Group Transfer Polymerization of Acrylates Catalyzed by N-Heterocyclic Carbenes

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ABSTRACT: Group transfer polymerization (GTP) is an effective method for the synthesis of poly(methyl methacrylate) (pMMA) with controlled molecular weights and narrow polydispersities. Silyl ketene acetals initiate the polymerization of methyl methacrylate in the presence of either nucleophilic or Lewis acid catalysts. We report the use of N-heterocyclic carbenes (NHCs) as neutral nucleophilic catalysts for GTP of methyl methacrylate (MMA) and *tert*-butyl acrylate (TBA). For MMA, polymer molecular weights increase linearly with conversion and are predictable over a range of $[M]_0/[I]_0$ ratios. Polydispersities trend downward with conversion and approach 1.2 at >95% conversion. Significantly, NHCs were also shown to be effective for the controlled GTP of TBA, generating living polymers with predictable molecular weights, narrow molecular weight distributions ($M_w/M_n \leq 1.2$), and living chain ends, as illustrated by chain-extension experiments.

Introduction

Group transfer polymerization (GTP) is an efficient method for the controlled polymerization of acrylates and methacrylates at room temperature.[1−5] First reported in 1983 by Webster and Sogah,[1] GTP utilizes silyl ketene acetals as polymerization initiators in the presence of either nucleophilic or Lewis acid catalysts. In nucleophile-catalyzed GTP, silyl ketene acetals are activated by catalytic amounts of an anionic nucleophile such as bifluoride (HF_2^-),[1] difluoride (F_2^{2-}),[1,4] cyanide,[6,7] azide,[5] oxyanions,[8−10] or bioxyanions.[8,9,11]

The mechanism of nucleophilic GTP has stimulated considerable debate.[1−3,5,12−20] At the heart of this debate is the identity of the propagating species. In the original proposal,[1] the addition of fluoride was proposed to generate a hypervalent silicon intermediate[21] which coordinated the acrylate in an associative process to effect an intramolecular addition of the silyl enolate to the bound acrylate (Scheme 1, path a).[1−3,5,13−17] This hypothesis was questioned[18−20] on the basis of earlier studies of silyl enolates[22,23] and the behavior of anionic acrylate polymerization in the presence of silyl ketene acetals.[18,19] Quirk demonstrated the living polymerization of methacrylates with anionic initiators at room temperature in the presence of silyl ketene acetals and proposed that the rapid complexation of free enolate with the initiator generated a bis(enolato)siliconate.[18,19] Rate-determining breakdown of this complex generated the propagating enolate and 1 equiv of silyl ketene acetal (Scheme 1, path b). Kinetic studies demonstrating that the polymerization rate is inverse order in silyl ketene acetal is consistent with this proposal.[13]

Anionic catalysts perform admirably for methacrylates and are typically employed at very low concentrations, on the order of 0.1−1.0 mol % relative to initiator,[4] which enables these polymer solutions to be utilized directly without costly purification steps.[2] Nevertheless, nucleophilic catalysts are not as well-behaved for acrylates due to competitive enolization of the growing polymer and deprotonation reactions that lead to poor control over the molecular weight and chain-end fidelity.[24,25] To minimize these competitive processes, Lewis acid catalysts for GTP were introduced with the objective of enhancing monomer scope[3,26] and enabling control of polymer tacticity.[27−33] While the Lewis acid catalysts exhibit higher levels of control for acrylate polymerization, the higher catalyst concentrations required (typically on the order of 10−20% relative to initiator)[4] are a disadvantage of this approach.

Herein, we report the use of N-heterocyclic carbenes (NHCs) as neutral nucleophilic catalysts for the GTP of methacrylates and acrylates (Scheme 2).[34] N-Heterocyclic carbenes (NHCs) are stable singlet carbenes[35−38] that are useful both as ligands in organo-transition metal chemistry[37] and as nucleophilic organic catalysts.[39−42] The efficiency of N-heterocyclic carbenes as catalysts for the ring-opening polymerization of cyclic monomers[40,43−47] prompted us to investigate these complexes for group transfer polymerization of acrylates.[34,48]

Results and Discussion

GTP of Methyl Methacrylate. The carbene 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**)[49] was evaluated as a catalyst for the polymerization of methyl methacrylate (Table 1) and compared to the behavior of tris(dimethylamino)sulfur (trimethylsilyl)difluoride ($TASF_2SiMe_3$) under the conditions reported by Webster.[1] The carbene **1** is an effective catalyst; in the presence of the silyl ketene acetal initiator 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS, $[M]_0/[I]_0 = 35$), **1** catalyzes the polymerization of MMA in THF at room temperature to >95% conversion in 1 h to generate pMMA with a molecular weight $M_n = 4100$ and a polydispersity of $M_w/M_n = 1.72$ (Table 1, entry 2). Under comparable conditions, the activity of **1** is slightly lower, and the polydispersity is broader than that of a typical nucleophilic catalyst, $TASF_2SiMe_3$ (Table 1, entries 1 and 2).[1] Lower concentrations $[M]_0 = 1.2$ M resulted in a slower polymerization and a narrower PDI ($M_w/M_n = 1.14$), but this improvement came at the expense of control over molecular weight ($M_n = 7900$). Under optimal conditions $[C]_0 = 0.3$ mM and $[M]_0 = 2.2$ M (Table 1, entries 4 and 5), the carbene **1** exhibited excellent control to generate pMMA with polydispersities <1.35 and molecular weights up to 21 000 g/mol. Control experiments reveal that **1** does not initiate the polymerization of MMA in the absence of the silyl ketene acetal initiator.[50]

For the GTP of MMA catalyzed by **1**, the evolution of the molecular weight (M_n) and polydispersity as a function of MMA conversion (Figure 1) reveal that the experimentally determined

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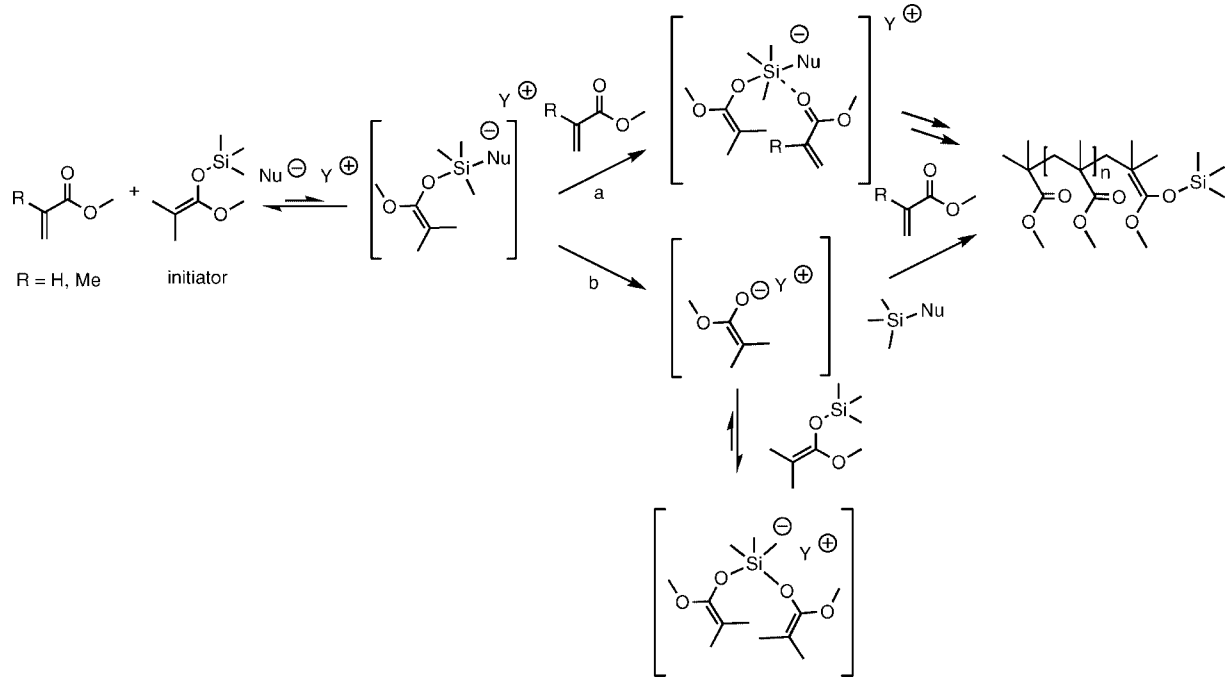
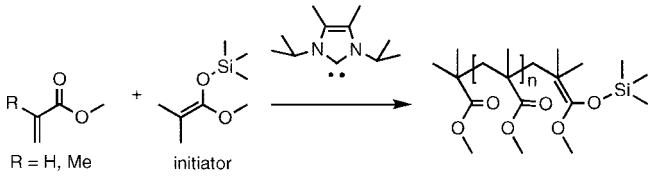
Scheme 1. Group Transfer Polymerization with Nucleophilic Catalysts



Scheme 2. N-Heterocyclic Carbene (NHC)-Catalyzed Group Transfer Polymerization of Acrylates



molecular weights are similar to that predicted by the starting concentration of monomer to initiator, but some systematic deviations are evident, particularly at low conversion. In the early stages of polymerization, M_n values are higher than predicted. In GTP studies by Bandermann, this observation was attributed to slow initiation relative to propagation.[9] This hypothesis is consistent with the trends observed in the molecular weight distribution as a function of conversion. Relatively broad polydispersities of 1.5−1.8 are observed at low conversion, as typically observed in polymerizations where initiation is slow relative to propagation.[51,52] These distributions drop precipitously to values in the range of 1.1−1.2 as statistical chain sampling progresses. Such trends in polydispersity are commonly observed in polymerizations involving reversible activation/deactivation equilibria.[51,52]

The kinetics of MMA polymerization catalyzed by **1**/MTS are complex and do not conform to first-order kinetics (Figure 2). The first-order kinetic plot for these polymerizations deviates from linearity; at low conversion, a relatively shallow slope indicative of slow initiation gives rise to a steeper more linear region as polymerization proceeds, indicative of an induction period.[9,13] The initial rate of polymerization was studied as a function of the initial monomer concentration and indicates that the initial rates double when the initial monomer concentration doubles (Supporting Information).

The most notable feature of Figure 2 is the dependence of polymerization rate on the concentration of silyl ketene acetal initiator. The polymerization rate increases dramatically as the concentration of initiator decreases. This inverse-order dependence in initiator is consistent with the studies of Müller[13,15] and Quirk.[18,19] Quirk had proposed that nucleophilic catalysts generate free enolates that react with silyl ketene acetals to generate a bis(enolato)siliconate;[18,19] rate-determining breakdown of the silicate leads to formation of the propagating enolate and 1 equiv of silyl ketene acetal (Scheme 1). The reversible formation of dormant (or less active) bis(enolato)siliconates would lead to inhibition by initiator, as observed. Furthermore, the induction period observed at low conversion can be understood by a reduced concentration of propagating chains as a result of enolate trapping by MTS. On the basis of these observations, we propose (Scheme 3) that the carbene **1** activates the silyl ketene acetal to generate free enolates, which reversibly complex to silyl enolates (either the initiator at low conversion or silyl enolate chain ends at higher conversion). A similar mechanism was proposed for the Mukaiyama aldol reaction catalyzed by N-heterocyclic carbenes.[53,54] We favor a dissociative mechanism involving an enolate/trimethylsilyl imidazolium[55] ion pair, as the tacticity of PMMA derived from the sterically demanding carbene **1** (*mm*/*mr*/*rr* = 0.09/0.46/0.45) is similar to that obtained from $TASF_2SiMe_3$ (*mm*/*mr*/*rr* = 0.06/0.43/0.51), and it is unlikely that the steric demands of **1** would accommodate an associative mechanism where the imidazolium enolsilicate binds to acrylate to effect an intramolecular Michael addition.[48]

GTP of *tert*-Butyl Acrylate. The N-heterocyclic carbene **1** is also a remarkably effective catalyst for the group transfer polymerization of acrylates (Table 2). The polymerization of *tert*-butyl acrylate (TBA) with **1** (Table 2, entries 2−5) proceeds rapidly at room temperature in THF to generate poly(TBA) with narrow polydispersities ($M_n/M_w < 1.2$). Catalyst activity remains high down to a concentration of 10 μM with a calculated turnover number in the range of 1×10^5 (entry 4). Furthermore, the monomer-to-initiator ratio can be adjusted to target higher molecular weights approaching $M_n = 20\,000$ g/mol.

These results are noteworthy as typical nucleophilic catalysts are ineffective for the group transfer polymerization of acrylates.[5,7,56−59] In the GTP of TBA catalyzed by $TASF_2SiMe_3$ at room temperature, uncontrolled polymerization is observed as evidenced by low monomer conversion and a bimodal molecular weight distribution (entry 1). Nucleophilic catalysis is typically

Table 1. Group Transfer Polymerization of Methyl Methacrylate in THF at Room Temperature[a]

entry	[F⁻] (mM)	[NHC] (mM)	$[I]_0$ (mM)	$[M]_0$ (M)	$[M]_0/[I]_0$	time (h)	TON[b]	% conv	M_n predicted	M_n (GPC)[c]	PDI
1	0.3	0	160	5.6	35	0.1	17700	>95	3300	6000	1.32
2	0	0.3	160	5.6	35	1	17700	>95	3300	4100	1.72
3[d]	0	0.1	32	1.2	40	17	11400	>95	3600	7900	1.14
4	0	0.3	38	2.2	57	1.6	5900	81	4600	4100	1.35
5[e]	0	0.3	9.4	2.2	230	0.8	6700	91	21 300	18900	1.18
6	0	0.3	0	5.6		17	0	0	0		

[a] $[F^-] = TASF_2SiMe_3$; NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; I = 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene. [b] Turnover number calculated from ($[M]_0/[catalyst]_0$) × conversion. [c] M_n determined by GPC calibrated to pMMA standards. V_{total} = 5 mL for entries 1−4. [d] V_{total} = 23 mL. [e] V_{total} = 13 mL.

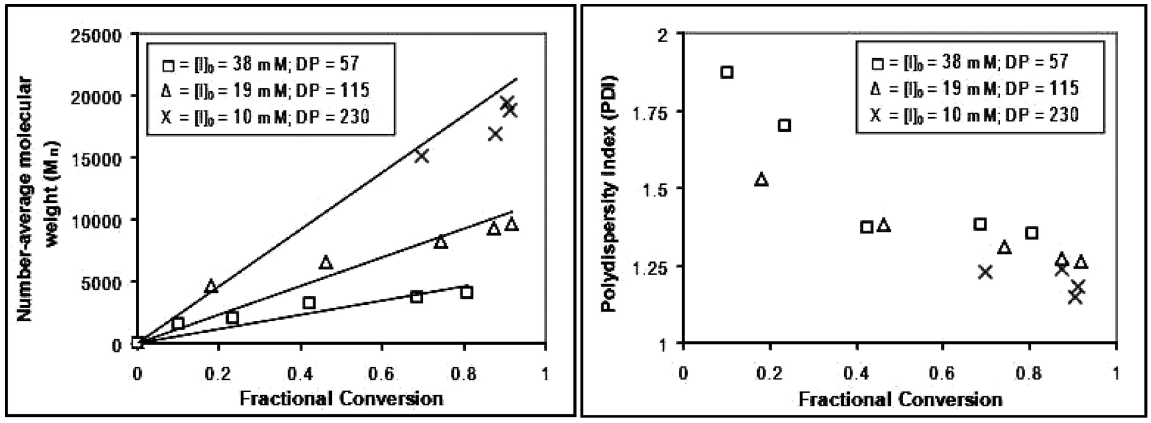


Figure 1. Dependence of polymer molecular weight (M_n) and polydispersity (PDI) on monomer conversion for GTP of MMA catalyzed by NHC **1**, as determined by GPC with pMMA calibration. DP = targeted degree of polymerization based on $[M]_0/[I]_0$ ratio. V_{total} for each run is 13 mL, with $[I]_0$ = 38, 19, and 10 mM for DP = 57, 115, and 230, respectively. $[M]_0$ = 2 M, $[NHC]_0$ = 0.3 mM, T = 25 °C, THF. Solid line represents theoretical M_n based on $[M]_0/[I]_0$ ratio.

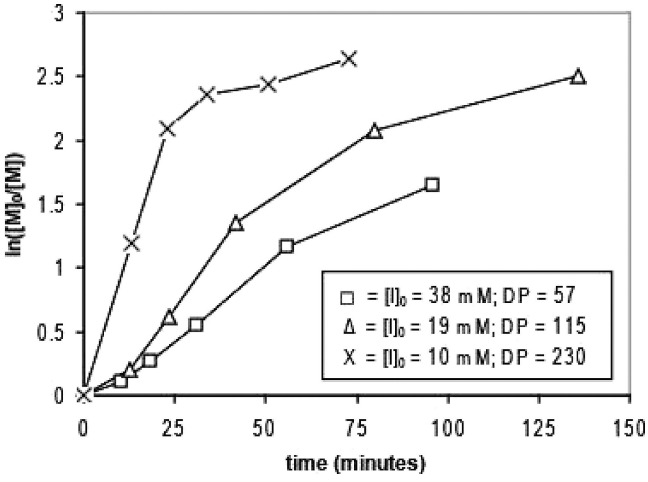


Figure 2. First-order kinetic plots for GTP of methyl methacrylate using NHC catalyst 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; I = 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS); DP = $[M]_0/[I]_0$; [NHC] = 0.3 mM; $[M]_0$ = 2 M, T = 25 °C, THF with V_{total} = 13 mL.

less effective for GTP due to a variety of competing processes[60] that can make GTP of acrylates difficult to control. Specific examples include enolization and branching along the polymer backbone,[57] deprotonation at the α-position on the monomer to yield a ketene and alkoxide salt,[24] and backbiting of the propagating chain end.[25] The higher selectivity in the presence of **1** may be a consequence of the stability of the trimethylsilylimidazolium[55] counterion and the low concentration of enolates modulated by the reversible formation of bis(enolato)-siliconates.

Control experiments reveal that in the absence of initiator a catalytic amount of NHC **1** initiates polymerization of TBA that reaches 25% monomer conversion after 16 h (entry 6). The background process may result from monomer deprotonation as proposed by Börner and Heitz[24] or addition of the carbene directly to the monomer to generate a zwitterionic enolate initiator.[61] The M_n of the isolated polymer is similar to the value predicted if the NHC were to behave as an initiator. Silyl ketene acetal also initiates a slow and uncontrolled polymerization in the absence of catalyst, perhaps due to initiation off the borosilicate glass surface as observed for MMA. After 22 h, 83% of the monomer is consumed with poor initiator efficiency and broad distribution of molecular weights. Given the rates of these reactions compared to the catalytic reactions and the absence of high molecular weight fractions in the GPC analysis of the crude polymer obtained in the presence of both **1** and MTS, it is unlikely that these background processes are competitive with the catalytic GTP in the presence of **1**.

Chain extension experiments also provide evidence for living behavior (Figure 3). Addition of a second TBA charge to a sample of poly(TBA) (M_n = 4000, M_w/M_n = 1.13) prepared from **1**/MTS resulted in an increase in molecular weight of the macroinitiator. GPC analysis of the resulting polymer (M_n = 10 500, M_w/M_n = 1.18) gave no evidence of a low molecular weight shoulder or substantial broadening of molecular weight distribution. The end group fidelity of the pMMA chains is also supported by ^{1}H NMR studies of the chain ends. In d_8-THF solution, a sharp singlet for the silyl ketene acetal initiator is observed at 0.21 ppm. As polymerization begins, this singlet gives rise to a broadened singlet that is shifted slightly upfield to 0.24 ppm. At full conversion, the integration of this new singlet relative to those of the formed pMMA is consistent with the targeted degree of polymerization. This singlet persists up to 4 days following completion of the polymerization and reacts quantitatively with 1 equiv of benzyl alcohol to generate benzyl trimethylsilyl ether.

Block copolymers can also be prepared with this strategy. Addition of TBA to a p(MMA) prepared by **1**/MTS (M_n = 6976, M_w/M_n = 1.18) generated a p(MMA)-*b*-p(TBA) block copoly-

Scheme 3. Proposed Mechanism for NHC-Catalyzed GTP of Acrylates

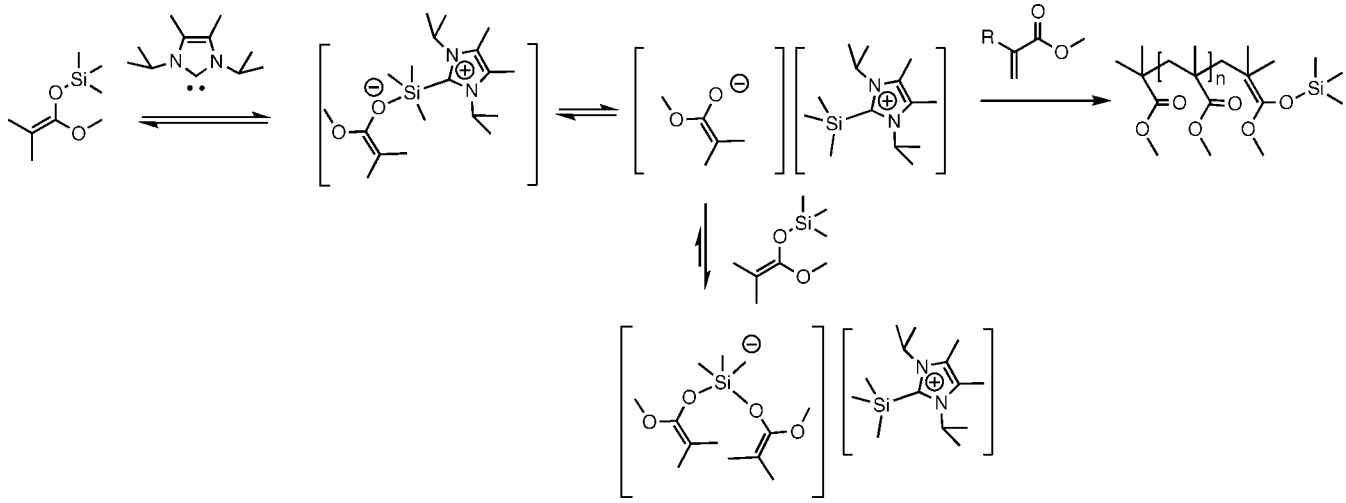


Table 2. Group Transfer Polymerization of *tert*-Butyl Acrylate in THF at Room Temperature[a]

entry	$[F^-]$ (mM)	[NHC] (mM)	$[I]_0$ (mM)	$[M]_0$ (M)	$[M]_0/[I]_0$	time (h)	TON[b]	conv (%)	M_n pred	M_n (GPC)[c]	PDI
1	0.5	0	150	4	30	22	1600	20	800	bimodal	
2	0	0.4	150	4	30	0.1	9500	>95	3700	7800	1.20
3	0	0.1	32	1	30	0.1	9500	>95	3700	9800	1.14
4	0	0.01	38	1.5	40	1	143000	>95	5100	6100	1.16
5	0	0.1	8.8	1.5	170	0.3	14300	>95	20800	16300	1.16
6	0	0.4	0	4		16	2500	25	320500[d]	205100	1.47

[a] $[F^-] = TASF_2SiMe_3$; NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; I = 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene. $V_{total} = 5$ mL for entries 1−4; for entries 5−7 $V_{total} = 13$ mL. [b] Turnover number calculated from $([M]_0/[catalyst]_0) \times$ conversion. [c] M_n determined by GPC calibrated to pMMA standards. [d] M_n predicted if NHC behaves as an initiator.

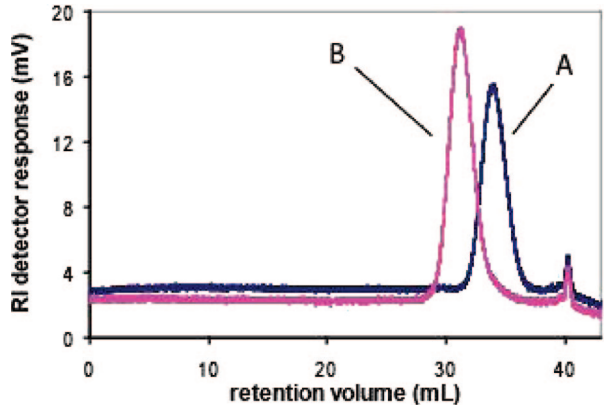


Figure 3. Chain extension of poly(TBA) with addition of a second monomer charge. (A) $M_n = 4000$; PDI = 1.13; >95% conversion after 20 min. $[M]_0 = 1.4$ M, $[I]_0 = 50$ mM, [NHC] = 0.2 mM in 10 mL of THF. (B) $M_n = 10\,500$; PDI = 1.18; >95% conversion after 40 min.

mer of $M_n = 11\,800$ with a monomodal molecular weight distribution ($M_w/M_n = 1.14$). However, attempts to generate a similar block copolymer by addition of MMA to a p(TBA) ($M_n = 4974$, $M_w/M_n = 1.11$) generated the p(MMA)-*b*-p(TBA) block copolymer ($M_n = 10\,900$, $M_w/M_n = 1.32$) contaminated with a small amount of the unreacted p(TBA), as evidenced by a small shoulder in the GPC trace of the block copolymer.

In conclusion, N-heterocyclic carbenes are effective neutral nucleophilic catalysts for the group transfer polymerization of methyl methacrylate and *tert*-butyl acrylate. High activities typical of nucleophilic GTP catalysts are observed, but in contrast to typical anionic nucleophilic catalysts the neutral N-heterocyclic carbenes are effective for the controlled polymerization of acrylate monomers. Furthermore, this system demonstrates characteristics of a living polymerization, where reversible activation/deactivation equilibria involving dormant bis(enolato)siliconates modulate the concentration of the propagating enolates.

Experimental Section

General Methods. Tetrahydrofuran was dried with heating over sodium benzophenone ketyl and collected by vacuum transfer. Methyl methacrylate (Acros, 99%, stabilized with 10−20 ppm MEHQ) was washed twice with 5% aqueous NaOH and twice with water and allowed to stand over $CaCl_2$ pellets for 1 h. The dried monomer was stirred over calcium hydride for a minimum of 16 h, degassed by three freeze−pump−thaw cycles, collected by vacuum transfer at room temperature, and stored under nitrogen at −20 °C. Tris(dimethylamino)sulfur (trimethylsilyl)difluoride was purchased from Aldrich, stored at −30 °C in a drybox, and used as received. 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS) was purchased from Aldrich Chemical and degassed by three freeze−pump−thaw cycles prior to use. 1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**) was prepared as described by Kuhn et al.[49] All polymerizations were conducted in a drybox under a nitrogen atmosphere at room temperature with less than 3 ppm oxygen present.

Polymer Characterization. Gel permeation chromatography (GPC) using tetrahydrofuran mobile phase and poly(methyl methacrylate) calibration were used to determine number-average molecular weight (M_n) and polydispersity (PDI) of all isolated polymers. Data were acquired on a Viscotek GPC equipped with 5 μm Waters columns (300 mm × 7.7 mm) connected in series with increasing pore size (10, 100, 1000, 10^5, 10^6 Å). A Viscotek S3580 refractive index detector and Viscotek GPCmax autosampler were employed at a flow rate of 1 mL/min at 35 °C.

Polymerization of MMA Using Fluoride Catalyst. Using the original conditions of Webster et al.,[1] tris(dimethylamino)sulfur (trimethylsilyl)difluoride ($TASF_2SiMe_3$, Aldrich, 3.4 mg, 0.01 mmol) was dissolved in 1 mL of THF. From this solution, 0.1 mL was withdrawn and added to a vial containing 2.0 mL of THF equipped with a magnetic stir bar. To this vial was added MTS (0.15 mL, 0.74 mmol) and 0.2 mL of toluene (internal standard).

With stirring, 3.0 mL (28.3 mmol) of methyl methacrylate was added over 3 min at room temperature. Immediate bubbling of the reaction mixture and marked increase in solution viscosity were observed. After 10 min bubbling had ceased, and the reaction was quenched with excess methanol. The precipitated polymer was washed three times with 5 mL portions of methanol. Residual solvent was removed under vacuum, yielding poly(methyl methacrylate), 1.56 g, 55.1%. ^{1}H NMR 500 MHz ($CDCl_3$): δ (ppm) = 0.81 [br s, backbone CH_3 *rr* triad, 51.2%], 1.00 [br s, backbone CH_3 *mr* triad, 43.3%], 1.2 [br s, backbone CH_3 *mm* triad, 5.6%], 1.41 [br m, backbone CH_2 of varying stereochemistry], 1.76−2.06 [br m, backbone CH_3 tetrads of varying stereochemistry], 3.58 [br s, OCH_3]. GPC (pMMA calibration): M_n = 6019, PDI = 1.32.

Polymerization of MMA Using NHC Catalyst. NHC **1** (1.8 mg, 0.01 mmol) was dissolved in 1 mL of THF. From this solution, 0.1 mL was withdrawn and added to a vial containing 1.9 mL of THF equipped with a magnetic stir bar. To this vial was added MTS (0.17 mL, 0.84 mmol). With stirring, 3.0 mL (28.3 mmol) of methyl methacrylate was added over 3 min at room temperature. Within 10 min, bubbling of the reaction mixture and increased solution viscosity were observed. After 10 min bubbling had ceased and the reaction was quenched with excess methanol. The precipitated polymer was washed three times with 5 mL portions of methanol. Residual solvent was removed under vacuum, yielding poly(methyl methacrylate), 2.1 g, 74.2%. ^{1}H NMR 500 MHz ($CDCl_3$): δ (ppm) = 0.81 [br s, backbone CH_3 *rr* triad, 44.9%], 0.99 [br s, backbone CH_3 *mr* triad, 46.1%], 1.2 [br s, backbone CH_3 *mm* triad, 9.0%], 1.41 [br m, backbone CH_2 of varying stereochemistry], 1.73−2.18 [br m, backbone CH_3 tetrads of varying stereochemistry], 3.58 [br s, OCH_3]. GPC (pMMA calibration): M_n = 4098, PDI = 1.72.

Kinetics. MMA was purified as described in the General Methods section and titrated with tri-*n*-octylaluminum (0.3 M solution in heptane) until the solution was a pale yellow color. Monomer was collected from this solution by vacuum transfer and used immediately. In a typical experiment, NHC **1** (2.4 mg, 0.013 mmol) was weighed into a vial and dissolved in 0.1 mL of d_8-THF. To a J-Young NMR tube was added 0.8 mL of d_8-THF, 2 μL of the NHC stock solution, 5.2 μL of the MTS initiator, and 5.2 μL of toluene (internal standard). To initiate polymerization, 0.1 mL of MMA was added. Monomer conversion was monitored by ^{1}H NMR at room temperature by integrating olefinic proton resonances against those of the toluene internal standard. At the end of the run, the experiment was repeated holding all conditions constant, except 0.2 mL of MMA was added to initiate polymerization.

Kinetics of of MMA Polymerization. Representative procedure for $[M]_0/[I]_0$ = 57. NHC **1** (1.8 mg, 0.01 mmol) was dissolved in 1 mL of THF. From this solution, 0.1 mL was withdrawn and added to a 20 mL vial containing 9 mL of THF, 1 mL of toluene (internal standard), and a magnetic stir bar. To this vial was added MTS (0.1 mL, 0.49 mmol). With stirring, 3.0 mL (28.3 mmol) of methyl methacrylate was added over 30 s. At predetermined intervals, 1 mL aliquots of the reaction mixture were removed for analysis. Of these samples, 20 μL was diluted in 0.8 mL of $CDCl_3$ and conversion determined by ^{1}H NMR integration using toluene as an internal standard. The remainder of each sample was quenched with excess methanol, and solvent was removed under vacuum. To target higher degrees of polymerization, $[I]_0$ was systematically reduced. For $[M]_0/[I]_0$ = 115 and 230, 0.05 and 0.025 mL of MTS were added, respectively.

Poly(*tert*-butyl acrylate)-*block*-*co*-poly(methyl methacrylate). A stock solution of catalyst was prepared by dissolving 5.8 mg of **1** in 1 mL of THF. Of this stock solution, 0.1 mL was added to a 20 mL glass vial equipped with a magnetic stir bar containing 10 mL of THF. To this vial was also added 0.1 mL of neat MTS. With stirring at room temperature, *tert*-butyl acrylate (3 mL, 20.5 mmol) was added dropwise over 8 min. After 1 h, ^{1}H NMR analysis demonstrated quantitative monomer conversion. A 1 mL aliquot of the reaction mixture was retained for analysis (95% conversion, M_n = 4974, M_w/M_n = 1.11). To this reaction mixture, 3 mL (28.3 mmol) of methyl methacrylate was added over 5 min. After 20 min, gentle boiling of the reaction mixture was observed, and after 1 h ^{1}H NMR analysis demonstrated only a trace amount of residual monomer. The reaction mixture was quenched with excess methanol and solvent removed under vacuum. Residual solvent was removed after 2 days in a vacuum oven set to 80 °C and 30 mmHg. Yield: 3.43 g. ^{1}H NMR assignments based on similar work by Kriz et al.[62] ^{1}H NMR 400 MHz ($CDCl_3$): δ (ppm) = 0.82 [br s, backbone CH_3 *rr* triad, pMMA block], 1.01 [br s, backbone CH_3 *mr* triad, pMMA block], 1.20 [br s, backbone CH_3 *mm* triad, pMMA block], 1.43 [br s, *tert*-butyl side chains on p-tBuA block], 1.53 [br s, CH_2 of p-tBuA block], 2.1−1.8 [CH_2 tetrads of different tacticity on pMMA block], 2.22 [α-CH of p-tBuA block], 3.59 [br s, OCH_3 side chains on pMMA block], 3.64 [m, OCH_3 end group signal from MTS]. GPC: M_n = 10 931, M_w/M_n = 1.32.

Poly(methyl methacrylate)-*block*-*co*-poly(*tert*-butyl acrylate). Analogous to the procedure above, initiated from pMMA (95% conversion, M_n = 6976, M_w/M_n = 1.18). Yield: 2.08 g. GPC: M_n = 11 812, M_w/M_n = 1.14.

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Supporting Information Available: Representative GPC traces, kinetic data, and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706–5708.
(2) Webster, O. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2855–2860.
(3) Webster, O. W. S. D Y. Group transfer and aldol group transfer polymerization. In *Comprehensive Polymer Science*; Pergamon: New York, 1989; Vol. *4*, pp 163−169.
(4) Aida, T. Group Transfer Polymerization. In *Catalysis in Precision Polymerization*; Kobayashi, S., Ed.; Wiley: New York, 1997; pp 323−335.
(5) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473–1488.
(6) Bandermann, F.; Speikamp, H. D. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 335–339.
(7) Schubert, W.; Bandermann, F. *Makromol. Chem.* **1989**, *190*, 2721–2726.
(8) Brittain, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 7440–7444.
(9) Schmalbrock, U.; Bandermann, F. *Makromol. Chem.* **1993**, *194*, 2543–2551.
(10) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4034–4041.
(11) Gnaneshwar, R.; Sivaram, S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2514–2531.
(12) Webster, O. W. *J. Macromol. Sci., Chem.* **1994**, *A31*, 927–935.
(13) Mai, P. M.; Muller, A. H. E. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 99–107.
(14) Mai, P. M.; Muller, A. H. E. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 247–253.
(15) Muller, A. H. E. *Macromolecules* **1994**, *27*, 1685–1690.
(16) Muller, A. H. E.; Litvinenko, G.; Yan, D. Y. *Macromolecules* **1996**, *29*, 2339–2345.
(17) Muller, A. H. E.; Litvinenko, G.; Yan, D. Y. *Macromolecules* **1996**, *29*, 2346–2353.
(18) Quirk, R. P.; Bidinger, G. P. *Polym. Bull.* **1989**, *22*, 63–70.
(19) Quirk, R. P.; Ren, J. *Macromolecules* **1992**, *25*, 6612–6620.
(20) Jenkins, A. D. *Eur. Polym. J.* **1991**, *27*, 649–649.
(21) Chuit, C.; Corriu, R. J. P.; Reye, C. *J. Organomet. Chem.* **1988**, *358*, 57–66.
(22) Noyori, R.; Nishida, I.; Sakata, J.; Nishizawa, M. *J. Am. Chem. Soc.* **1980**, *102*, 1223–1225.
(23) Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598–1608.
(24) Borner, H. G.; Heitz, W. *Macromol. Chem. Phys.* **1998**, *199*, 1815–1820.
(25) Brittain, W. J.; Dicker, I. B. *Macromolecules* **1989**, *22*, 1054–1057.
(26) Hertler, W. R.; Sogah, D. Y.; Webster, O. W.; Trost, B. M. *Macromolecules* **1984**, *17*, 1415–1417.

(27) Tomasi, S.; Weiss, H.; Ziegler, T. *Organometallics* **2006**, *25*, 3619–3630.
(28) Holscher, M.; Keul, H.; Hocker, H. *Macromolecules* **2002**, *35*, 8194–8202.
(29) Caporaso, L.; Gracia-Budria, J.; Cavallo, L. *J. Am. Chem. Soc.* **2006**, *128*, 16649–16654.
(30) Collins, S.; Ward, D. G.; Suddaby, K. H. *Macromolecules* **1994**, *27*, 7222–7224.
(31) Deng, H. S.; Shiono, T.; Soga, K. *Macromolecules* **1995**, *28*, 3067–3073.
(32) Giardello, M.; Yamamoto, Y.; Brard, L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 3276–3277.
(33) Zhang, Y.; Chen, E. Y. X. *Macromolecules* **2008**, *41*, 36–42.
(34) A preliminary communication of this work has appeared. Scholten, M. D.; Hedrick, J. L.; Waymouth, R. M. *Polym. Prepr.* **2007**, *48*, 167–168.
(35) Wanzlick, H. W. *Angew. Chem., Int. Ed.* **1962**, *1*, 75–80.
(36) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–91.
(37) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309.
(38) Arduengo, A. J. *Acc. Chem. Res.* **1999**, *32*, 913–921.
(39) Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719–3726.
(40) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* **2007**, *107*, 5813–5840.
(41) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606–5655.
(42) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951–961.
(43) Culkin, D. A.; Jeong, W. H.; Csihony, S.; Gomez, E. D.; Balsara, N. R.; Hedrick, J. L.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2627–2630.
(44) Jeong, W.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2007**, *129*, 8414–8415.
(45) 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.
(46) Lohmeijer, B. G. G.; Dubois, G.; Leibfarth, F.; Pratt, R. C.; Nederberg, F.; Nelson, A.; Waymouth, R. M.; Wade, C.; Hedrick, J. L. *Org. Lett.* **2006**, *8*, 4683–4686.
(47) Rodriguez, M.; Marrot, S.; Kato, T.; Sterin, S.; Fleury, E.; Baceiredo, A. *J. Organomet. Chem.* **2007**, *692*, 705–708.
(48) While this manuscript was under review, related studies of NHC-catalyzed GTP was reported by Gnanou and Taton: Raynaud, J.; Ciolino, A.; Baceiredo, A.; Destarac, M.; Bonnette, F.; Kato, T.; Gnanou, Y.; Taton, D. *Angew. Chem.* **2008**, *120*, 5470–5473.
(49) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561–562.
(50) Control experiments reveal a slow (3% after 22 h) and uncontrolled polymerization of MMA with MTS in the absence of carbene (M_n = 115 000). The absence of a detectable high molecular weight fraction in the GPC analysis of the polymers generated in the presence of carbene 1 indicates that this process is not competitive with the catalyzed process.
(51) Litvinenko, G.; Muller, A. H. E. *Macromolecules* **1997**, *30*, 1253–1266.
(52) Matyjaszweski, K. Overview: Fundamenals of Controlled/Living Radical Polymerization. In *Controlled Radical Polymerization*; Matyjaszweski, K., Ed.; ACS Symposium Series 695; American Chemical Society: Washington, DC, 1998.
(53) Song, J.; Tan, Z.; Reeves, J. T.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2007**, *9*, 1013–1016.
(54) Song, J.; Tan, Z.; Reeves, J. T.; Fandrick, D. R.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2008**, *10*, 877–880.
(55) Kuhn, N.; Kratz, T.; Blaser, D.; Boese, R. *Chem. Ber.* **1995**, *128*, 245–250.
(56) Masar, B.; Vlcek, P.; Kriz, J.; Kovarova, J. *Macromol. Chem. Phys.* **1994**, *195*, 289–302.
(57) Masar, B.; Vlcek, P. *Macromol. Chem. Phys.* **1994**, *195*, 671–678.
(58) Schubert, W.; Sitz, H. D.; Bandermann, F. *Makromol. Chem.* **1989**, *190*, 2193–2201.
(59) Schubert, W.; Bandermann, F. *Makromol. Chem.* **1989**, *190*, 2161–2171.
(60) Baskaran, D. *Prog. Polym. Sci.* **2003**, *28*, 521–581.
(61) Johnston, D. S. *Adv. Polym. Sci.* **1982**, *42*, 51–106.
(62) Kriz, J.; Masar, B.; Vlcek, P. *Makromol. Chem.* **1993**, *194*, 1435–1444.

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