of all NHC-derived block copolymers are provided in Table 3, and SEC traces (RI detector) are shown in Figure 6.

Results and Discussion

1. GTP of Methyl Methacrylate. GTPs of MMA were triggered in the presence of either NHC **1** and **2**, namely, 1, 3-bis-(diisopropyl)imidazol-2-ylidene and 1,3-bis-(di-*tert*-butyl)imidazol-2-ylidene, respectively. As already discussed in our previous works,[2,24] these two catalysts were selected for their relative ease of synthesis and purification by distillation or by sublimation, affording catalysts free of any metallic residues. When using 1-methoxy-2-methyl-1-trimethylsiloxypropene (MTS) as initiator, both NHCs **1** and

Table 2. Group Transfer Polymerization of *tert*-Butyl Acrylate and *n*-Butyl Acrylate Catalyzed by *N*-Heterocyclic Carbenes (NHCs)

expt	solvent	monomer	NHC	[NHC]/[MTS]/[M]	time (h)	convn (%)	$M_{n,th}$[a]	$M_{n,exp}$[b]	PDI[b] (M_w/M_n)
8	THF	tBA	1	0.01/1/80	1	100	10200	12800	1.15
9	THF	tBA	1	0.1/−/80	24	40	41000	230000	2.1
10	THF	nBA	1	0.01/1/80	1	100	10200	9000	1.6
11	THF	nBA	2	0.01/1/80	1	100	10200	11900	1.4
12	THF	nBA	2	0.01/1/200	1	95	24400	27300	1.4
13	THF	nBA	2	0.1/−/80	24	55	56000	150000	2.3
14	toluene	tBA	1	0.01/1/100	3	100	25600	22200	1.19
15	toluene	nBA	1	0.01/1/100	2	100	25600	19700	1.6
16	toluene	nBA	2	0.01/1/100	2	100	25600	21400	1.5

[a] Theoretical molar masses ($M_{n,th}$) = ([monomer]/[I]) × convn × MMU + MI, where MMU and MI are the molar masses of the monomer unit and the initiator: Methyl (trimethylsilyl)dimethylketene acetal = MTS, and convn is the monomer conversion determined by gravimetry and/or NMR. [b] Experimental molar masses ($M_{n,exp}$) and polydispersities obtained by size exclusion chromatography (SEC) in tetrahydrofuran (THF) using polystyrene standards for calibration and adjustment with a PMMA/PS correction factor obtained using a laser light scattering detector.

Table 3. Sequential Group Transfer Polymerization Catalyzed by *N*-Heterocyclic Carbenes (NHCs) for the Synthesis of All Acrylic Block Copolymers

expt	solvent	block-copolymers	NHC	[NHC]/[MTS]/[M]	time (h)	$M_{n,th}$[a]	$M_{n,exp}$[b]	PDI[b] (M_w/M_n)
17	THF	PMMA-*b*-PtBA-*b*-PMMA	1	0.01/1/30	16	3000	2900	1.25
				0.01/1/30	24[c]	6800	6500	1.35
				0.01/1/60	48[c]	12800	12600	1.4
18	THF	PMMA-*b*-PnBA	2	0.01/1/50	16	5000	4800	1.17
				0.01/1/100	40[c]	17800	16000	1.5
19	THF	PMMA-*b*-PnBA-*b*-PMMA	2	0.01/1/200	16	20000	23100	1.08
				0.01/1/500	24[c]	84000	72000	1.5
				0.01/1/200	48[c]	104000	130000	1.6
20	toluene	PMMA-*b*-PtBA	1	0.05/1/100	16	10000	10900	1.3
				0.05/1/80	40[c]	20200	21900	1.3
21	toluene	PMMA-*b*-PnBA	2	0.05/1/100	16	10000	11600	1.3
				0.05/1/80	40[c]	20200	18200	1.6

[a] Theoretical molar masses ($M_{n,th}$) = ([monomer]/[I]) × convn × MMU + MI, where MMU and MI are the molar masses of the monomer unit and the (macro)initiator: Methyl (trimethylsilyl-)dimethylketene acetal (MTS) or polymer precursor respectively, and conv. is the monomer conversion determined by gravimetry. [b] Experimental molar masses ($M_{n,exp}$) and polydispersities obtained by size exclusion chromatography (SEC) in tetrahydrofuran (THF) using polystyrene standards for calibration and adjustment with a PMMA/PS correction factor obtained by obtained using a laser light scattering detector. [c] Cumulated time of the experiment.

2 catalyze the GTP of MMA in THF at room temperature, leading to PMMAs with controlled molar masses from 10 000 g·mol^{-1} to 300 000 g·mol^{-1} and polydispersities lower than 1.3 (Table 1). It is worth pointing out that in all these experiments, MMA was slowly added dropwise into the solution containing both the NHC catalyst and the MTS initiator (starved conditions, see Experimental Section). Importantly, polymerizations could also be performed in an apolar solvent such as toluene.

The polymerization kinetics of MMA was then investigated in THF under very similar conditions to those described by Hedrick, Waymouth et al.[3] who used, however, **3**, a NHC of slightly different structure from ours (Figure 1). In particular, the [MMA]/[MTS] molar ratio was varied to determine the kinetic order in initiator. These experiments were performed in a specifically designed device that allowed us to withdraw aliquots at different intervals to determine both the monomer conversion and molar masses by ^{1}H NMR and SEC, respectively, at various stages of the polymerization. Figure 2 shows a typical ^{1}H NMR spectrum of a GTP-derived PMMA obtained in the presence of NHC **1**, whereas Figure 3 indicates that these PMMAs exhibit symmetrical SEC traces, even at low monomer conversion.

From these data, the kinetic variation of $\ln[M]_0/[M]$ versus time could be plotted, assuming a first-order in monomer. The results are summarized in Figures 4 and 5 where are also represented the data reported by Hedrick, Waymouth et al.[3] In our case, the first-order kinetic plots for NHC **1**-catalyzed GTPs of MMA evolves linearly in the initial phase then deviates from linearity at higher monomer conversions. The results reported by Hedrick, Waymouth et al. showed in contrast an induction period due to a slow initiation with NHC **3** as catalyst.[3] The most significant difference between their observations and ours concerns the dependence of the GTP rate on the concentration of MTS initiator. Figure 4 clearly shows that the polymerization rate increases upon increasing the concentration of initiator. From a technical point of view, it was difficult to take more aliquots and thus obtain more data points especially at the early stage of the polymerization. Indeed, the device that was designed to monitor the kinetics of GTP has to be properly washed between two aliquots to ensure that no deactivation of the active chain ends occurred. The initial slopes of the pseudo-first order kinetic plot thus correspond to the apparent initial rate constants, denoted as k^0_{app}. It has to be acknowledged, however, that there is possible error associated with this determination of the rate constants. The evolution of k^0_{app} versus [MTS] indicates a linear evolution (Figure 5), confirming a first order dependence on initiator for the GTP of MMA catalyzed by NHC **1** (Figure 4).

The direct dependence on initiator observed in our case supports the associative mechanism (Scheme 1), in agreement with theoretical arguments established by Muller and co-workers in the 1990s.[30,31,34−39] When the rate of polymerization is inversely dependent on the concentration on initiator, as observed by Hedrick, Waymouth et al.,[3] the active species responsible for the polymerization are enolates. The latter anionic species can indeed further react with one equivalent of silyl ketene acetal groups and generate bis(enolato)siliconates (Scheme 1). As a matter of fact, the polymerization rate decreases upon increasing the concentration in MTS. The induction period—which is not observed in our case—can be explained by the trapping of

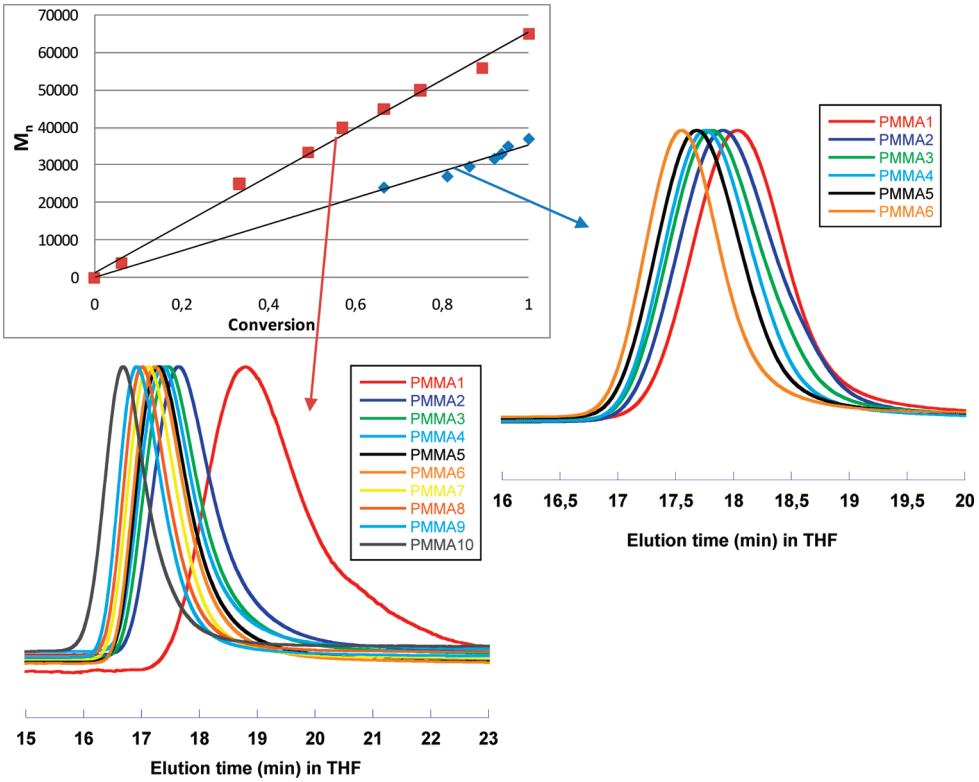


Figure 3. Evolution of molar masses with monomer conversion and corresponding size exclusion chromatography traces during group transfer polymerization of methyl methacrylate catalyzed by the *N*-heterocyclic carbene **1**. (a) Molar masses (M_n) vs conversion from experiments 1 and 4 completed by total conversions in both cases taken after several days. (b SEC traces (RI detector) of PMMAs from kinetic withdrawals of experiment 1 (Table 1). (c) SEC traces (RI detector) of PMMAs from kinetic withdrawals of experiment 4 (Table 1) and an additional withdrawal just before chain extension.

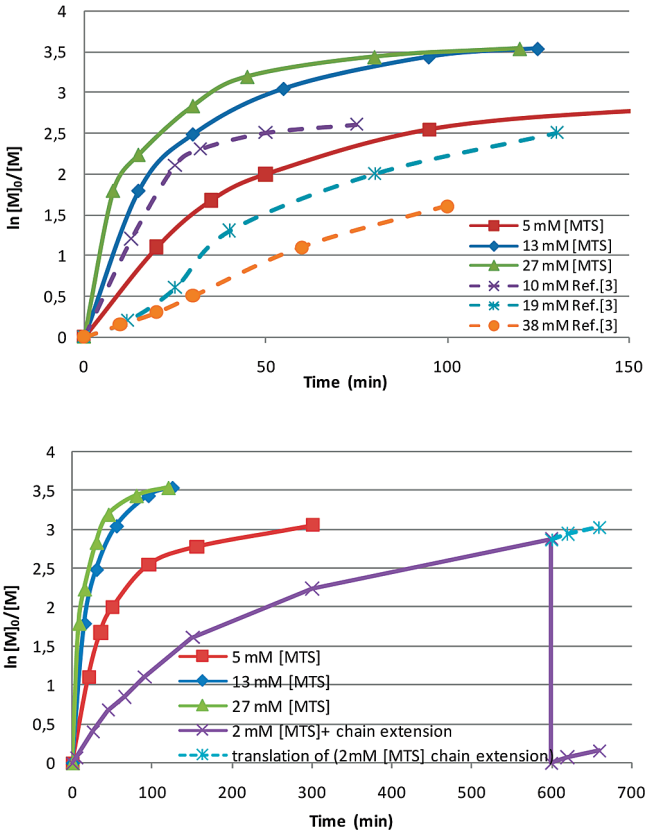


Figure 4. Evolution of the k_{app} vs time as a function of the concentration of initiator ([MTS]) and comparison with ref 3 during *N*-heterocyclic carbene-catalyzed group transfer polymerization of methyl methacrylate.

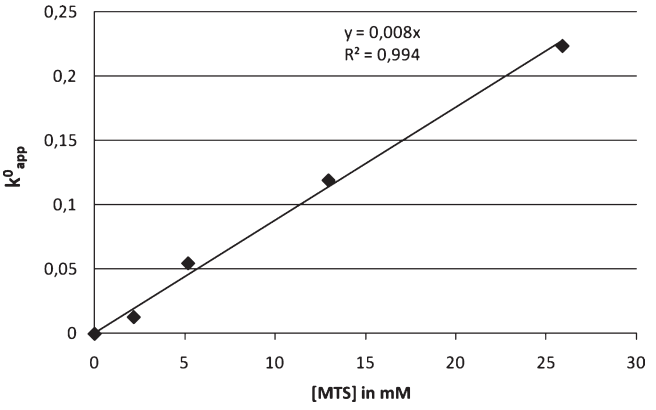


Figure 5. Evolution of initial apparent constant (k^0_{app}) (min^{-1}) vs the concentration of initiator ([MTS]) during group transfer polymerization (GTP) of methyl methacrylate (MMA) catalyzed by *N*-heterocyclic carbene **1**.

propagating enolates by MTS and the reversible formation of dormant bis(enolato)siliconates.

The evolution of PMMA molar masses and polydispersity as a function of MMA conversion is consistent with a controlled/living GTP (Figure 3).[30,31,38,39] Indeed, experimental molar masses correspond closely to the initial [MMA]/[MTS] ratio from the early stage of the polymerization and PDI values are lower than 1.3.

GTPs of MMA induced by NHC could also be achieved in toluene.[2] As shown in Figure 6, the kinetics is slower in this apolar solvent compared to THF; however, good control over molar mass and polydispersity is again observed though the molar mass distribution is somewhat broader, indicative

of a slow exchange between active and dormant chain-ends (Table 1, entry 5).

As mentioned above, the first-order kinetic plots in Figure 4 deviate from linearity at high MMA conversion, which is not expected from a reportedly controlled/living polymerization process. This intriguing behavior which has been previously observed by others[3] is to be commented on. It can be hypothesized that the diffusion of the catalyst and its access to the $SiMe_3$ carried by polymer chain ends are reduced as the molar mass of PMMA increases, due to the viscosity of the medium. We indeed noticed a build-up in viscosity at high conversion whenever high molar masses were targeted. It has to be reminded that catalyst loadings are very low (1−5% mol. relative to the initiator and thus to the polymer chain ends). The fact that the rate of catalyst diffusion decreases with the increase of the polymer chain length affects the overall rate of polymerization. The nature of the catalyst also plays a role in the kinetic behavior. For instance, NHC **1** proved more efficient than **2** in GTP of MMA,[2] presumably due to its higher silicophilicity as compared to **2**. In spite of the rate breakdown with monomer conversion, GTP retains its controlled/living character. Indeed, a seven-day aged solution of living PMMA (M_n = 55 000 g·mol^{-1}; PDI = 1.19, entry 4, Table 1) grown by NHC **1**-catalyzed GTP was subjected to chain extension via fresh monomer addition, which resulted in an extended PMMA of M_n = 102 000 g·mol^{-1} and PDI of 1.2.

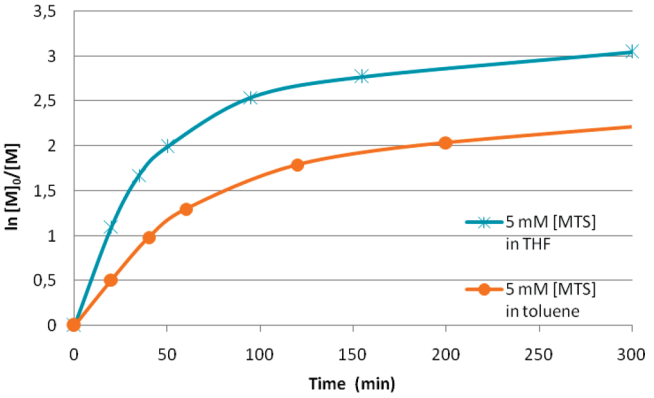
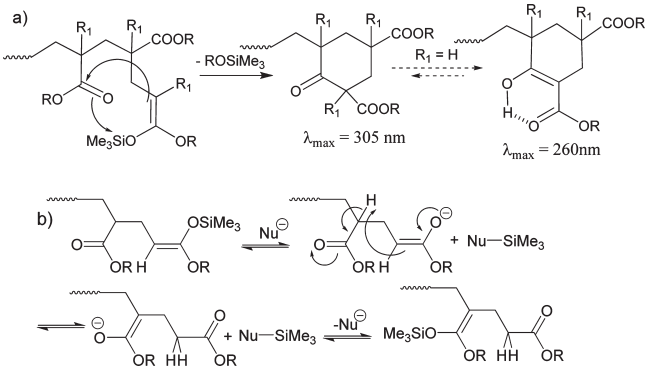


Figure 6. Differences of $k_{app}(\ln\{[M]_0/[M]\})$ vs time between tetrahydrofuran and toluene as solvents during group transfer polymerization of methyl methacrylate catalyzed by *N*-heterocyclic carbene **1**.

Scheme 2. Possible Side Reactions Encountered in Group Transfer Polymerization: (a) backbiting; (b) C−O isomerization

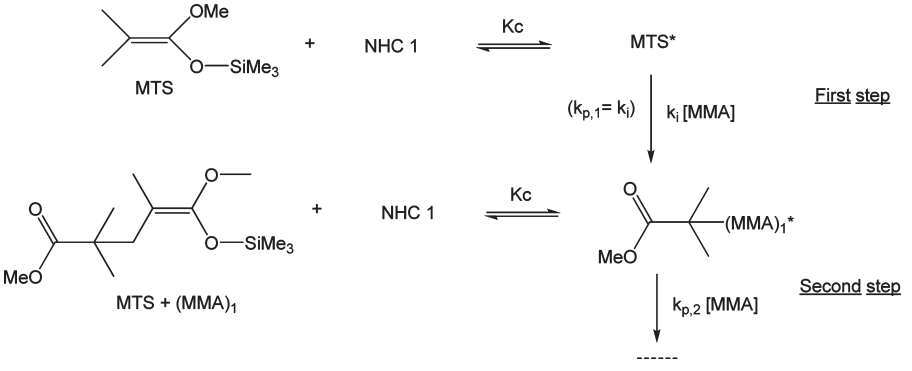


Based on all these observations, we postulate that NHCs **1** and **2** activate silyl ketene acetal moieties in a first instance before catalyzing the GTP of MMA by an associative mechanism, which involves the formation of activated silicon intermediates and the concerted insertion of upcoming monomers (Scheme 1). This is followed by group transfer of the $SiMe_3$ groups onto the new monomer unit to generate new associated active chain-ends. Noteworthy, the aforementioned intermediates consist of bulky activated imidazolium siliconates which prevent—or at least minimize to a large extent—backbiting termination reactions (Scheme 2) from occurring. Related activated (hypervalent) siliconate intermediates have been thoroughly investigated in the past literature in inorganic molecular chemistry.[40−42]

Another clue in favor of the associative mechanism is the living/controlled character exhibited by the polymerization when initiated by adducts formed by reaction of NHC and MTS in a 1/1 molar ratio (see section 4). The polymerization went to completion affording PMMAs with controlled molar masses and relatively low polydispersities (M_n = 31 000 g·mol^{-1}, PDI = 1.35 and 27 000 g·mol^{-1}, PDI = 1.4 for NHC **1** and **2**, respectively, the theoretical M_n value being 33 000 g·mol^{-1}). A 1/1 of MTS/NHC **2** adduct kept for several months in a NMR tube was even able to bring about a controlled polymerization of MMA (M_n = 21 300 g/mol and PDI = 1.5 for a targeted M_n value of 25 000 g/mol). These results again substantiate the proposed associative mechanism. Should the dissociative mechanism occur, such a high load in NHC would have quantitatively transform MTS into enolate-type active species whose tendency to undergo backbiting reactions would have rapidly resulted in a loss of control of the polymerization.

A more quantitative treatment of these NHC-catalyzed GTPs can be proposed, as briefly discussed below, though this will be the topic of a forthcoming publication (a detailed investigation would be beyond the scope of the present study). As reported by Muller et al. and Brittain, a kinetic treatment for both initiation and propagation steps of GTP has been developed.[34,35,43] On the basis of a first kinetic order

Scheme 3. Kinetic Model for Initiation of Group Transfer Polymerization Catalyzed by N-Heterocyclic Carbene 1



in MTS of NHC-catalyzed GTP of MMA, Scheme 3 can be used for the initiation step.

In this model, the asterisk indicates the catalyst complex, K_c is the equilibrium constant for the formation of the pentacoordinated silicon, k_i is the rate constant for the first propagation step which is equivalent here to the initiation step, $k_{p,2}$ is the rate constant for the second propagation step.

The propagation rate of the first step can be established as follows:

$$R_{p,1} = -d[MMA]/dt = k_i[MMA][MTS^*]$$

with

$$[MTS^*] = K_c[MTS][NHC]$$

Neglecting the differences between $k_{p,1}$ ($=k_i$) and $k_{p,2}$ (and so on), one can write $k_{p,1} \sim k_{p,2} \ldots = k_p$, where k_p is the propagation rate constant. Thus

$$R_p = k_p K_c[MMA][MTS][NHC]$$

where [MMA] is the monomer concentration at time t, [MTS*] is the concentration of active centers that is equal to the concentration in MTS initiator, and [NHC] is the concentration in carbene **1**.

After integration, one obtains

$$\ln([MMA]_o/[MMA]) = k_{app}t$$

$$k_{app} = k_p K_c[MTS][NHS]$$

where $[MMA]_0$ is the initial monomer concentration and k_{app} is the apparent rate constant of reaction. As mentioned above, we have considered the initial slopes of the pseudo-first order kinetic plots (Figure 4), which correspond to the initial apparent rate constant k^0_{app}. Hence,

$$k_{app}{}^0 = k_p K_L[MTS][NHC]$$

$$k_{app}{}^0 = 0.0088 \times [MTS](L \cdot mmol^{-1} \cdot min^{-1})$$

$$= 0.147 \times [MTS](L \cdot mol^{-1} \cdot s^{-1})$$

With $[NHC] = 0.3 \times 10^{-3}$M, the following value is obtained:

$$k_p K_a \approx 500\ L^2 \cdot mol^{-2} \cdot s^{-1}$$

This value is in between that found for tris-(piperidino)sulfonium (TPS) benzoate and TPS bibenzoate used as catalysts for GTP of MMA, as reported by Brittain.[43] These two catalysts being recognized as favoring an associative pathway, this again supports that NHC **1** follows the same mechanism.

2. GTP of Alkyl Acrylates (*t*BA and nBA). A key advantage of using NHCs is their ability to catalyze the GTP of both alkyl acrylates and methacrylates,[2,3] contrary to catalytic systems initially proposed.[7] In particular, Lewis bases used to catalyze the GTP of alkyl acrylates induce a termination reaction known as the internal isomerization (Scheme 2b), which results in a broadening of the molar mass distribution. In addition, growing polyacrylate chains—like their polymethacrylate homologues—are also prone to backbiting reactions which cause the formation of enolized cyclic β-keto ester end-groups seen at 260 nm by UV analysis (Scheme 2a).[29] In our previous report, we showed that the GTP of *t*BA exhibited a controlled/living character in THF, in the presence of NHC **1** or **2** as catalyst. Here we show that controlled polymerization of nBA can also be achieved, either in THF or in toluene as solvent (Table 2). The latter monomer being much more reactive than *t*BA, the corresponding active PnBA chain-ends should be less reactive than P*t*BA ones; however, it is well-documented that the monomer polymerizability is the driving force in such polymerizations.[29,44] Hence, a better control is expected with the least nucleophilic NHC **2**. It can be indeed verified that **2** affords narrower polydispersities (Table 2, entry 11 versus 10). However, this improved control over molar masses distribution at the expense the polymerization kinetics which is slower. In addition, the SEC traces of samples prepared did not show any signal released by the UV detector set at 260 nm, attesting to the absence of cyclic β-keto ester end-groups that would have formed by backbiting. Similar results were obtained with toluene as solvent, again at the expense of the polymerization rate (entries 15 and 16, Table 2).

These experiments confirm that the associative mechanism is responsible for the successful control of GTP of acrylates when catalyzed by NHC **1** and **2**, which is mirrored in the absence of backbiting or internal isomerization reactions of the pentacoordinate siliconate end groups (Scheme 1). GTP is indeed more prone to such termination reactions when true enolates are the propagating species.[45,46] We are currently investigated other NHCs of various nucleophilicity/silicophilicity to polymerize acrylic monomers of different reactivity via GTP.

3. Synthesis of "All Acrylic" Block Copolymers by Sequential NHC-Catalyzed GTP. As reminded above, anionic catalysts are well-suited for the GTP of methacrylates whereas Lewis acids work best for acrylates. We already reported the synthesis of a PMMA-*b*-P*t*BA-*b*-PMMA triblock copolymer by sequential GTP using NHCs.[2] Figure 7 now shows the formation of a PMMA-*b*-PnBA-*b*-PMMA triblock copolymer, which could serve as a thermoplastic elastomer with its two hard external PMMA blocks and its soft central PnBA block. All block copolymerization results are summarized in Table 3. Interestingly, the aforementioned triblock copolymers could be prepared either in THF or in toluene as solvent of sequential GTP.

Experiments 18, 19, and 21 (Table 3) involve a first step which is the formation of the PMMA-*b*-PnBA diblock copolymers. Their molar mass distributions tend to broaden after the growth of the PnBA block, likely due to a fast rate of nBA addition compared to that of activation of chain ends. However, this does not affect the quality of both the diblock and triblock copolymers formed. It is again argued that the triblock copolymer formation is favored by the associative mechanism. Indeed, had the active species taken the structure of true enolates, the obtainment of PMMA-*b*-PnBA would have been conceivable but that of PnBA-*b*-PMMA more questionable.[29] Indeed, this would not have complied with the reactivity scale of a purely anionic pathway which ranks PnBA living ends lower than PMMA ones in the ladder of reactivity.[29,44] It is worth mentioning that only a few examples of block copolymers made of either all methacrylic or all acrylic monomer units obtained by sequential GTP have been reported.[10,12] In the latter case, oxyanions and bioxyanions catalysts known to induce an associative mechanism were often used.[31] Because of the occurrence of the associative mechanism which forms unstable pentacoordinate silicon intermediates, the synthesis of such all acrylic block copolymers could be achieved, irre-

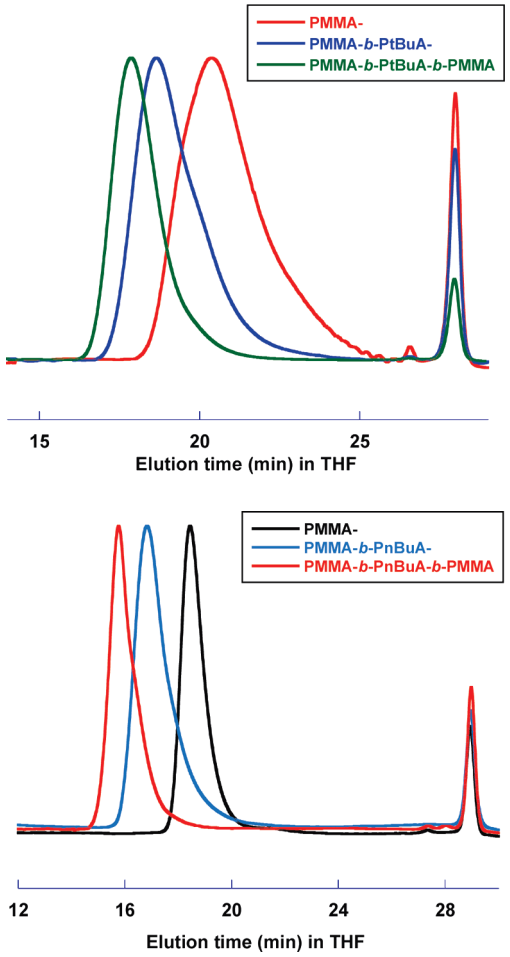


Figure 7. Size exclusion chromatography traces in tetrahydrofuran (THF) (refractometric detector) of triblock copolymers (entries 17 and 19, Table 1).

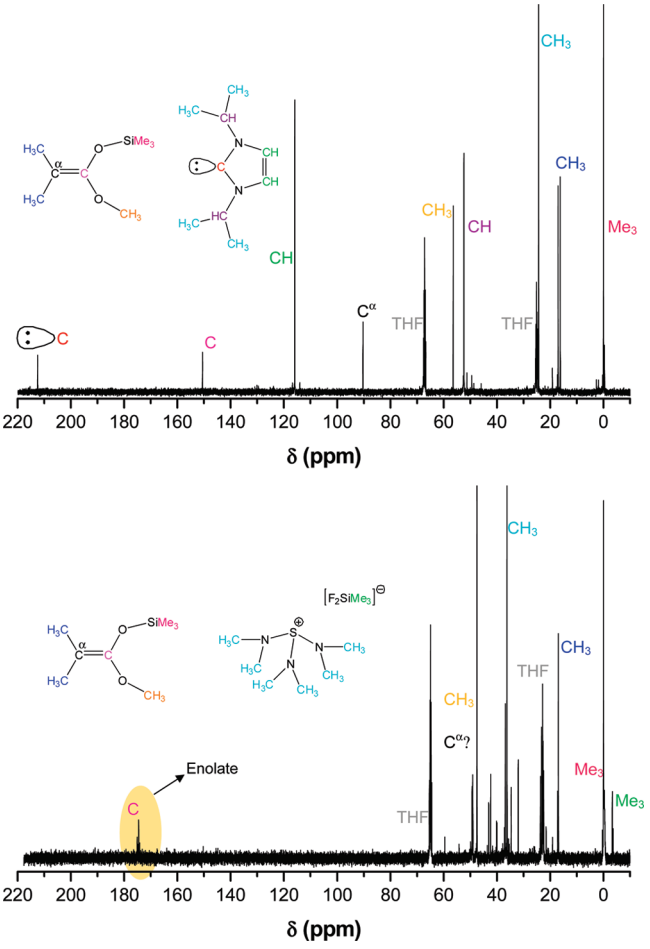
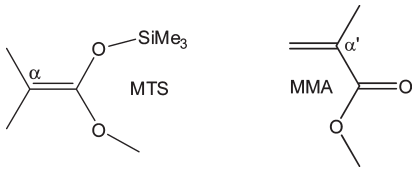


Figure 8. NMR ^{13}C spectra of equimolar model experiments (entries 23, 24 and 25, Table 4).

spective of the order of addition of the two monomers (Figure 8). This important development of NHC-catalyzed GTP opens new avenues for engineering all acrylic block copolymers by this polymerization method.

4. Investigation by NMR into Model Reactions. In these experiments, NHC and MTS were mixed in equimolar amounts in THF-d_8, the reaction being monitored by NMR in order to get a better insight into the product formed or the type of interactions between the two reagents. Tris(trimethylamino)sulfonium bifluorotrimethylsiliconate ($TASF_2SiMe_3$) known to form enolates upon reaction with MTS[31,32,42] was also mixed with the latter reagent for comparison purpose. Data from these experiments are provided in Tables 4 and 5 and are illustrated in Figure 8. A clear difference can be seen from the NMR spectra of the two types of 1/1 adducts. Table 4 indicates that the chemical shift for the peak due to the resonance of (**C**−O) of MTS, δ_{C-O} remains unchanged after addition of NHC **1** ($\delta_{C-O} \approx 151.2$ ppm before and 150.6 ppm after reaction). In contrast, a dramatic shift of this peak to lower fields (($\delta_{C-O} = 174$ ppm) can be observed after addition of $TASF_2SiMe_3$ to MTS. The peak of the carbon atom of MTS bearing the double bond and the two methyl groups, C_α, also shifts to higher fields. In addition, some white precipitate quickly formed at the bottom of the NMR tube in the case of $TASF_2SiMe_3$ unlike that of NHC. These observations are consistent with the formation of enolates that bring about a dissociative mechanism.[30,47−53] The absence of enolates in the case of NHC again supports the formation of activated-silicon intermediates,[40−42,54] as NHC **1** is obviously less silicophilic than $TASF_2SiMe_3$.

Characterization by ^{29}Si NMR confirmed the results obtained by ^{13}C spectroscopy (Table 5).[54] Indeed, addition of NHC to MTS hardly shifted the ^{29}Si signal of the $SiMe_3$ group of MTS to lower fields (from 17 to 19 ppm). This small shift can be ascribed to a weak interaction between the lone pair of electrons of NHC and the silicon atom, consistently with recent calculations.[22,28,55] Through simple room temperature NMR analysis, we could not however identify pentacoordinated silicon atoms whose chemical shifts are expected between −60 and −160 ppm and which are known to be very instable intermediates.[54] When $TASF_2SiMe_3$ was employed instead of NHC **1**, a drastic difference in the chemical shift of the peak due to $SiMe_3$ before and after addition of $TASF_2SiMe_3$ could be seen: an intense peak at −45 ppm appears, which can be attributed to the formation of the bifluorobis(trimethylsilyl) enolate (Scheme 1).



Other GTP experiments could be implemented to support the occurrence of the associative mechanism in particular, the determination of the activation energy and entropy of the

Table 4. ^{13}C NMR Spectroscopy Chemical Shifts in Deuterated Tetrahydrofuran (THF-d_8) of Various Characteristic Adducts or Model Reactions of Group Transfer Polymerization

expt	[A]:[B] = 1:1	δ(**C**−O) (ppm)	δ(**C**α) (ppm)	δ (**C**H$_3$) (ppm)	δ(O−H$_3$) (ppm)	δ(OSi−(**C**H$_3$)$_3$) (ppm)
22	MTS only	151.2	90	17.2; 16.1[a]	56.6	0.25
23	MTS:NHC1	150.6	90.3	17; 15.9[a]	56.6	0
24	MTS:NHC2	150.7	90.5	17.5; 16.3[a]	56.6	0.25
25	MTS:TASF$_2$SiMe$_3$	**174.7**	48[b]	17.3	36[b]	0 and **−3.2**

expt	[A]:[B] = 1:1	δ(**C**−O) (ppm)	δ(**C**α′) (ppm)	δ(**C**β)	δ(**C**H$_3$)	δ(O−H$_3$)
26	MMA only	165.7	135.5	123.2	16.5	49.8
27	MMA:NHC1	**174−188**[c]	precipitation: multiple peaks			
28	MMA:TASF$_2$SiMe$_3$	165.7	135.5	123.2	16.5	49.8

[a] Two different peaks due to slight differences in the chemical environment of the two methyl groups. [b] Multiple peaks probably due to some precipitation. [c] Multiple small peaks.

Table 5. ^{29}Si NMR Spectroscopy Chemical Shifts in Deuterated Tetrahydrofuran (THF-d_8) of Various Products

expt	[A]:[B] = 1:1	δ (O**Si**−(CH$_3$)$_3$) (ppm)	δ (F$_2$**Si**−(**C**H$_3$)$_3^-$) (ppm)
29	MTS only	17.3	
30	MTS:NHC1	19.2	
31	MTS:NHC2	19.1	
32	TASF$_2$SiMe$_3$ only		5.6
33	MTS:TASF$_2$SiMe$_3$	17.6 and **2.1** (broad) precipitation[a]	
34	MTS:TASF$_2$SiMe$_3$	17.6 and **−45.2**	7.2

[a] Some precipitate appeared at the bottom of the tube; after removal of the upper part, the tube was reanalyzed to give the following result.

polymerization by varying the temperature.[56−59] This will be the scope of a subsequent publication.

Concluding Remarks

The group transfer polymerization of (meth)acrylic monomers proceeds via an associative mechanism when catalyzed by *N*-heterocyclic carbenes—**1** and **2**—at room temperature in polar or apolar medium, in the presence of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MTS) as initiator. Several observations support the existence of such an associative mechanism; these include the following:

- The increase of the polymerization rate with the increase of the concentration of initiator with a first-order dependence.
- The absence of enolate-type species upon reacting **1** or **2** with the initiator in model experiments, as evidenced by ^{29}Si and ^{13}C NMR spectroscopy.
- The production of well-defined poly(methyl methacrylate)s using 1/1 adducts of **1** and MTS as initiating system.
- The controlled polymerization of n-butyl and *tert*-butylacryates in the presence of **1** or **2**, which suggests that backbiting and internal isomerization can be minimized, presumably because no enolate is generated.
- The preparation of block copolymers based on acrylate-type and methacrylate-type monomer units, irrespective of the order of addition of the two monomers, which would not be conceivable from pure enolates formed by a dissociative mechanism.

Thus, pentacoordinate siliconates are thought to be the key intermediates in the associative mechanism of GTP catalyzed by NHC **1** or **2**. It is very likely that other NHCs that would be more nucleophilic/silicophilic catalysts than **1** or **2** could bring about the GTP of (meth)acrylics *via* a dissociative pathway. On this basis, we are currently exploring the potential of other carbenes as GTP catalysts, in particular those that could favor stereoselective addition and the formation of syndiotactic polymers. These NHC-catalyzed GTPs open new avenues and should rejuvenate this polymerization method and in its use in macromolecular engineering.

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