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Expanding the Scope of Group Transfer Polymerization Using *N*-Heterocyclic Carbenes as Catalysts: Application to Miscellaneous (Meth)acrylic Monomers and Kinetic Investigations

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ABSTRACT: 1,3-Bis(di-*iso*propyl)imidazol-2-ylidene (**1**) and 1,3-bis(di-*tert*-butyl)imidazol-2-ylidene (**2**), which are *N*-heterocyclic carbenes (NHCs) are shown to catalyze the solution group transfer polymerization (GTP) of miscellaneous monomers in a controlled fashion at room temperature, in the presence of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MTS) as initiator. The ability of seven distinct monomers, methyl methacrylate (MMA), *tert*-butyl acrylate (*t*BA), *n*-butyl acrylate (nBA), *N*,*N*-dimethylaminoethyl acrylate (DMAEA), *N*,*N*-dimethyl acrylamide (DMA), *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA), and methacrylonitrile (MAN) to polymerize via GTP by NHC catalysis has been evaluated. The first-order kinetic plots, that is the evolution of $\ln[M]_0/[M]$ versus time, systematically deviate from linearity, with the noticeable exception of GTP of DMA. A direct dependence of the rate of GTP on the concentration in MTS initiator is observed in the case of *t*BA carried out in THF, that is, the rate of polymerization increases with [MTS], with a first-order dependence on [MTS]. These results suggest the formation of hypervalent siliconate intermediates in NHC-induced GTP of acrylic monomers which proceeds via an associative mechanism. The nonlinear variation of $\ln[M]_0/[M]$ with time in the terminal phase of the polymerization of both acrylates and methacrylates may be explained by the development of strong interactions between the NHC and pendant ester groups of poly(meth)acrylates, limiting the availability of the catalyst for chain end activation. In contrast, interactions between the NHC and amide-type units of poly(DMA) are unlikely, NHCs being not known as effective catalysts for transamidation reactions. A first-order kinetic plot with a linear variation of $\ln[M]_0/[M]$ with time is thus observed for the NHC-catalyzed GTP of DMA.

Introduction

Group transfer polymerization (GTP) finds its roots in molecular chemistry, for it is based on the repetition of a C−C bond forming reaction referred to as the Mukaiyama−Michael reaction[1] and is catalyzed by a Lewis base or a Lewis acid. In the context of GTP, the methacrylic monomer plays the role of the Michael acceptor while the silyl ketene acetal (SKA) serves as the initiator and mimics the dormant polymer chain ends. GTP thus enables the controlled polymerization of methacrylic monomers at ambient temperature and above.[2] Seminal works in the mid-1980s by Webster and co-workers at DuPont[3,4] have opened avenues for an application of GTP to the synthesis of tailor-made metal-free and colorless (co)polymers based on (meth)acrylate monomer units.[3,5−8] For instance, Patrickios et al. have extensively employed GTP as a tool for macromolecular engineering.[9−18] Numerous reports have also been devoted to the search of efficient GTP catalysts and to a comprehensive understanding of the related mechanism(s).[7,19−22] The main drawback of GTP as unveiled by Webster et al., however, was the absence of a unique catalytic system that could be generalized to both acrylic and methacrylic monomers. Anions such as fluoride or bifluoride (HF_2^-), oxyanions or bioxyanions associated with bulky metal-free counter-cations such as sulfoniums $[(CH_3)_3N]_3S^+$ or ammoniums $(n\text{-}C_4H_9)_4N^+$ that prevent backbiting termination reactions perform best for methacrylic monomers in polar solvents such as tetrahydrofuran (THF).[3,6] In contrast, large amounts of Lewis acid (approximately 10 mol % relative to the monomer concentration), such as AlR_2Cl or $ZnCl_2$ and apolar media (e.g., toluene) are well suited to acrylic monomers.[5,6] As a matter of fact, the synthesis all-(meth)acrylate di- and triblock copolymers by sequential addition of the two types of monomers is not straightforward. For this simple reason, GTP did not meet all of the initial expectations with respect to the production of specialty polymers on an industrial scale.[4,23−25]

In recent years, however, new developments in GTP catalysis have been proposed. For instance, Chen et al. have employed trityl tetrakis(pentafluorophenyl)borate ($[Ph_3C][B(C_6F_5)_4]$) to activate SKA moieties by a so-called "oxidative GTP mechanism" forming cationic silylium intermediates.[26−29] Oxidative GTP permits the synthesis of well-defined poly(*n*-butyl acrylate)s and poly(methyl methacrylate)s of high molar masses at ambient temperature. Kakuchi et al. have reported that trifluoromethanesulfonimide ($HNTf_2$) can be used as a Brönsted "superacid" in catalytic amounts to trigger GTP.[30] Not only methyl methacrylate[30] but also *N*,*N*-dimethylacrylamide[31] could be polymerized in this way under controlled fashion. Finally, Hedrick, Waymouth et al.[32] and our group have reported that GTP can be efficiently conducted using *N*-heterocyclic carbenes (NHCs) as nucleophilic organic catalysts,[33,34] confirming the great potential and versatility of NHCs in organocatalyzed polymerization reactions.[33−47] These reports have also reopened the debate on the exact mechanism that

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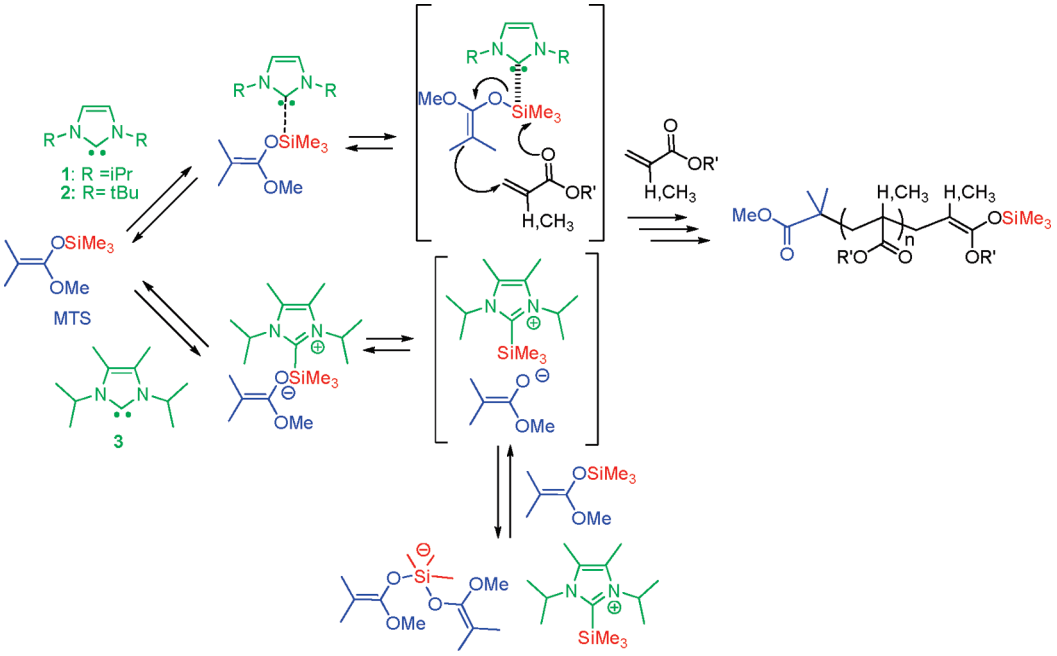
Scheme 1. Associative (top) *versus* Dissociative (bottom) Mechanism of Group Transfer Polymerization of (Meth)acrylic Monomers as a Function of the *N*-Heterocyclic Carbene Employed as Catalyst



operates in GTP (Scheme 1).[3,20,21,32−34,48] While Hedrick et al. have postulated a dissociative mechanism forming enolate-type species using NHC **3** as catalyst,[32] we have provided a series of experimental evidence suggesting that GTP occurs by an associative (concerted) mechanism, when catalyzed by NHC **1** or **2** (Scheme 1).[33,34] This discrepancy may eventually be explained by the difference in nucleophilicity/silicophilicity of the different NHCs used. NHC **3** is indeed slightly more nucleophilic than NHCs **1** and **2**, hence the occurrence of the two mechanisms depending on the NHC used is plausible. Yet, though the two mechanisms lead to the same polymer, the polymerization kinetics as well as the properties of the final polymers associated with each of them are different.[22,32−34] These NHC-catalyzed GTPs were further applied to the synthesis of all-acrylic block copolymers.[32−34]

In this contribution, we wish to exemplify the potential of NHCs **1** and **2** to activate the GTP of miscellaneous monomers, including not only acrylics (i.e., *n*-butyl acrylate, *tert*-butyl acrylate, and *N*,*N*-dimethylaminoethyl acrylate), methacrylics (methyl methacrylate and *N*,*N*-dimethylaminoethyl methacrylate), but also an acrylamido-type monomer, namely, *N*,*N*-dimethylacrylamide, and methacrylonitrile as well. NHCs **1** and **2**, respectively, 1,3-bis(di-*iso*propyl)imidazol-2-ylidene (**1**) and 1,3-bis(di-*tert*-butyl)imidazol-2-ylidene (**2**), have thus been used as GTP catalysts in the presence of methoxy-trimethylsilyloxy-dimethylketene acetal (MTS) as initiator. The polymerization kinetics of various monomers have been compared. In particular, GTP of *tert*-butyl acrylate has revealed a first-order dependence of the rate of polymerization on the concentration in MTS, again suggesting the occurrence of an associative mechanism.

Experimental Section

Materials. Methyl methacrylate (MMA), *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA), *n*-butyl acrylate (nBA), *tert*-butyl acrylate (*t*BA), *N*,*N*-dimethylaminoethyl acrylate (DMAEA), *N*,*N*-dimethylacrylamide (DMA), and methacrylonitrile (MAN) were all purchased in Aldrich or Fluka (purity: 97−99%) and were distilled over CaH_2 into burets. All other reagents were purchased from Aldrich. Methyl trimethylsilyl−ketene acetal (MTS; 95%) was distilled over CaH_2 and stored in a Schlenk tube kept at low temperature in a glovebox. Tetrahydrofuran (THF) (technical grade) was distilled over Na/benzophenone and toluene over PS−Li prior to use. Dimethylformamide (DMF; technical grade) was cryo-distilled over CaH_2 and stored over molecular sieves, and freshly cryo-distilled prior to use. NHCs **1** and **2** were prepared by slightly modifying already reported procedures:[49] the di-*iso*propyl-imidazolium salt was deprotonated with NaH and a catalytic amount of tBuOK and the di-*tert*-butyl-imidazolium salt with *n*Bu-Li. NHC **1** was purified by distillation under vacuum, and NHC **2** by sublimation under vacuum. Solutions of each catalyst were kept in a glovebox under argon atmosphere.

Instrumentation. ^{1}H NMR (400 MHz) spectra were recorded on Bruker AC-400 spectrometer in appropriate deuterated solvents. Molar masses of PMMAs, P*t*BuAs and PnBAs were determined by size exclusion chromatography (SEC) using a 3-column set of TSK gel TOSOH (G4000, G3000, G2000 with pore sizes of 20, 75, and 200 Å respectively, connected in series) calibrated with PMMA standards with THF as eluent (1 mL/min) and trichlorobenzene as a flow marker at 25 °C, using both refractometric and UV detectors (Varian).

SEC in DMF was used for the characterization of PDMAEMAs, PDMAEAs, PDMAs and PMANs, using a 3-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 (PS) standards with DMF as eluent (0.8 mL/min) and toluene as a flow marker at 60 °C, in the presence of LiBr (1 g/L) using both refractometric and UV detectors (Varian).

Group Transfer Polymerization of Methyl Methacrylate. Polymerization of MMA was carried out under a dry and inert atmosphere using Schlenk equipments. In a typical polymerization, 70 μL of a 1 M solution of NHC **1** (7×10^{-5} mol; 2 mM) and 70 μL of MTS (3.4×10^{-4} mol; 10 mM) (entry 1, Table 1) were introduced via a syringe in a vacuumed flame-dried Schlenk special apparatus equipped with a withdrawal digit on the side of main flask (ESI), kept in a glovebox under an argon atmosphere. After removal of the Schlenk from the glovebox, 30 mL of dry THF were added under vacuum. After homogenization, 4 mL (3.7×10^{-2} mol, final concentration 1 M) of MMA were introduced at 25 °C. The addition proceeded discontinuously over 5 min. After addition of first droplets, the color of the solution turned pink and then red-orange.

Table 1. Group Transfer Polymerization in Solution of Various Monomers Catalyzed by 1,3-Bis(diisopropyl)imidazol-2-ylidene (1) and 1,3-Bis(di-*tert*-butyl)imidazol-2-ylidene (2) in the Presence of 1-Methoxy-2-methyl-1-trimethylsiloxypropene (MTS) as Initiator at 25 °C

expt	monomer	NHC	Solvent	[*M*] (M)	[NHC] (mM)	[MTS] (mM)	$M_{n,th.}$[a] (g/mol)	$M_{n,expt}$[b] (g/mol)	convn[c] (%)	time (h)	D[d] (M_w/M_n)
1	MMA[e]	**1**	THF	1	2	10	20 000	19 000	100	2	1.07
2	*n*BA	**1**	THF	0.7	0.3	2.5	36 000	31 000	100	1	1.39
3		**2**	THF	0.7	0.3	2.5	36 000	33 000	100	1	1.31
4	*t*BA	**1**	THF	0.7	0.3	2.5	36 000	40 000	100	1	1.15
5		**1**	THF	0.7	0.3	6.25	14 600	15 200	100	1	1.09
6		**1**	THF	0.7	0.3	18.75	4800	5000	100	1	1.18
7		**1**	toluene	0.7	0.3	18.75	4800	5100	100	30	1.25
8		**1**	toluene	0.7	0.625	6.25	14 600	14 000	100	10	1.27
9		**1**	toluene	0.7	3.125	6.25	14 600	13 900	100	5	1.38
10		**1**	toluene	0.7	6.25	6.25	14 600	13 100	100	3	1.45
11		**1**	THF	1	2	10	25 800	24 000	100	0.5	1.19
12	DMAEMA	**1**	THF	1	0.5	20	8000	6500	95	40	1.11
13		**2**	THF	1	0.5	10	15 900	18 000	100	50	1.19
14		**1**	THF	1	0.5	5	31 600	34 000	95	70	1.10
15		**1**	THF	1	2	10	15 900	13 000	95	40	1.15
16	DMAEA	**1**	THF	1	2	10	14 500	23 000	90	24	1.46
17	DMA	**1**	THF	0.7	0.3	2.5	28 000	42 000	100	5	1.15
18		**1**	THF	2.1	0.9	7.5	28 000	24 000	100	3	1.15
19		**2**	THF	0.7	0.3	2.5	28 000	37 000	100	8	1.17
20	MAN	**1**	DMF	1	0.5	20	3500	5000	90	12	1.51
21		**1**	DMF	1	0.5	3	22 500	18 000	100	24	1.37

[a] $M_{n,th.}$: theoretical average molar mass, M_n = ([monomer])/([MTS]) × M_{UM} × convn (M_{UM} is the molar mass of the monomer unit). [b] $M_{n,expt}$: experimental number-average molar mass obtained by SEC in THF or in DMF (60 °C, 0.1% LiBr) (calibration is based on PMMA standards). [c] convn: monomer conversion calculated from ^{1}H NMR analysis and double-checked by gravimetry (after kinetic measurements). [d] D: molar mass distribution or dispersity = M_w/M_n with M_w mass average weight molar mass (obtained by SEC). [e] More data related to the NHC-catalyzed GTP of MMA can be found in ref33,34.

At precise time intervals, aliquots were withdrawn thanks to the vacuum flame-dried digit. A droplet of degassed MeOH was then introduced, and the reaction mixture in the digit became colorless. The aliquot was removed from the withdrawal digit attached to the flask. Its volume was given by transfer to a small tarred container with a precise syringe. The conversions were determined by ^{1}H NMR (ESI) and double-checked by gravimetry. Molecular characteristics of NHC-derived PMMAs are provided in Table 1.

Group Transfer Polymerization of *n*-Butyl Acrylate and *tert*-Butyl Acrylate. The polymerization procedures are similar to the one used for the NHC-catalyzed GTP of MMA. In a typical polymerization, 100 μL of a 0.1 M solution of NHC **2** (10^{-5} mol; 0.3 mM) and 20 μL of MTS (10^{-4} mol; 2.5 mM) (entry 3, Table 1) were introduced via a syringe into a vacuumed flame-dried Schlenk kept in a glovebox under an argon atmosphere. After removal of the Schlenk from the glovebox, 30 mL of dry THF were added under vacuum. After homogenization, 3.5 mL (2.4×10^{-2} mol, giving a final concentration of 0.7M) of nBA were introduced at 25 °C). A droplet of degassed MeOH was introduced after completion of the reaction. Molecular characteristics of these NHC-derived PnBAs and P*t*BAs are provided in Table 1.

Group Transfer Polymerization of *N*,*N*-Dimethylaminoethyl Methacrylate and *N*,*N*-Dimethylaminoethyl acrylate. The polymerization procedures are similar to that described for the GTP-derived PMMA's. In a typical polymerization (entry 12, Table 1), 180 μL of a 0.1 M solution of NHC **1** (1.8×10^{-5} mol; 0.5 mM) and 150 μL of MTS (7.5×10^{-4} mol; 20 mM) were introduced via a syringe into a vacuumed flame-dried Schlenk kept in a glovebox under an argon atmosphere. After removal of the Schlenk from the glovebox, 30 mL of dry THF were added under vacuum. After homogenization, 6 mL (3.6×10^{-2} mol, giving a final concentration of 1 M) of DMAEMA were introduced at 25 °C. A droplet of degassed MeOH was introduced after completion of the reaction. Molecular characteristics of all NHC-derived PDMAEMAs and PDMAEAs are provided in Table 1.

Group Transfer Polymerization of *N*,*N*-Dimethylacrylamide. In a typical polymerization (entry 17, Table 1), 100 μL of a 0.1 M solution of NHC **1** (10^{-5} mol; 0.3 mM) and 20 μL of MTS (10^{-4} mol; 2.5 mM) were introduced via a syringe into a vacuumed flame-dried Schlenk kept in a glovebox under an argon atmosphere. After removal of the Schlenk from the glovebox, 30 mL of dry THF was added under vacuum. After homogenization, 2.5 mL (2.4×10^{-2} mol, giving a final concentration of 0.7M) of DMA was introduced at 25 °C. A droplet of degassed MeOH was introduced after completion of the reaction. Molecular characteristics of NHC-derived PDMAs are provided in Table 1.

Group Transfer Polymerization of Methacrylonitrile. The polymerization procedures are similar to the one used for PMMA but using DMF as solvent to ensure homogeneous conditions. For instance, in a typical polymerization (entry 20, Table 1), 180 μL of a 0.1 M solution of NHC **1** (1.8×10^{-5} mol; 0.5 mM) and 150 μL of MTS (7.5×10^{-4} mol; 20 mM) were introduced via a syringe into a vacuumed flame-dried Schlenk kept in a glovebox under an argon atmosphere. After removal of the Schlenk from the glovebox, 30 mL of dry DMF were added under vacuum. After homogenization, 3 mL (3.5×10^{-2} mol; 1 M) of MAN were introduced at 25 °C. A droplet of degassed MeOH was introduced after completion of the reaction. Molecular characteristics of the two NHC-derived PMANs are provided in Table 1.

Results and Discussion

"Group transfer polymerization" was coined by Webster et al.[3] to account for the putative transfer of the trimethylsilyl moiety ($SiMe_3$) from the polymer chain-end to the just inserted monomer. In other words, an associative (concerted) mechanism was originally put forward by the authors (see Scheme 1). This pathway has been further questioned and has been the subject of a heated debate.[3,4,6,20,21,50−56] The occurrence of either the reversible or the irreversible dissociative or the associative mechanism actually depends on the overall polymerization conditions and, most of all, on the nature of the employed catalyst. NHCs have themselves been reported to induce either the first or the second mechanism in independent studies by Hedrick, Waymouth et al.[32] and by our group.[33,34] In both cases, NHCs have enabled the controlled GTP of both acrylic and methacrylic monomers, in sharp contrast to the catalysts used so far. Here we provide new evidence for the efficient control of GTP of both families of monomers. In addition, we report for the first time the

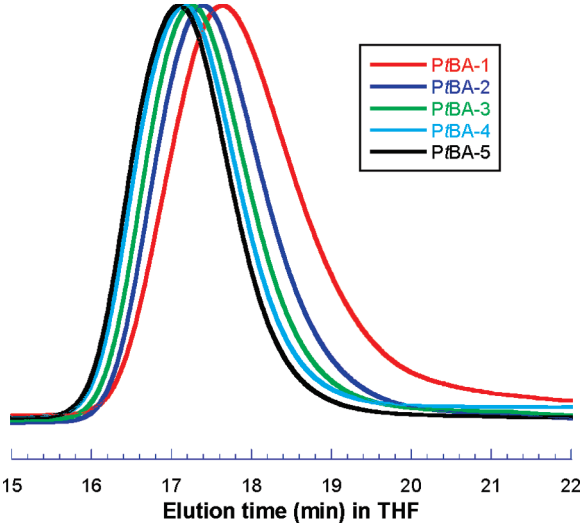


Figure 1. SEC traces in THF (RI detection) of polymers obtained by group transfer polymerization of *t*BA in the presence of 1,3-bis-(di-*iso*propyl)imidazol-2-ylidene (NHC **1**).

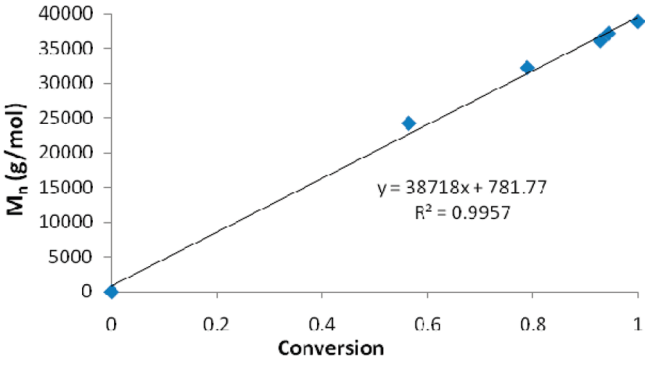


Figure 2. M_n vs conversion of polymers obtained by group transfer polymerization of *t*BA catalyzed by 1,3-bis(di-*iso*propyl)imidazol-2-ylidene (NHC **1**).

synthesis of well-defined poly(*N*,*N*-dimethyl acrylamide)s and poly(methacrylonitrile)s by a NHC-catalyzed GTP. Table 1 summarizes the different experiments and the molecular characteristics of the GTP-derived polymers.

1-GTP of *tert*-Butyl Acrylate. In our previous reports, we showed that the controlled polymerization of nBA and *t*BA could be achieved either in THF or in toluene.[33,34] Investigation into the polymerization kinetics is very instructive and a possible means to discriminate between the two mechanisms discussed above (Scheme 1).[7,20,21,24,52,53,57−59] A new series of experiments was thus performed to evaluate the effect of the initiator concentration ([MTS]) on the polymerization kinetics of *t*BA catalyzed by NHC **1** (entries 4−6, Table 1). Aliquots were withdrawn 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 (ESI). Figure 1 shows that poly(*tert*-butyl acrylate)s (P*t*BAs) exhibit narrow molar mass distributions, with experimental molar masses close to expected values, even at low monomer conversions (Figure 1).

The polymerization kinetics of *t*BA was then investigated in THF for different [*t*BA]/[MTS] initial molar ratios. For each ratio, the kinetic variation of $\ln[M]_0/[M]$ versus time could be plotted, assuming a first-order in monomer (Figures 2 and 3). As previously observed for the NHC-catalyzed GTP of MMA,[34] the first-order kinetic plots of GTP of *t*BA catalyzed by NHC **1** deviate from linearity at high monomer conversions.

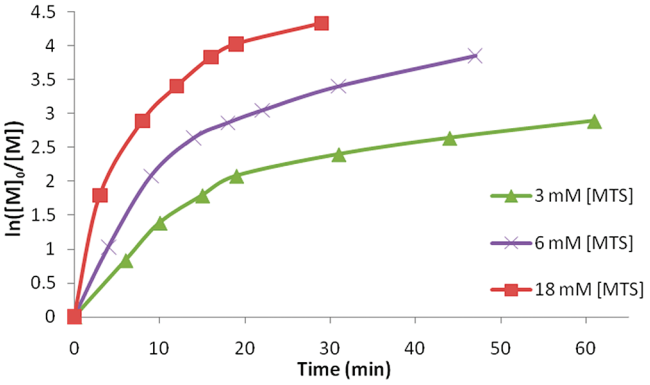


Figure 3. Evolution of $\ln([M]_0/[M])$ vs time of polymers obtained by group transfer polymerization of *t*BA catalyzed by 1,3-bis(di-*iso*propyl)imidazol-2-ylidene (NHC **1**) (entries 4−6, Table 1).

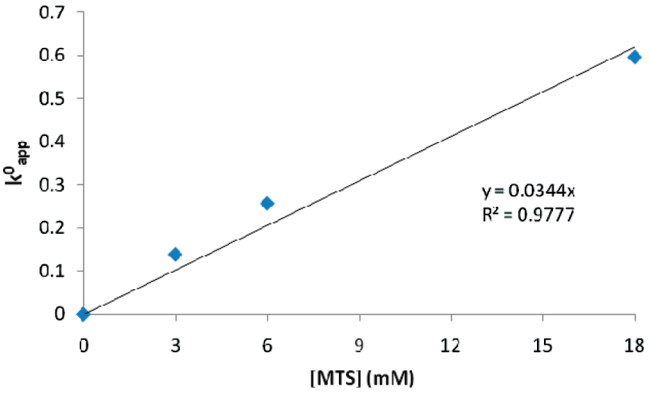


Figure 4. Evolution of k^0_{app} (min^{-1}) vs [MTS] of polymers obtained by group transfer polymerization of *t*BA catalyzed by 1,3-bis(di-*iso*propyl)imidazol-2-ylidene (NHC **1**).

In addition, no induction period is observed, and the polymerization rate is directly proportional to the initial concentration in MTS initiator. The apparent initial rate constant, k^0_{app}, that can be deduced from the *initial slopes of these pseudo-first order kinetic plots,* varies linearly with a first order dependence in MTS (Figure 4). In other words, the polymerization rate is faster upon increasing the concentration in MTS. This suggests that, alike the polymerization of MMA, GTP of *t*BA follows an associative mechanism when NHC **1** is used as catalyst.[34]

In the case of the GTP of MMA, we have postulated the nonlinear evolution of $\ln[M]_0/[M]$ versus time as being due to a limited availability of NHC for activation of chain ends, in particular as their molar mass builds up. New arguments can be brought here in light of the kinetics of NHC **1**-catalyzed GTP of *t*BA and its comparison with that of DMA (see further). As a matter of fact, NHCs are likely trapped within the poly(meth)acrylate chains due to their strong interactions with the pendant ester groups reducing the concentration of NHC actually available for GTP catalysis. It is well documented indeed that NHCs efficiently catalyze transesterification reactions through carbonyl activation.[36,40,60−64]

On the basis of a first kinetic order in MTS, one can determine the k_iK_c product for the NHC-catalyzed GTP of *t*BA, where K_c is the equilibrium constant of the formation of the pentacoordinated silicon and k_i is the rate constant of initiation (i.e., the first propagation step).[7,34] To the best of our knowledge, no k_iK_c value has been reported for GTP of acrylates using regular nucleophilic catalysts, *i.e.*, (bi)fluorides or (bi)oxyanions. This is due to the fact that

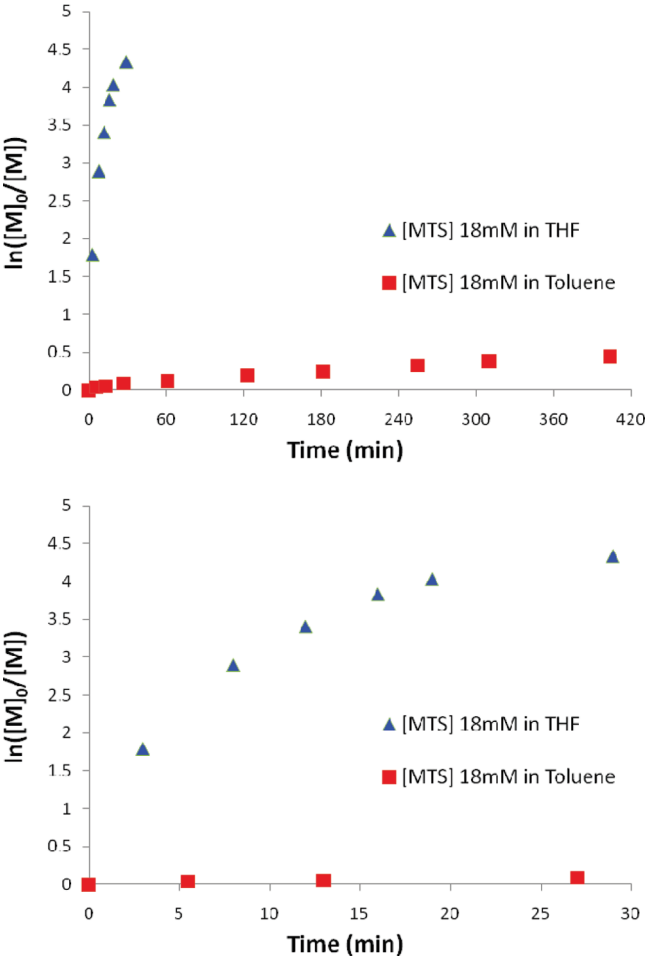


Figure 5. Kinetics of group transfer polymerization of *t*BA catalyzed by 1,3-bis(di-*iso*propyl)imidazol-2-ylidene (NHC **1**) in THF and in toluene: extended view (top) and zoom (down).

such catalysts do not bring about a well-controlled polymerization of these monomers. One can write:

$$k^0_{app} = k_i K_c[\text{MTS}][\text{NHC}]$$

From Figure 4, one obtains:

$$k^0_{app} = 0.0344 \times [\text{MTS}](\text{L}\cdot\text{mmol}^{-1}\cdot\text{min}^{-1})$$

or

$$k^0_{app} = 0.573 \times [\text{MTS}](\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1})$$

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

$$k_i K_c \cong 2000\ \text{L}^2\cdot\text{mol}^{-2}\cdot s^{-1}$$

This value is approximately 4 times higher than that found for the NHC-catalyzed GTP of MMA under the same conditions,[34] which is consistent with the higher monomer reactivity of acrylates compared to methacrylates.

Thereafter, we compared the kinetics of the NHC-catalyzed GTP of *t*BA in THF and in toluene (entries 4−10, Table 1; see also ESI). Figure 5 shows the evolution of $\ln([M]_0/[M])$ versus time corresponding to the two series of experiments. The polymerization rate is undoubtedly slower

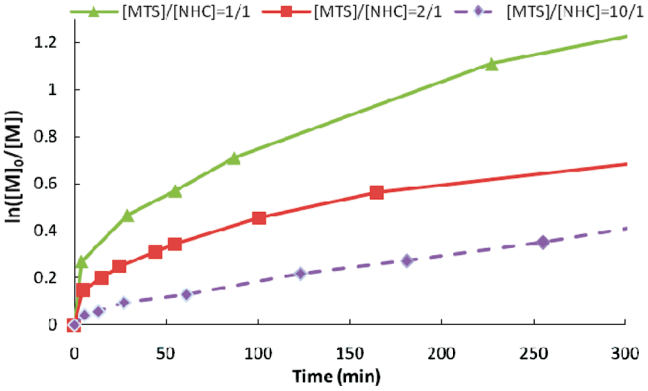


Figure 6. Kinetics of group transfer polymerization in toluene of *t*BA catalyzed by 1,3-bis(di-*iso*propyl)imidazol-2-ylidene (NHC **1**) using a ratio [MTS]/[NHC] = 10/1; 2/1 and 1/1 (entries 8, 9, and 10 respectively, Table 1).

in toluene than in THF. In the former solvent, one obtains 50% of monomer conversion after 12 h, and the reaction reaches completion after 30 h. Importantly, GTP retains its controlled character in both solvents, as verified by SEC after chain extension experiments (ESI). Noteworthyly, the polymerization rate was only slightly affected in the case of the GTP of MMA in toluene using NHC **1** as catalyst,[34] while the same apolar solvent dramatically slows down the kinetics of *t*BA.

Finally, we investigated the effect of the NHC concentration on the results of GTP of *t*BA in toluene, with a [MTS]/[NHC **1**] ratio of 1/1, 2/1, and 10/1 (entries 7−10, Table 1). Toluene was chosen as solvent because GTP in THF would have been too fast to monitor with our sampling method. It is worth reminding that with (bi)fluoride as catalyst, an increase of the catalyst concentration favors the dissociative mechanism, and "*can even ruins the polymerization due to the predominance of side reactions*".[2,24] This is due to a too high concentration of bare enolates that can cause termination reactions by backbiting and by C−O isomerization in the case of acrylics.

In our previous study, we reported that MTS and NHC **1** when mixed in 1/1 molar ratio do not form enolate-type species as shown by ^{29}Si or ^{13}C NMR spectroscopy,[34] which indirectly supports the prevalence of the associative mechanism. As can be seen in Figure 6, a higher concentration in NHC accelerates the polymerization of *t*BA, while control of chain growth is retained, a feature that is again consistent with the associative mechanism.

Determination of the original slopes allowed us to plot k^0_{app} (min^{-1}) vs [NHC] from which a first-order variation with respect to the NHC catalyst could be drawn (Figure 7). The same observation was made by Brittain in the case of GTP of MMA catalyzed by (bi)benzoates.[7] In contrast, bifluoride catalysts gave second-order kinetics, which was explained by the reaction of two HF_2^- anions onto one MTS molecule, leading to the formation of both $H_2F_3^-$ and 1:1 [MTS−fluoride] complex. The complex would further dissociate, forming enolate-type species by a dissociative mechanism.

In a similar manner to that discussed above, the k_iK_c value could be determined in toluene:

$$k^0_{app} = 0.0108 \times [\text{NHC}](\text{L}\cdot\text{mmol}^{-1}\cdot\text{min}^{-1})$$

$$= 0.18 \times [\text{NHC}](\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1})$$

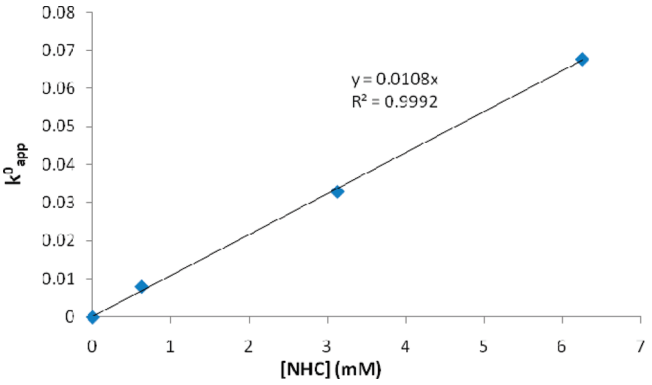


Figure 7. Evolution of k^0_{app} (min^{-1}) vs [NHC] of group transfer polymerization in toluene of *t*BA catalyzed by 1,3-bis(di-*iso*propyl)imidazol-2-ylidene (**1**).

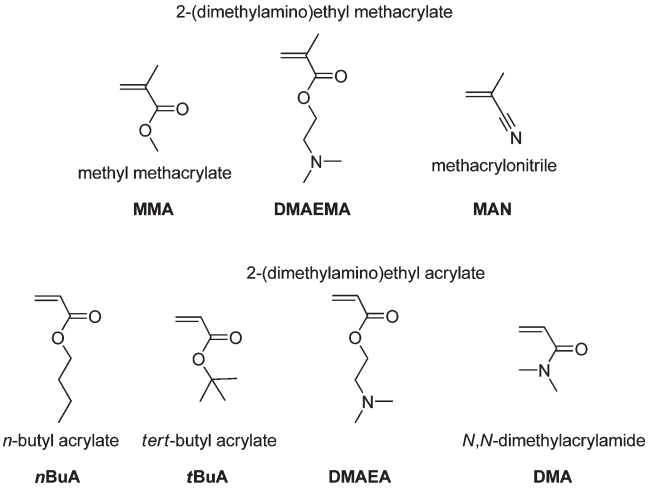


Figure 8. (Meth)acrylic monomers polymerized in this study.

with $k^0_{app} = k_i K_c$[MTS][NHC], and [MTS] = 6,25 × 10^{-3} M

The following value was obtained:

$$[k_i K_c]_{Toluene} \cong 30\ L^2 \cdot mol^{-2} \cdot s^{-1}$$

This value found in toluene is approximately 60 times smaller than the one in THF, which is consistent with experimental observations: complete monomer conversion is achieved in less than half an hour in THF, whereas about 30 h are required to reach completion in toluene.

Thus, investigations into the kinetics of GTP of *t*BA catalyzed by NHC **1** and initiated by MTS confirm the occurrence of the associative mechanism, as shown for the GTP of MMA using the same NHC catalyst (Scheme 1). Increasing the catalyst concentration speeds up the polymerization without loss of control over molar masses and dispersities ($D \leq 1.5$ for a 1:1 molar ratio of [NHC]/[MTS]).

2-NHC-Catalyzed GTP of Miscellaneous (Meth)acrylic Monomers. As already mentioned, one drawback of earlier GTP systems was the absence of a unique class of catalysts that could trigger the polymerization of both acrylic and methacrylic monomers. It is demonstrated here that the same NHC can efficiently catalyze the GTP of various (meth)acrylic monomers, including *N*,*N*-dimethylaminoethyl acrylate (DMAEA), *N*,*N*-dimethyl acrylamide (DMA), and *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) (Figure 8). Preliminary experiments of GTP of methacrylonitrile (MAN) are also shown, whereas results related to the GTP of MMA are presented for a comparison purpose.

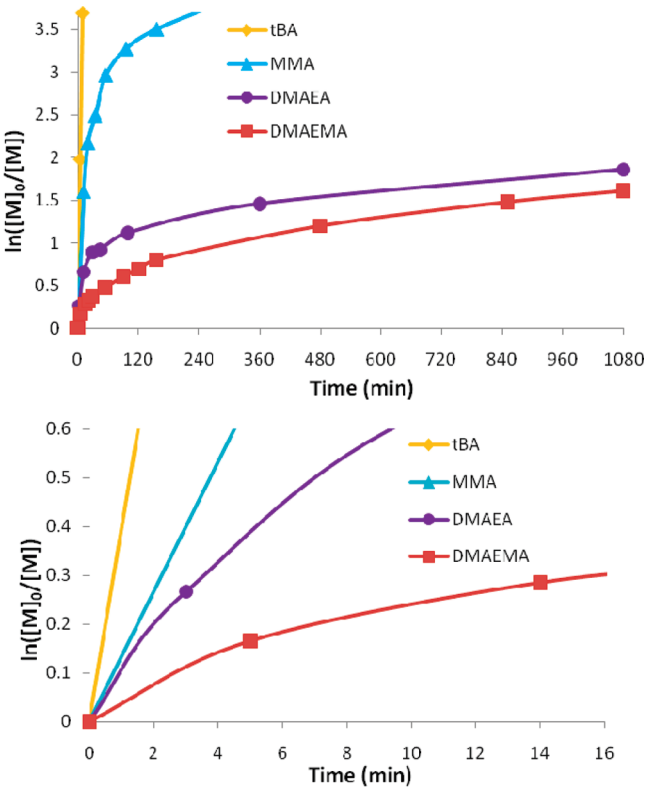
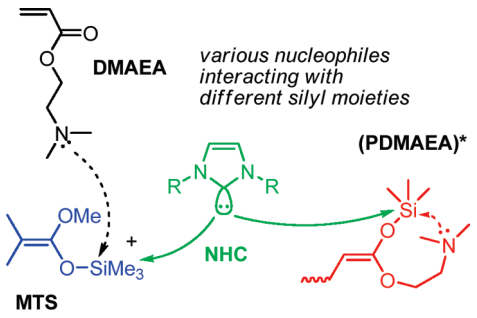


Figure 9. Kinetic of the group transfer polymerization of (meth)acrylic monomers in THF in the presence of 1,3-bis(di-*iso*propyl)imidazol-2-ylidene (NHC **1**), for the whole experiment (top) and for the first instants of the polymerization (down), (entries 1;11;15;16, Table 1).

Scheme 2. Side Interactions That Could Disrupt the NHC-Catalyzed Group Transfer Polymerization of DMAEA



Both poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) and poly[2-(dimethylamino)ethyl acrylate] (PDMAEA) are useful polymer components in drug delivery systems, as being water-soluble, temperature-sensitive and weak polybases whose lateral amino groups can be protonated, providing efficient polycationic interacting agents for nonviral-DNA.[65−67] On the other hand, control of the polymerization of MAN has been a long-standing issue,[2,22,24,68] owing to the occurrence of side reactions such as the attack of the anionic propagating species onto the cyano group. In addition, MAN is extremely reactive and the corresponding poly(methacrylonitrile) (PMAN), which can serve as precursor for carbon fibers exhibits poor solubility in common solvents. In particular, attempts to carry out the GTP of MAN with 2-(trimethylsilyl)isobutyronitrile as initiator met with limited success with respect to the control of molar masses of the PMAN samples formed.[68] As for poly(*N*,*N*-dimethylacrylamide) (PDMA), it is widely used in pharmaceutical/personal care

applications, owing to its water solubility and biocompatibility. *N*,*N*-Dialkyl acrylamides have seldom been polymerized by GTP, and their polymerization was limited to low molar masses, broad dispersities and poor conversions with conventional catalysts.[2,24,69]

Figure 9 shows the comparative evolution of $\ln([M]_0/[M]) = f(t)$ for the four tested (meth)acrylic-type monomers, i.e. MMA, DMAEMA, *t*BA, and DMAEA, which allows us to rank them according to their reactivity in GTP catalyzed by NHC **1**. The polymerization rates vary in the following order: DMAEMA < DMAEA < MMA < *t*BA. With a complete conversion in about 10 min, the GTP of *t*BA is the most rapid of all these polymerizations (Figure 9). One can note then that the GTP of MMA is noticeably faster than that of amino-containing monomers, DMAEMA and DMAEA. Yet DMAEA, which is an acrylate-type monomer, should be more reactive than methacrylics. This may be rationalized as follows. In the case of the GTP of DMAE(M)A monomers, the trimethylsilyl groups carried by the SKA polymer chain ends that are expectedly activated by the NHC can competitively interact with the tertiary lateral amino groups of PDMAE(M)A, and thus perturb the polymerization kinetics (Scheme 2).

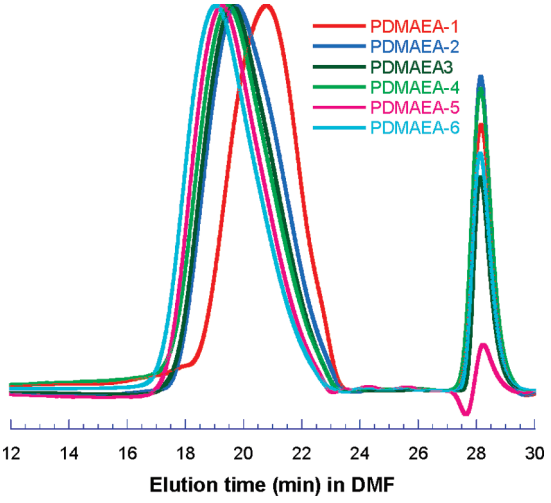


Figure 10. SEC (DMF) traces of polymers obtained by group transfer polymerization of DMAEA in THF in the presence of NHC **1** (RI detection), (entry 16, Table 1).

Formation of pentavalent siliconates stabilized by nitrogen-containing ligands has indeed been reported.[56]

Well-defined PDMAEAs could nonetheless be achieved, with a monomer conversion that reaches 90% after 1 day; Figure 10 shows the fairly symmetrical and unimodal shapes of the chromatograms ($D < 1.5$). To avoid possible interactions of PDMAEA with the SEC columns with THF as solvent, the analysis by SEC was carried out using DMF at 60 °C in the presence of 0.1% LiBr.

The kinetics of GTP of these monomers were compared in THF at 25 °C using a ratio [MTS]/[NHC **1**] equal to 5 (entries 1;11;15;16, Table 1); the monomer conversion could be monitored by ^{1}H NMR spectroscopy (ESI). As expected, DMAEMA is less reactive than DMAEA and exhibits the lowest reactivity in this series (Figure 11). The same hypotheses than in the case DMAEA can be made to account for the kinetics of the GTP of this monomer (Scheme 2). Low molar mass distributions ($D < 1.2$) and PDMAEMAs with predicted molar masses could be readily obtained from both NHCs 1 and 2 as organic catalysts, as illustrated in Figure 11.

Owing to its acrylamido-type structure, DMA is to be considered separately with respect to the previous series. As shown in Figure 12, catalysis by NHC-1 provides an excellent control over the GTP of this monomer (see also Table 1). The first-order kinetic plots of GTP of *t*BA and that of DMA are compared in Figure 13. Remarkably, the $\ln[M]_0/[M]$ vs time plot shows a perfectly linear variation in the case of DMA, in contrast to the case of all aforementioned monomers. As discussed above, the nonlinearity of $\ln[M]_0/[M] = f(t)$ can be explained by the interactions of the catalyst with the carbonyl groups of poly(meth)acrylates;[70] these interactions would reduce the concentration of carbene really available for chain end activation, in particular at high conversions. In contrast, NHCs are not known to catalyze transamidation reactions. Interactions between the NHC catalyst and the amide moieties of PDMA are thus less probable (Scheme 3), letting the catalyst free to activate SKA-type PDMA chain ends. This may explain the linear variation of the first-order kinetic curves in this case.

To check whether the overall concentration of the medium and its viscosity play any role in the kinetics of polymerization, two experiments of GTP of DMA were performed at two different concentrations using the same molar ratio, ([NHC]/[MTS]/[DMA] = 0.1/1/280). As can be seen in Figure 14, the plot of $\ln[M]_0/[M]$ vs time evolves linearly in

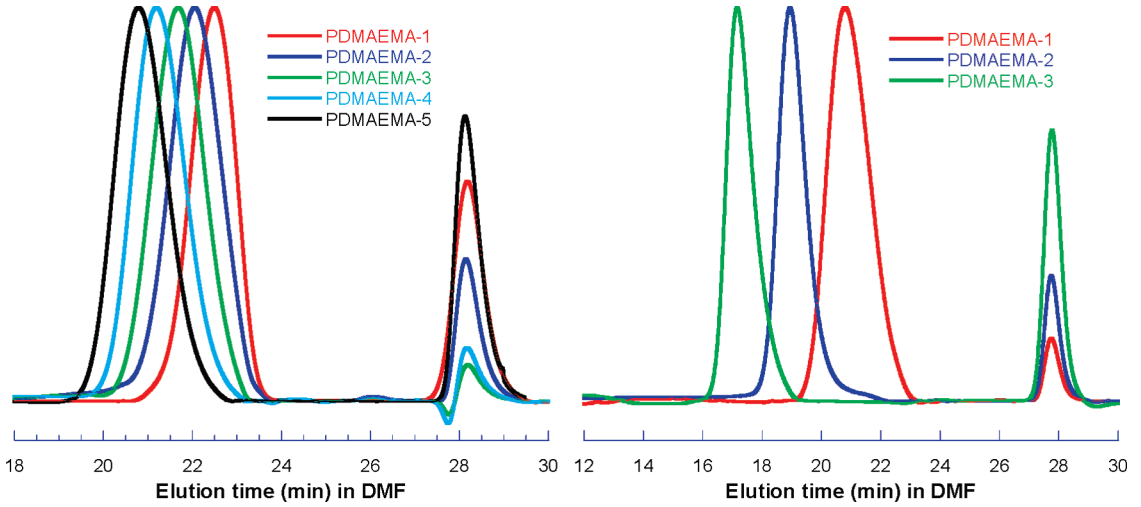


Figure 11. SEC (DMF) traces of polymers obtained by NHC-catalyzed group transfer polymerization of DMAEMA (RI detection), for the kinetics experiment (left, entry 15, Table 1) and for additional experiments (right, entries 12−14, Table 1).

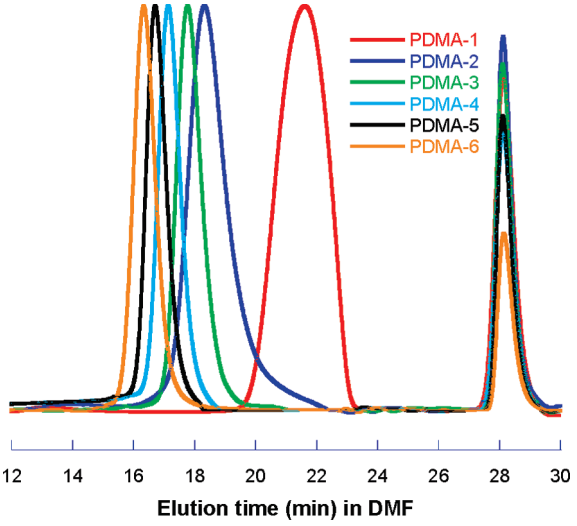


Figure 12. SEC traces of polymers obtained by group transfer polymerization of DMA in THF using NHC **1** as catalyst (RI detection), (entry 17, Table 1).

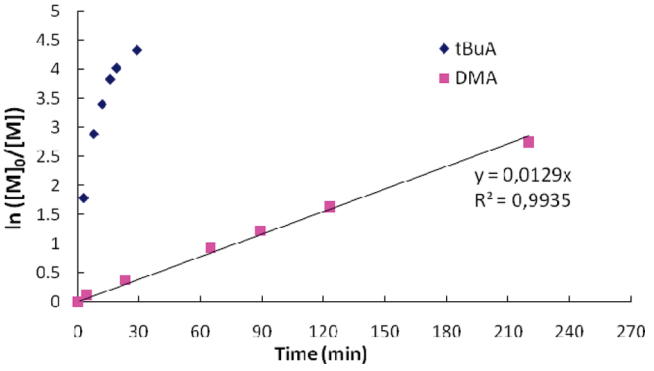
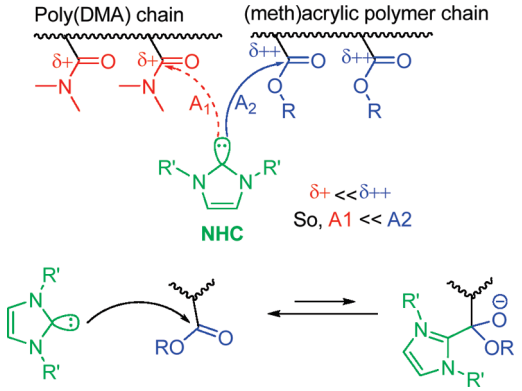


Figure 13. Kinetics of the group transfer polymerization of DMA and of *t*BA in THF in the presence of NHC **1** (entries 4 and 17, Table 1).

Scheme 3. Affinities of NHCs toward Carbonyl Moieties of Ester and Amide Groups



both cases, with a higher polymerization rate for the NHC-catalyzed GTP of DMA in the more concentrated THF solution, as expected. This result further supports the assumption that interactions of the NHC with amide moieties of PDMA, if existing, do not affect the availability of the catalyst, irrespective of the viscosity of the reaction mixture.

Finally, the GTP of MAN triggered by NHC catalysis was attempted. To this end, DMF was used as polymerization solvent due to the poor solubility of PMAN in THF.

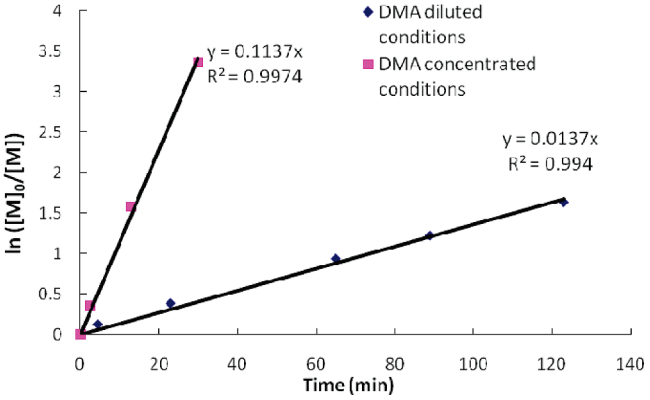


Figure 14. Kinetic comparison of group transfer polymerization of DMA in diluted conditions (blue) and concentrated conditions (pink), (entries 17 and 18, Table 1).

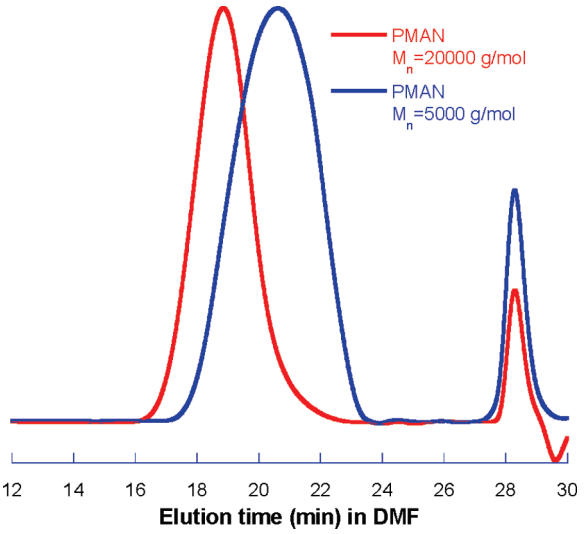


Figure 15. SEC (DMF) traces (RI detection) of PMANs obtained by NHC 1-catalyzed group transfer polymerization of MAN in DMF initiated by MTS (entries 20 and 21, Table 1).

As preliminary results, two PMAN samples with experimental molar masses close to expected values and relatively narrow dispersities ($D < 1.5$) could be obtained (Figure 15). However, a more systematic study and optimization of the polymerization of this monomer are ongoing in our group.

Conclusion

N-Heterocyclic carbenes prove efficient organic catalysts for the group transfer polymerization of a variety of monomers in THF or toluene at room temperature, in the presence of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MTS) as initiator. Monomers include not only alkyl acrylates and methacrylates, but also an acrylamido-type monomer such as *N*,*N*-dimethylacrylamide. NHC-catalyzed MTS-initiated GTP of methacrylonitrile using DMF as solvent has also been demonstrated. The nonlinearity of the first-order kinetic plots, $\ln[M]_0/[M]$ vs time, in the GTP of (meth)acrylates is the result of interactions developing between the NHC and the ester moieties of poly(meth)acrylate chains, reducing the concentration of the catalyst really available for GTP activation. The rate of polymerization consequently decreases, but it does not prevent NHC-GTPs to exhibit a "controlled/living" character.

Investigations into the kinetics of GTP of *tert*-butyl acrylate catalyzed by NHC support our previous argumentation in favor of the associative mechanism, with in particular a direct dependence of

the polymerization rate with the concentration in initiator. We are currently exploring the possibilities offered by NHCs as organic catalysts in GTP, in particular to favor a stereoselective polymerization via the associative (concerted) mechanism with the view of manipulating the polymer syndiotacticity. Application of NHC catalysis to sequential GTP for the synthesis of miscellaneous block copolymers is also ongoing in our group.

Supporting Information Available: Text and figures describing the synthesis and characterization of *N*-heterocyclic carbenes **1** and **2**, the determination of the conversion of the different monomers by ^{1}H NMR spectroscopy, and SEC traces of chain extension experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Mukaiyama, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 5590–5614.
(2) Webster, O. W. *Adv. Polym. Sci.* (*New Synth. Methods*) **2004**, 1–34.
(3) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706–5708.
(4) Webster, O. W. *J. Polym. Sci., Part A* **2000**, *38*, 2855–2860.
(5) Hertler, W. R.; Sogah, D. Y.; Webster, O. W.; Trost, B. M. *Macromolecules* **1984**, *17*, 1415–1417.
(6) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473–1488.
(7) Brittain, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 7440–7444.
(8) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4034–4041.
(9) Patrickios, C. S.; Hertler, W. R.; Abbott, N. L.; Hatton, T. A. *Macromolecules* **1994**, *27*, 2364–2364.
(10) Triftaridou, A. I.; Kafouris, D.; Vamvakaki, M.; Georgiou, T. K.; Krasia, T. C.; Themistou, E.; Hadjiantoniou, N.; Patrickios, C. S. *Polym. Bull.* **2007**, *58*, 185−190 [and references herein].
(11) Triftaridou, A. I.; Vamvakaki, M.; Patrickios, C. S. *Biomacromolecules* **2007**, *8*, 1615–1623.
(12) Georgiou, T. K.; Patrickios, C. S. *Biomacromolecules* **2007**, *9*, 574–582.
(13) Rikkou, M. D.; Patrickios, C. S. *Macromolecules* **2008**, *41*, 5957–5959.
(14) Kafouris, D.; Gradzielski, M.; Patrickios, C. S. *Macromolecules* **2009**, *42*, 2972–2980.
(15) Hadjiantoniou, N. A.; Triftaridou, A. I.; Kafouris, D.; Gradzielski, M.; Patrickios, C. S. *Macromolecules* **2009**, *42*, 5492–5498.
(16) Rikkou, M. D.; Loizou, E.; Porcar, L.; Butler, P.; Patrickios, C. S. *Macromolecules* **2009**, *42*, 9412–9421.
(17) Hadjiantoniou, N. A.; Krasia-Christoforou, T.; Loizou, E.; Porcar, L.; Patrickios, C. S. *Macromolecules* **2010**, *43*, 2713–2720.
(18) Kassi, E.; Patrickios, C. S. *Macromolecules* **2010**, *43*, 1411–1415.
(19) Brittain, W. J.; Dicker, I. B. *Macromolecules* **1989**, *22*, 1054–1057.
(20) Quirk, R. P.; Ren, J. *Macromolecules* **1992**, *25*, 6612–6620.
(21) Müller, A. H. E. *Macromolecules* **1994**, *27*, 1685–1690.
(22) Baskaran, D. *Prog. Polym. Sci.* **2003**, *28*, 521–581.
(23) Webster, O. W. *Science* **1991**, *251*, 887–893.
(24) Brittain, W. J. *Rubber Chem. Technol.* **1992**, *65*, 580–600.
(25) Webster, O. W. *New Synthetic Methods* **2004**, 257–266.
(26) Zhang, Y.; Chen, E. Y. X. *Macromolecules* **2008**, *41*, 36–42.
(27) Zhang, Y.; Chen, E. Y. X. *Macromolecules* **2008**, *41*, 6353–6360.
(28) Chen, E. Y. X. *Chem. Rev.* **2009**, *109*, 5157–5214.
(29) Zhang, Y.; Ning, Y.; Caporaso, L.; Cavallo, L.; Chen, E. Y. X. *J. Am. Chem. Soc.* **2010**.
(30) Kakuchi, R.; Chiba, K.; Fuchise, K.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42*, 8747–8750.
(31) Fuchise, K.; Sakai, R.; Satoh, T.; Sato, S.-i.; Narumi, A.; Kawaguchi, S.; Kakuchi, T. *Macromolecules* **2010** ASAP.
(32) Scholten, M. D.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2008**, *41*, 7399–7404.
(33) Raynaud, J.; Ciolino, A.; Baceiredo, A.; Destarac, M.; Bonnette, F.; Kato, T.; Gnanou, Y.; Taton, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 5390–5393.
(34) Raynaud, J.; Gnanou, Y.; Taton, D. *Macromolecules* **2009**, *42*, 5996–6005.
(35) Dove, A. P.; Pratt, R. C.; Lohmeijer, B. G. G.; Culkin, D. A.; Hagberg, E. C.; Nyce, G. W.; Waymouth, R. M.; Hedrick, J. L. *Polymer* **2006**, *47*, 4018–4025.
(36) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* **2007**, *107*, 5813–5840.
(37) Nederberg, F.; Lohmeijer, B. G. G.; Leibfarth, F.; Pratt, R. C.; Choi, J.; Dove, A. P.; Waymouth, R. M.; Hedrick, J. L. *Biomacromolecules* **2007**, *8*, 153–160.
(38) Jeong, W.; Shin, E. J.; Culkin, D. A.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2009**, *131*, 4884–4891.
(39) Kamber, N. E.; Jeong, W.; Gonzalez, S.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2009**, *42*, 1634–1639.
(40) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43*, 2093–2107.
(41) Raynaud, J.; Absalon, C.; Gnanou, Y.; Taton, D. *J. Am. Chem. Soc.* **2009**, *131*, 3201–3209.
(42) Raynaud, J.; Absalon, C.; Gnanou, Y.; Taton, D. *Macromolecules* **2010**, *43*, 2814–2823.
(43) Raynaud, J.; Ottou, W. N.; Gnanou, Y.; Taton, D. *Chem. Commun.* **2010**, *46*, 3203–3205.
(44) Rodriguez, M.; Marrot, S.; Kato, T.; Stérin, S.; Fleury, E.; Baceiredo, A. *J. Organomet. Chem.* **2007**, *692*, 705–708.
(45) Marrot, S.; Bonnette, F.; Kato, T.; Saint-Jalmes, L.; Fleury, E.; Baceiredo, A. *J. Organomet. Chem.* **2008**, *693*, 1729–1732.
(46) Pinaud, J.; Vijayakrishna, K.; Taton, D.; Gnanou, Y. *Macromolecules* **2009**, *42*, 4932–4936.
(47) Guo, L.; Zhang, D. *J. Am. Chem. Soc.* **2009**, *131*, 18072–18074.
(48) Quirk, R. P.; Bidinger, G. P. *Polym. Bull.* **1989**, *22*, 63–70.
(49) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.
(50) Mai, P. M.; Müller, A. H. E. *Makromol. Chem. Rapid Comm.* **1987**, *8*, 99–107.
(51) Mai, P. M.; Müller, A. H. E. *Makromol. Chem. Rapid Comm.* **1987**, *8*, 247–253.
(52) Müller, A. H. E.; Litvinenko, G.; Yan, D. *Macromolecules* **1996**, *29*, 2339–2345.
(53) Müller, A. H. E.; Litvinenko, G.; Yan, D. *Macromolecules* **1996**, *29*, 2346–2353.
(54) Litvinenko, G.; Müller, A. H. E. *Macromolecules* **1997**, *30*, 1253–1266.
(55) Simon, P. F. W.; Müller, A. H. E. *Macromolecules* **2004**, *37*, 7548–7558.
(56) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371–1448.
(57) Jenkins, A. D. *Eur. Polym. J.* **1993**, *29*, 449–450.
(58) Müller, A. H. E.; Yan, D.; Litvinenko, G.; Zhuang, R.; Dong, H. *Macromolecules* **1995**, *28*, 7335–7338.
(59) Müller, A. H. E.; Zhuang, R.; Yan, D.; Litvinenko, G. *Macromolecules* **1995**, *28*, 4326–4333.
(60) Grasa, G. A.; Kissling, R. M.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 3583–3586.
(61) Nyce, G. W.; Lamboy, J. A.; Connor, E. F.; Waymouth, R. M.; Hedrick, J. L. *Org. Lett.* **2002**, *4*, 3587–3590.
(62) Nair, V.; Bindu, S.; Sreekumar, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 5130–5135.
(63) Dove, A. P.; Pratt, R. C.; Lohmeijer, B. G. G.; Li, H.; Hagberg, E. C.; Waymouth, R. M.; Hedrick, J. L. In *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley VCH: New York, 2006; p 275.
(64) Marion, N.; Díez-González, S.; Nolan, Steven P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988–3000.
(65) Bütün, V.; Armes, S. P.; Billingham, N. C. *Polymer* **2001**, *42*, 5993–6008.
(66) Rungsardthong, U.; Ehtezazi, T.; Bailey, L.; Armes, S. P.; Garnett, M. C.; Stolnik, S. *Biomacromolecules* **2003**, *4*, 683–690.
(67) Plamper, F. A.; Ruppel, M.; Schmalz, A.; Borisov, O.; Ballauff, M.; Müller, A. H. E. *Macromolecules* **2007**, *40*, 8361–8366.
(68) Bandermann, F.; Witkowski, R. *Makromol. Chem.* **1986**, *187*, 2691–2696.
(69) Eggert, M.; Freitag, R. *J. Polym. Sci., Part A* **1994**, *32*, 803–813.
(70) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606–5655.