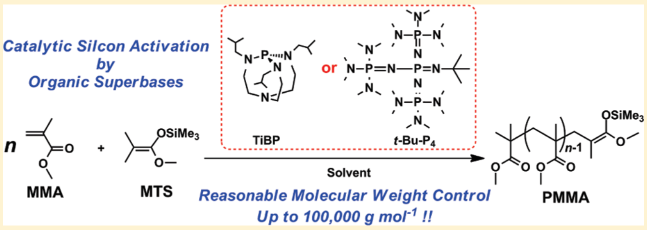
Macromolecules
ARTICLE
pubs.acs.org/Macromolecules

Organic Superbase as an Efficient Catalyst for Group Transfer Polymerization of Methyl Methacrylate

Toyoji Kakuchi,* Yougen Chen, Junsuke Kitakado, Kota Mori, Keita Fuchise, and Toshifumi Satoh

Division of Biotechnology and Macromolecular Chemistry, Faculty of Engineering, Hokkaido University, Sapporo, 060-8628, Japan

ABSTRACT: Organic superbases, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), proazaphosphatranes ($P(RNCH_2CH_2)_3N$: R = CH_3, TMP; R = *i*-Bu, TiBP), and phosphazene bases (1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-$2\Lambda^5,4\Lambda^5$-catenadi(phosphazene), *t*-Bu-P_2; 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-$2\Lambda^5,4\Lambda^5$-catenadi(phosphazene), *t*-Bu-P_4) were employed to determine the catalytic activity in the group transfer polymerization (GTP) of methyl methacrylate (MMA). Among the superbases used, TiBP and *t*-Bu-P_4 effectively catalyzed the polymerization to afford poly(methyl methacrylate) (PMMA) with controlled molecular weight and narrow polydispersity. In particular, the molecular weight of the PMMA obtained from the *t*-Bu-P_4-catalyzed GTP was up to 109 600 g mol^{-1}. Only one series of peaks was observed in the MALDI−TOF MS spectra of the PMMAs obtained from the TiBP- and *t*-Bu-P_4-catalyzed GTPs, indicating that both polymerizations proceeded without any side reactions. A postpolymerization experiment further supported the living nature of the TiBP- and *t*-Bu-P_4-catalyzed GTPs of MMA. Furthermore, a mechanistic study of the TiBP- and *t*-Bu-P_4-catalyzed GTPs of MMA was attempted by determining the stereoregularity of the obtained PMMAs and obtaining a series of NMR spectra for the equimolar mixtures of MTS and TiBP or *t*-Bu-P_4.



INTRODUCTION

Recent developments in metal-free catalysis, so-called organocatalysis, have rapidly been innovating a wide range of organic reactions, such as the Friedel−Crafts reaction,[1−3] the Mukaiyama aldol reaction,[4] the aza-Henry reaction,[5,6] the Diels−Alder reaction,[7−9] and the Morita−Baylis−Hillman reaction,[10,11] without the aid of metal-based catalysts. Organocatalysis has provided not only a revision of the well-established organic reactions but also conceptually and synthetically new organic reactions. However, the metal-free approach is assumed to be an important subject not only for organic synthesis but also for polymer chemistry[12−15] because metallic residues derived from metallic catalysts are difficult to remove from the polymer materials,[16−18] which has prevented the practical use of polymer materials for biomedical[19] and electronic applications.[20] Hence, it is of great importance to further explore the potential of organocatalysis that is suitable for polymer synthesis.

Organic bases are one of the important organocatalysts for synthetic chemistry and have been developed to optimize the basicity and to reduce the nucleophilicity, thus leading to various new synthetic methodologies. In particular, Verkade et al. and Schwesinger et al. established a new category of organic superbases, such as proazaphosphatranes[21,22] and phosphazene bases.[23−25] Nucleophilicity of these bases are substantially lower than that of organometallic bases. The strong basicity and low nucleophilicity allow organic superbases to be very promising organocatalysts for polymer syntheses. In fact, various types of organic bases have been used in polymer synthesis. For example, Hedrick et al. reported that conventional organic bases, such as 4-dimethylaminopyridine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), were effective for the living ring-opening polymerization (ROP) of cyclic monomers.[26−28] In addition, Müller et al. reported that a phosphazene base, *t*-Bu-P_4, could promote the ROP of ethylene oxide.[29] Moreover, the combinations of alcohol derivatives and phosphazene bases have been reported to promote the ROP of strained cyclic monomers including octamethylcyclotetrasiloxane,[30] lactide, and δ-valerolactone.[31,32] However, recent advances in organic superbase chemistry revealed that proazaphosphatranes and phosphazene bases have not only high Brønsted basicity but also silicon activation ability.[33−35] Verkade et al. and Kondo et al. have independently reported that proazaphosphatranes and phosphazene bases could activate organosilicon compounds to catalyze the Mukaiyama aldol reaction and related reactions based on an interaction between a silyl group and the bases.[36−38] Proazaphosphatranes and phosphazene bases were expected to be applicable to group transfer polymerization (GTP) because the mechanism of the Mukaiyama aldol reaction is similar to that of the Mukaiyama−Michael reaction[39] that is extensively accepted to be the initiating and propagation reactions of GTP.[40−49] However, the silicon activation ability of proazaphosphatranes and phosphazene bases has never been examined in synthetic polymer chemistry while the Brønsted basicity of the organic superbases was revealed to be efficient for the ROP of cyclic monomers (vide supra).[30−32] In addition,

Received: December 14, 2010
Revised: May 14, 2011
Published: May 26, 2011

Scheme 1. GTP of MMA Mediated by Superbases Such as DBU, Proazaphosphatranes (TMP and TiBP), and Phosphazene Bases (t-Bu-P$_2$ and t-Bu-P$_4$)

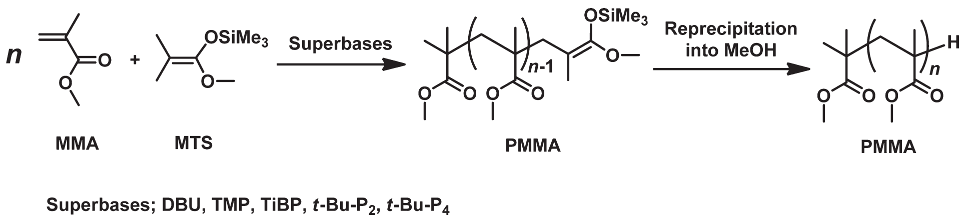


Table 1. GTP of MMA with MTS as the Initiator and Superbases as the Catalyst at 25 °C [a]

run	catalyst	solvent	time (h)	$[\text{catalyst}]_0/[\text{MTS}]_0$	convn (%)[b]	$M_{n,\text{theor}}$ (g mol^{-1})[c]	M_n (g mol^{-1})[d]	M_w/M_n[d]
1	DBU	THF	1.0	0.1	6.9	790	4400	1.43
2	DBU	toluene	1.0	0.1	0	-	-	-
3	TMP	THF	1.0	0.05	21.9	2290	6600	1.48
4	TMP	toluene	1.0	0.05	0	-	-	-
5	TiBP	THF	1.0	0.01	>99	10 100	12 700	1.04
6	TiBP	toluene	1.0	0.01	77.1	7820	22 800	1.35
7	t-Bu-P$_2$	THF	1.0	0.05	0	-	-	-
8	t-Bu-P$_2$	toluene	1.0	0.05	0	-	-	-
9	t-Bu-P$_4$	THF	1.0	0.01	>99	10 100	11 100	1.45
10	t-Bu-P$_4$	toluene	0.5	0.01	>99	10 100	10 200	1.17

[a] $[\text{MMA}] = 2.0$ mol L^{-1}; $[\text{MMA}]_0/[\text{MTS}]_0 = 100$. [b] Determined by ^{1}H NMR in CDCl$_3$. [c] Calculated as follows: $M_{n,\text{theor}} = ([\text{MMA}]_0/[\text{MTS}]_0) \times \text{convn} \times (\text{MW of MMA}) + (\text{MW of MTS}_{\text{residual}} = 102.13)$. [d] Determined by SEC in THF using PMMA standards.

applications of organocatalysts to vinyl polymerization are still limited in several examples of anionic polymerization[50,51] and GTP,[52−62] while organocatalysts have been intensively applied to ROPs.[12,13]

Therefore, we turned our attention to evaluating the scope and limit of the organic superbases with low nucleophilicity, i.e., proazaphosphatranes and phosphazene bases, as the organocatalyst for the GTP of MMA in order to investigate their silicon activation ability. In this article, we employed DBU, proazaphosphatranes ($\text{P(RNCH}_2\text{CH}_2)_3\text{N}$: R = CH$_3$, TMP; R = i-Bu, TiBP) and phosphazene bases (1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2Λ^5,4Λ^5-catenadi(phosphazene), t-Bu-P$_2$; 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene), t-Bu-P$_4$) in order to clarify the effect of the basicity and structure of the organic superbases on the GTP process (Scheme 1).This article describes (1) the evaluation and optimization of the proazaphosphatranes and phosphazene bases as catalysts for the GTP of MMA, and (2) a mechanistic insight into the TiBP- and t-Bu-P$_4$-catalyzed GTPs of MMA.

EXPERIMENTAL SECTION

Materials. Toluene (>99.5%), tetrahydrofuran (THF, > 99.5%), dichloromethane (CH$_2$Cl$_2$, > 99%), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from the Kanto Chemical Co., Inc. Toluene was distilled over CaH$_2$, degassed, and then distilled under an argon atmosphere over LiAlH$_4$ and stored under an argon atmosphere. THF was distilled from sodium benzophenone ketyl. DBU was distilled over CaH$_2$. 2,8,9-Trimethyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane (TMP), 2,8,9-triisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane (TiBP) (>97%), and the phosphazene bases, 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2Λ^5,4Λ^5-catenadi(phosphazene) (t-Bu-P$_2$) (2.0 mol L^{-1} in THF) and 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino) phosphoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene) (t-Bu-P$_4$) (1.0 mol L^{-1} in hexane), were available from the Sigma-Aldrich Chemicals Co. TiBP was distilled under an argon atmosphere prior to use. 1-Methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS), methyl methacrylate (MMA), and benzoic acid were purchased from the Tokyo Kasei Kogyo Co., Ltd. MTS was used after distillation under reduced pressure. MMA was used after distillation from CaH$_2$. Tetrahydrofuran-d_8 (THF-d_8, 99.5+ atom% D) and toluene-d_8 (99.5 atom % D) were purchased from Acros organics, and distilled from CaH$_2$ by trap-to-trap technique. For the determination of the stereoregularity of the obtained poly(methyl methacrylate) (PMMA), the obtained PMMA was purified using preparative size exclusion chromatography (preparative SEC).

Instruments. The ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{29}Si (79.5 MHz) NMR spectra were recorded using JEOL JNM-A400II (^{1}H and ^{13}C), Bruker MSL400 (^{29}Si), and JEOL-ECP-400 (^{1}H) instruments. The preparation of the polymerization solution was carried out in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere (H$_2$O, O$_2$ < 1 ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 and an MB-OX-SE 1 respectively. The size exclusion chromatography (SEC) was performed at 40 °C in THF (1.0 mL min^{-1}) using a Jasco GPC-900 system equipped with a set of Waters Ultrastyragel 7 mm columns (linear, 7.8 mm × 300 mm) and two Shodex KF-804 L columns (linear, 8 mm × 300 mm). The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a PMMA calibration. The preparative SEC was performed in CHCl$_3$ (3.5 mL min^{-1}) at 23 °C using a JAI LC-9201 equipped with a JAI JAIGEL-3H column (20 mm ×600 mm; exclusion limit, 7×10^4) and a JAI RI-50s refractive index detector. Matrix-assisted laser desorption

Chart 1. Structures of DBU, Proazaphosphatranes (TMP and TiBP), and Phosphazene Bases (t-Bu-P$_2$ and t-Bu-P$_4$)

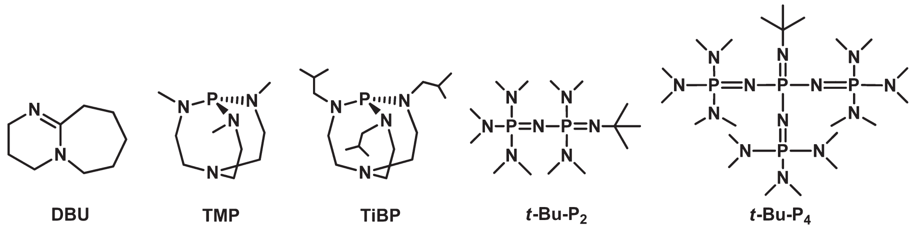


Table 2. TiBP- and t-Bu-P$_4$-Catalyzed GTPs of MMA with Various $[\mathrm{MMA}]_0/[\mathrm{MTS}]_0$ Ratios [a]

run	catalyst	solvent	time (h)	$[\mathrm{MMA}]_0/[\mathrm{MTS}]_0/[\mathrm{catalyst}]_0$	convn (%)[b]	$M_{\mathrm{n,theor}}$ (g mol^{-1})[c]	M_n (g mol^{-1})[d]	$M_\mathrm{w}/M_\mathrm{n}$[d]
11	TiBP	THF	0.5	50/1/0.02	>99	5100	6500	1.07
12			1.0	100/1/0.02	>99	10 100	13 300	1.05
13			1.0	200/1/0.02	>99	20 100	22 800	1.08
14			1.0	300/1/0.02	>99	30 100	34 400	1.10
15			1.0	500/1/0.05	>99	50 200	55 900	1.14
16	t-Bu-P$_4$	toluene	0.5	50/1/0.01	>99	5100	6500	1.16
10			0.5	100/1/0.01	>99	10 100	10 200	1.17
17			1.0	200/1/0.01	>99	20 100	22 600	1.15
18			1.0	300/1/0.01	>99	30 100	30 400	1.15
19			1.0	1000/1/0.01	98.2	98 400	109 600	1.32

[a] $[\mathrm{MMA}]_0 = 2.0$ mol L^{-1}; Ar atmosphere; temp, 25 °C. [b] Determined by ^{1}H NMR in CDCl$_3$. [c] Calculated as follows: $M_{\mathrm{n,theor}} = ([\mathrm{MMA}]_0/[\mathrm{MTS}]_0) \times \mathrm{convn} \times (\mathrm{MW\ of\ MMA}) + (\mathrm{MW\ of\ MTS_{residual}} = 102.13)$. [d] Determined by SEC in THF using PMMA standards.

ionization time-of-flight mass spectrometry (MALDI−TOF MS) of the obtained polymers was performed using an Applied Biosystems Voyager-DE STR-H equipped with a 337 nm-nitrogen laser (3 nm pulse width). Two hundred shots were accumulated for the spectra at a 25 kV acceleration voltage in the reflector mode, and calibrated using insulin (TAKARA BIO, Inc.) as the external standard. Samples for the MALDI−TOF MS were prepared by mixing the polymer (10 mg mL^{-1}, 30 μL), the matrix (1,8-dihydroxy-9(10H)-anthracenone, 30 mg mL^{-1}, 90 μL) and the cationizing agent (sodium trifluoroacetate, 10 mg mL^{-1}, 30 μL) in THF.

Polymerization of MMA. A typical procedure for the polymerization (Table 1, run 10) is as follows: To a toluene solution (7.00 mL) with a toluene stock solution (162 μL) of MTS (38.0 μL, 188 μmol) and a toluene stock solution (200 μL) of t-Bu-P$_4$ (1.19 mg, 1.88 μmol) was added MMA (2.00 mL, 18.8 mmol) over 10 min at 25 °C. The polymerization was quenched after 30 min by the addition of a small amount of benzoic acid. Before the addition of the benzoic acid, we obtained a portion of the polymerization mixtures for determining the MMA conversion that was directly determined from the ^{1}H NMR measurements of the polymerization mixtures. The polymer was isolated by reprecipitation from CH$_2$Cl$_2$ in methanol. Yield: 1.86 g (99.0%). SEC (RI): M_n = 10 200 g mol^{-1}; $M_\mathrm{w}/M_\mathrm{n}$ = 1.17.

Polymerizations using other catalysts were carried out using the same procedure.

Postpolymerization Experiments. The polymerizations of MMA catalyzed by TiBP and t-Bu-P$_4$ were first carried out under the conditions of $[\mathrm{MMA}]_0/[\mathrm{MTS}]_0/[\mathrm{TiBP}]_0 = 100/1/0.02$ and $[\mathrm{MMA}]_0 = 2.0$ mol L^{-1} in THF or $[\mathrm{MMA}]_0/[\mathrm{MTS}]_0/[t\text{-Bu-P}_4]_0 = 100/1/0.01$ and $[\mathrm{MMA}]_0 = 2.0$ mol L^{-1} in toluene using the above procedure for 30 min at 25 °C. Subsequently, the postpolymerization was started by adding 50 equiv of MMA to the reaction mixture after aliquots were taken from the reaction mixture for determining the conversion of MMA and the M_n value of the PMMA obtained from the first polymerizations. After 30 min the postpolymerization was quenched by adding a small amount of benzoic acid to the reaction mixture. The products were purified by reprecipitation from CH$_2$Cl$_2$ in methanol. For TiBP-catalyzed GTP (Table 3, run 20): SEC (RI): M_n = 11,300 g mol^{-1}, $M_\mathrm{w}/M_\mathrm{n}$ = 1.11 (first polymerization); M_n = 17 000 g mol^{-1}, $M_\mathrm{w}/M_\mathrm{n}$ = 1.08 (postpolymerization). For t-Bu-P$_4$-catalyzed GTP (Table 3, run 21): SEC (RI): M_n = 9000 g mol^{-1}, $M_\mathrm{w}/M_\mathrm{n}$ = 1.18 (first polymerization); M_n = 12 400 g mol^{-1}, $M_\mathrm{w}/M_\mathrm{n}$ = 1.16 (postpolymerization).

■ RESULTS AND DISCUSSION

GTP of MMA Using Organic Superbases. In order to provide a fundamental insight into the GTP of MMA catalyzed by a superbase, several organic superbases, such as DBU, TMP, TiBP, t-Bu-P$_2$, and t-Bu-P$_4$, were selected to investigate the effect of basicity and structures of each of the bases on the catalytic activity for the GTP (Chart 1). The order of their Brønsted basicity in acetonitrile was reported to be DBU < TMP ≈ TiBP ≈ t-Bu-P$_2$ < t-Bu-P$_4$ (pK_{BH} = 24.34, 32.90, 33.63, 33.4, and 42.7, respectively).[63−65] Table 1 summarizes the results for the GTP of MMA with MTS as the initiator and the base catalysts in THF or toluene at 25 °C. The polymerization with DBU under the condition of $[\mathrm{MMA}]_0/[\mathrm{MTS}]_0/[\mathrm{DBU}]_0 = 100/1/0.1$ gave a 6.9% conversion of MMA in THF (run 1) and no conversion of MMA in toluene (run 2). In addition, the polymerization with TMP under the condition of $[\mathrm{MMA}]_0/[\mathrm{MTS}]_0/[\mathrm{TMP}]_0 = 100/1/0.05$ showed similar results (runs 3 and 4). Furthermore, t-Bu-P$_2$ did not exhibit any catalytic activity for the polymerization under the condition of $[\mathrm{MMA}]_0/[\mathrm{MTS}]_0/[t\text{-Bu-P}_2]_0 = 100/1/0.05$ (runs 7 and 8). These results obviously indicated that DBU, TMP and t-Bu-P$_2$ showed very low catalytic activity for the GTP of MMA both in THF and toluene even when using a large amount of the catalysts. On the other hand, when TiBP or t-Bu-P$_4$ was employed as the catalyst, the polymerization rapidly

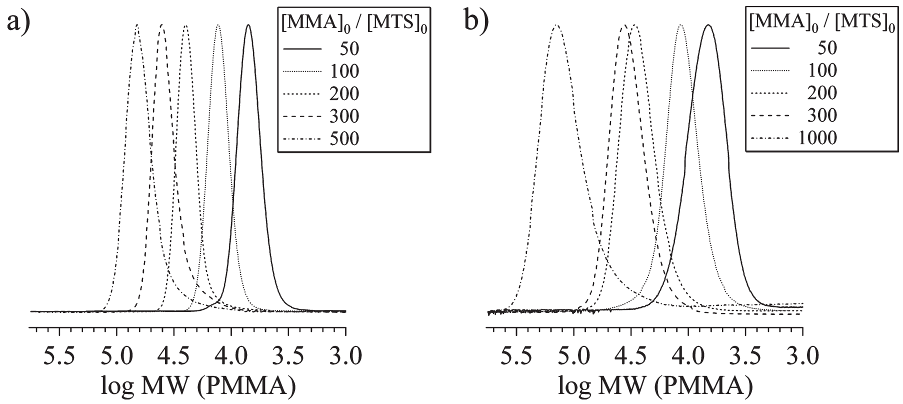


Figure 1. SEC traces of PMMAs obtained from (a) the TiBP-catalyzed GTP (runs 11−15), and (b) the *t*-Bu-P$_4$-catalyzed GTP (runs 10, 16−19) (eluent, THF; flow rate, 1.0 mL min^{-1}).

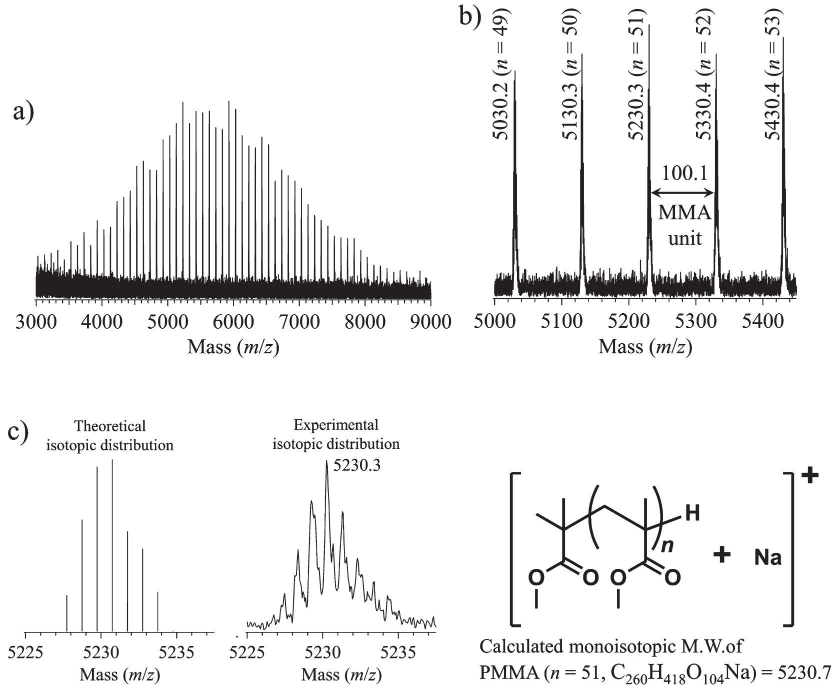


Figure 2. MALDI−TOF MS spectra of the PMMA obtained from run 11 measured in reflector mode.

proceeded in a homogeneous solution. The TiBP-catalyzed GTP of MMA under the condition of [MMA]$_0$/[MTS]$_0$/[TiBP]$_0$ = 100/1/0.01 in THF quantitatively produced PMMA, whose number-average molecular weight (M_n) and polydispersity (M_w/M_n) estimated from SEC calibrated by PMMA standards were 12 700 g mol^{-1} and 1.04, respectively (run 5). In addition, the *t*-Bu-P$_4$-catalyzed GTP of MMA under the condition of [MMA]$_0$/[MTS]$_0$/[*t*-Bu-P$_4$]$_0$ = 100/1/0.01 in toluene afforded PMMA with M_n = 10 200 g mol^{-1} and M_w/M_n = 1.17 (run 10), indicating that relatively stronger bases, such as TiBP and *t*-Bu-P$_4$, among the utilized bases showed high catalytic activity even when using a small amount of catalysts (1% relative to the initiator). Interestingly, TMP, TiBP, and *t*-Bu-P$_2$ showed different catalytic activity in the GTP of MMA in spite of their similar Brønsted basicity. It was clarified that the silicon activation process during the GTP of MMA was determined not only by the basicity but also by the structure of the superbases. Moreover, the polymerization solvent had a significant effect on the base-catalyzed GTP of MMA. The TiBP- and *t*-Bu-P$_4$-catalyzed GTPs of MMA will be discussed below in more detail.

Proof of the Living Nature of TiBP- and *t*-Bu-P$_4$-Catalyzed GTPs. In order to characterize the living nature of the TiBP- and *t*-Bu-P$_4$-catalyzed GTPs of MMA, we first carried out the polymerization with various ratios of [MMA]$_0$/[MTS]$_0$ (Table 2). The TiBP-catalyzed GTP of MMA in THF under the conditions of [MMA]$_0$/[MTS]$_0$ = 50, 100, 200, 300, and 500 (runs 11−15) produced PMMAs with M_ns in a range of 6500−55 900 g mol^{-1} and M_w/M_ns in a range of 1.05−1.14. Similarly, the *t*-Bu-P$_4$-catalyzed GTP of MMA in toluene under the conditions of [MMA]$_0$/[MTS]$_0$ = 50, 100, 200, 300, and 1000 (runs 10 and 16−19) produced PMMAs with M_ns in a range of 6500−109 600 g mol^{-1} and M_w/M_ns in a range of 1.15−1.32.

Table 3. Post-Polymerization of TiBP- and *t*-Bu-P_4-catalyzed GTPs of MMA [a]

run		catalyst	solvent	time (h)	$[MMA]_0$ / $[MTS]_0$	convn (%)[d]	$M_{n,theor}$ (g mol^{-1})[e]	M_n (g mol^{-1})[f]	M_w/M_n[f]
20[b]	first	TiBP	THF	0.5	100	>99	10 100	11 300	1.11
	second			0.5	50	>99	15 100	17 000	1.08
21[c]	first	*t*-Bu-P_4	toluene	0.5	100	>99	10 100	9000	1.18
	second			0.5	50	>99	15 100	12 400	1.16

[a] Ar atmosphere; temp, 25 °C. [b] $[TiBP]_0/[MTS]_0 = 0.02$. [c] $[t\text{-Bu-P}_4]_0/[MTS]_0 = 0.01$. [d] Determined by ^{1}H NMR in $CDCl_3$. [e] Calculated as follows: $M_{n,theor} = ([MMA]_0/[MTS]_0) \times \text{convn} \times (\text{MW of MMA}) + (\text{MW of MTS}_{residual} = 102.13)$. [f] Determined by SEC in THF using PMMA standards.

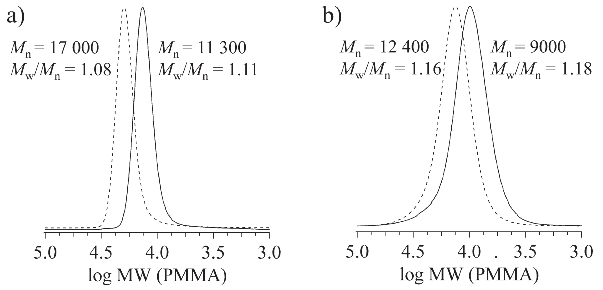


Figure 3. SEC traces of PMMA obtained from the first polymerization (solid line) and following postpolymerization (dashed line) catalyzed by (a) TiBP (run 20) and (b) *t*-Bu-P_4 (run 21) (eluent, THF; flow rate, 1.0 mL min^{-1}).

All the obtained PMMAs from these polymerizations showed monomodal molecular weight distribution (Figure 1). The M_n values of all the obtained polymers agreed fairly well with the theoretical molecular weights ($M_{n,theor}$) predicted from $[MMA]_0/[MTS]_0$ of each polymerization. Importantly, the TiBP- and *t*-Bu-P_4-catalyzed GTPs of MMA were able to afford PMMAs with M_ns up to 55 900 g mol^{-1} and 109 600 g mol^{-1}, respectively, though the GTP system was usually unsuitable for the synthesis of polymers with high molecular weight. These results strongly supported that the TiBP- and *t*-Bu-P_4-catalyzed GTPs of MMA proceeded in a living manner to afford PMMA with predictable molecular weight and narrow M_w/M_n.

In order to provide a detailed insight into the polymerization reaction, a MALDI–TOF MS spectrum of the PMMA obtained from the TiBP-catalyzed GTP (run 11) was observed, as shown in Figure 2. Only one series of peaks was observed in the spectrum, and the observed *m*/*z* values of each peak agreed fairly well with the molecular weight of the PMMA depicted in Figure 2. This result means that the TiBP-catalyzed GTP proceeded in a living manner without any side reactions, such as a backbiting reaction.[66] A similar spectrum was observed from the PMMA obtained from the *t*-Bu-P_4-catalyzed GTP.

For further evidence of the living nature of the TiBP- and *t*-Bu-P_4-catalyzed GTPs of MMA, we carried out postpolymerization experiments (Table 3). For the TiBP-catalyzed GTP of MMA in THF under the condition of $[MMA]_0/[MTS]_0/[TiBP]_0$ = 100/1/0.02 at 25 °C for 30 min, MMA was quantitatively consumed to produce a PMMA with M_n = 11 300 g mol^{-1} and M_w/M_n = 1.11. The polymerization was further carried out by the subsequent addition of 50 equiv of MMA to afford a PMMA with M_n = 17 000 g mol^{-1} and M_w/M_n = 1.08 (run 20). Similarly, for the *t*-Bu-P_4-catalyzed GTP of MMA under the condition of $[MMA]_0/[MTS]_0/[t\text{-Bu-P}_4]_0$ = 100/1/0.01 in toluene at 25 °C for 30 min, MMA was completely consumed to produce a PMMA with M_n = 9000 g mol^{-1} and M_w/M_n = 1.18. The postpolymerization was carried out for 30 min by adding 50 equiv of MMA to give a PMMA with M_n = 12 400 g mol^{-1} and M_w/M_n = 1.16 (run 21). Figure 3 shows the SEC traces of the obtained PMMAs before and after the postpolymerizations. In the postpolymerization, the chain extension for both the TiBP- and *t*-Bu-P_4-catalyzed GTPs of MMA was speculated along with an increase in the molecular weight without increasing the M_w/M_n after the addition of the second MMA, showing that the silyl enol ether at the chain end of the propagating PMMA possessed a truly living nature.

Mechanistic Aspects of the TiBP- and *t*-Bu-P_4-Catalyzed GTPs of MMA. We carried out control experiments to confirm that the polymerization of MMA with the combination of MTS and TiBP or *t*-Bu-P_4 proceeded through the group transfer mechanism because superbases by themselves are well-known to cause the anionic polymerization of MMA.[50] Table 4 summarizes the polymerization results. When the polymerization of MMA was carried out in the absence of MTS for 1 h at 25 °C, no polymer was obtained (runs 22 and 23). In addition, the polymerization of MMA in the absence of the superbase catalysts did not produce any polymers (runs 24 and 25). These results demonstrated that the active intermediates derived from MTS and TiBP or *t*-Bu-P_4 were crucially important for the polymerization. In addition, it was revealed that the TiBP- and *t*-Bu-P_4-catalyzed polymerizations of MMA proceeded through the group transfer mechanism rather than an anionic polymerization process. Thus, we successfully applied the silicon activation ability of proazaphosphatranes and phosphazene bases to the precise synthesis of PMMA for the first time.

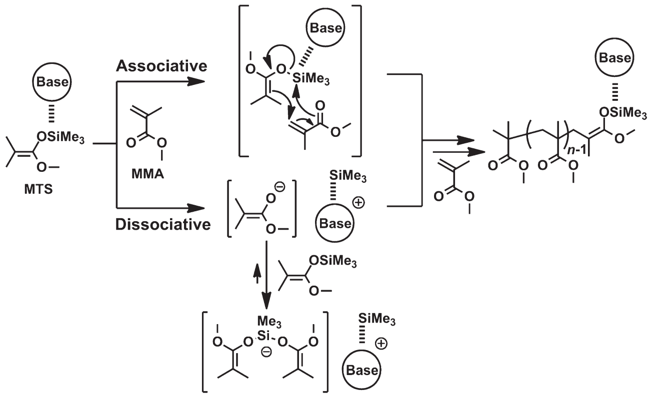
We finally focused on the mechanistic aspect of the TiBP- and *t*-Bu-P_4-catalyzed GTPs, because two GTP mechanisms, namely, the associative (via a formation of pentacoordinate siliconates) and dissociative (via a formation of enolate anions) mechanisms, have been proposed for the GTP of (meth)acrylates catalyzed by Lewis bases, as shown in Scheme 2. In order to provide a preliminary insight into the polymerization mechanism of the TiBP- and *t*-Bu-P_4-catalyzed GTPs, we determined the stereoregularity of the obtained PMMAs by ^{1}H NMR measurements (Figure 4). The stereoregularity, *mm*/*mr*/*rr*, of the PMMAs obtained from the TiBP- (run 14) and the *t*-Bu-P_4-catalyzed GTPs (run 10) were 0.05/0.40/0.55 and 0.06/0.39/0.55, respectively, which was quite similar to that of the PMMA obtained from the GTP of MMA catalyzed by tris(dimethylamino)sulfonium hydrogen bifluoride at 20 °C in THF (*mm*/*mr*/*rr* = 0.05/0.39/0.56).[43] The observed stereoregularity of the PMMAs suggested that both polymerizations proceed via the dissociative mechanism because it is well-known that hydrogen bifluoride anion reacted with MTS to generate an enolate anion.[67−69]

Table 4. GTP of MMA in the Absence of MTS or the Superbases at 25 °C [a]

run	catalyst	solvent	time (h)	$[MMA]_0/[MTS]_0/[catalyst]_0$	convn (%)[b]	$M_{n,theor}$ (g mol^{-1})[c]	M_n (g mol^{-1})[d]	M_w/M_n[d]
12	TiBP	THF	1.0	100/1/0.02	>99	10 100	13 300	1.05
22	TiBP	THF	1.0	100/0/0.02	0	-	-	-
10	*t*-Bu-P_4	toluene	0.5	100/1/0.01	>99	10 100	10 200	1.17
23	*t*-Bu-P_4	toluene	1.0	100/0/0.01	0	-	-	-
24	-	THF	1.0	100/1/0	0	-	-	-
25	-	toluene	1.0	100/1/0	0	-	-	-

[a] [MMA] = 2.0 mol L^{-1}. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated as follows: $M_{n,theor} = ([MMA]_0/[MTS]_0) \times$ convn $\times$ (MW of MMA) + (MW of $MTS_{residual}$ = 102.13). [d] Determined by SEC in THF using PMMA standards.

Scheme 2. Possible Mechanisms for the TiBP- and *t*-Bu-P_4-Catalyzed GTP of MMA



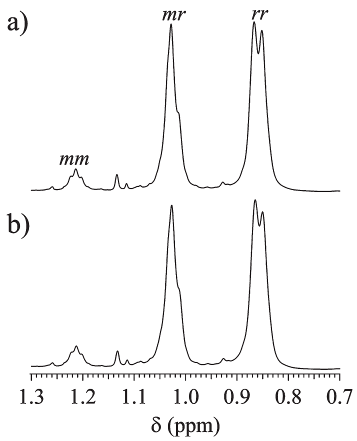


Figure 4. ^{1}H NMR spectra of the PMMAs obtained from (a) the TiBP-catalyzed GTP (run 14, *mm*/*mr*/*rr* = 0.05/0.40/0.55) and (b) the *t*-Bu-P_4-catalyzed GTP (run 10, *mm*/*mr*/*rr* = 0.06/0.39/0.55) of MMA measured in $CDCl_3$ at 50 °C.

In addition, we attempted to directly observe the generation of an enolate anion in equimolar mixtures of TiBP and MTS in THF-d_8 and *t*-Bu-P_4 and MTS in toluene-d_8 by ^{1}H, ^{13}C, and ^{29}Si NMR measurements. However, no new signals and no peak shifts were observed in any spectra though Taton et al. effectively utilized NMR measurements to presume the polymerization mechanism of the GTP catalyzed by *N*-heterocyclic carbenes.[61] Verkade et al. have proposed that the Mukaiyama aldol reaction catalyzed by proazaphosphatranes proceeded along with the generation of an enolate anion from MTS.[36] Similarly, Kondo et al. reported that all the reactions related to organosilicon compounds catalyzed by *t*-Bu-P_4 proceeded through the generation of anionic species.[38] These reports suggested that the TiBP- and *t*-Bu-P_4-catalyzed GTPs proceeded through the dissociative mechanism, though we could not obtain obvious evidence to determine the polymerization mechanism at this moment.

Although detailed discussions including a kinetic investigation[70−74] are required for decisive proof of the polymerization mechanism, the results obtained in this study showed that the silicon activation ability of proazaphosphatranes and phosphazene bases offers a fruitful feature for polymer chemists.

■ CONCLUSIONS

The silicon activation ability of TiBP and *t*-Bu-P_4 turned out to be the effective driving force for the GTP of MMA, which could easily produce a high molecular weight PMMA with a predictable molecular weight and reasonable polydispersity without the aid of metals. To the best of our knowledge, this is the first demonstration of the silicon activation ability of proazaphosphatranes and phosphazene bases as a facile driving force for precise syntheses of polymers, which provides a new concept in synthetic polymer chemistry.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone and Fax: +81-11-706-6602. E-mail: kakuchi@poly-bm.eng.hokudai.ac.jp.

■ ACKNOWLEDGMENT

This study was supported by the Global COE Program (Catalysis as the Basis for Innovation in Materials Science) of the Ministry of Education, Culture, Sports, Science and Technology. Y.-G. Chen was partly supported by a Grant-in-Aid for the Japan Society for the Promotion of Science (JSPS) Fellows.

■ REFERENCES

(1) Enders, D.; Seppelt, M.; Beck, T. *Adv. Synth. Catal.* **2010**, *352*, 1413–1418.

(2) Yu, P.; He, J.; Guo, C.-. X. *Chem. Commun.* **2008**, 2355–2357.

(3) Zhang, Y.-. G.; Zhao, L.; Lee, S.-. S.; Ying, J.-. Y. *Adv. Synth. Catal.* **2006**, *348*, 2027–2032.

(4) Adachi, S.; Harada, T. *Org. Lett.* **2008**, *10*, 4999–5001.

(5) Fini, F.; Sgarzami, V.; Pettersen, D.; Herrena, R. P.; Bernardi, L.; Ricci, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 7975–7978.

(6) Palomo, C.; Oiarbide, M.; Laso, A.; Lopéz, R. *J. Am. Chem. Soc.* **2005**, *127*, 17622–17623.

(7) Ahrendt, K. A.; Borths, C.; MacMillan, W. C. *J. Am. Chem. Soc.* **2000**, *122*, 4243–4244.

(8) Schreiner, P. R.; Wittkopp, A. *Org. Lett.* **2002**, *4*, 217–220.

(9) Nakashima, D.; Yamamoto, H. *J. Am. Chem. Soc.* **2006**, *128*, 9626–9627.

(10) Iwabuchi, Y.; Nakatani, M.; Yokoyama, N.; Hatakeyama, S. *J. Am. Chem. Soc.* **1999**, *121*, 10219–10220.

(11) Nakano, A.; Kawahara, S.; Akamatsu, S.; Morokuma, K.; Nakatani, M.; Iwabuchi, Y.; Takahashi, K.; Ishihara, J.; Hatakeyama, S. *Tetrahedron* **2006**, *62*, 381–389.

(12) Kamber, N. E.; Jeong, W-. H.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* **2007**, *107*, 5813–5840.

(13) Kiesewetter, M. K.; Shin, E-. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43*, 2093–2107.

(14) Hoyle, C. E.; Lowe, A. B.; Bowman, C. N. *Chem. Soc. Rev.* **2010**, *39*, 1355–1387.

(15) Mansfeld, U.; Pietsch, C.; Hoogenboom, R.; Becer, C. R.; Schubert, U. S. *Polym. Chem.* **2010**, *1*, 1560–1598.

(16) Tsarevsky, N. V.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5098–5112.

(17) Schwach, G.; Coudane, J.; Vert, E. M. *Polym. Bull.* **1996**, *37*, 771–776.

(18) Maji, M. S.; Pfeifer, T.; Studer, A. *Chem.—Eur. J.* **2010**, *16*, 5872–5875.

(19) Albertsson, A-.C.; Varma, I. K. *Biomacromoelcules* **2003**, *4*, 1466–1486.

(20) Hedrick, J. L.; Magbitang, T.; Connor, E. F.; Glauser, T.; Volksen, W.; Hawker, C. J.; Lee, V. Y.; Miller, R. D. *Chem.—Eur. J.* **2002**, *8*, 3300–3319.

(21) Verkade, J. G.; Kisanga, P. B. *Tetrahedron* **2003**, *59*, 7819–7858.

(22) Kisanga, P. B.; Verkade, J. G.; Schwesinger, R. *J. Org. Chem.* **2000**, *65*, 5431–5432.

(23) Schwesinger, R. *Chimia* **1985**, *39*, 269–271.

(24) Schwesinger, R.; Schlemper, H. *Angew. Chem., Int. Ed.* **1987**, *26*, 1167–1169.

(25) Schwesinger, R.; Hasenfratz, C.; Schlemper, H.; Walz, L.; Peters, E-. M.; Peters, K.; von Schnering, H. G. *Angew. Chem., Int. Ed.* **1993**, *32*, 1361–1363.

(26) Nederberg, F.; Connor, E. F.; Möller, M.; Glauser, T.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 2712–2715.

(27) Lohmeijer, B. G. G.; Pratt, R. C.; Leibfarth, F.; Logan, J. W.; Long, D. A.; Dove, A. P.; Nederberg, F.; Choi, J-. S.; Wade, C.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 8574–8583.

(28) Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 4556–4557.

(29) Schmalz, H.; Lanzendörfer, M. G.; Abetz, V.; Müller, A. H. E. *Macromol. Chem. Phys.* **2003**, *204*, 1056–1071.

(30) Hupfield, P. C.; Taylor, R. G. *J. Inorg. Organomet. Polym.* **1999**, *9*, 17–34.

(31) Zhang, L.; Nederberg, F.; Pratt, R. C.; Waymouth, R. M.; Hedrick, J. L.; Wade, C. G. *Macromolecules* **2007**, *39*, 4154–4158.

(32) Zhang, L.; Nederberg, F.; Messman, J. M.; Pratt, R. C.; Hedrick, J. L.; Wade, C. G. *J. Am. Chem. Soc.* **2007**, *129*, 12610–12611.

(33) Wang, Z.; Kisanga, P.; Verkade, J. G. *J. Org. Chem.* **1999**, *64*, 6459–6461.

(34) Wang, Z.; Fetterly, B.; Verkade, J. G. *J. Organomet. Chem.* **2002**, *646*, 161–166.

(35) Suzawa, K.; Ueno, M.; Wheatley, A. E. H.; Kondo, Y. *Chem. Commun.* **2006**, *46*, 4850–4852.

(36) Chintareddy, V. R.; Wadhwa, K.; Verkade, J. G. *J. Org. Chem.* **2009**, *74*, 8118–8132.

(37) Wadhwa, K.; Verkade, J. G. *J. Org. Chem.* **2009**, *74*, 4368–4371.

(38) Kobayashi, K.; Ueno, M.; Kondo, Y. *Chem. Commum.* **2006**, 3128–3130.

(39) Mukaiyama, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 5590–5614.

(40) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706–5708.

(41) Webster, O. W. *J. Polym. Sci., Part A.* **2000**, *38*, 2855–2860.

(42) Webster, O. W. *Adv. Polym. Sci.* **2004**, 1–34.

(43) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473–1488.

(44) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4034–4041.

(45) Bandermann, F.; Speikamp, H. D. *Makromol. Chem. Rapid Commun.* **1985**, *6*, 335–339.

(46) Schmalbrock, U.; Bandermann, F. *Makromol. Chem.* **1993**, *194*, 2543–2551.

(47) Schubert, W.; Bandermann, F. *Makromol. Chem.* **1989**, *190*, 2721–2726.

(48) Brittain, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 7440–7444.

(49) Gnaneshwar, R.; Sivaram, S. *J. Polym. Sci., Part A* **2007**, *45*, 2514–2531.

(50) Pietzonka, T.; Seebach, D. *Angew. Chem., Int. Ed.* **1993**, *32*, 716–717.

(51) Börner, H. G.; Heitz, W. *Macromol. Chem. Phys.* **1998**, *199*, 1815–1820.

(52) Kakuchi, R.; Chiba, K.; Fuchise, K.; Sakai, R.; Sato, T.; Kakuchi, T. *Macromolecules* **2009**, *42*, 8747–8750.

(53) Fuchise, K.; Sakai, R.; Sato, T.; Sato, S.; Narumi, A.; Kawaguchi, S.; Kakuchi, T. *Macromolecules* **2010**, *43*, 5589–5594.

(54) Zhang, Y.; Chen, E.Y.-X. *Macromolecules* **2008**, *41*, 36–42.

(55) Zhang, Y.; Chen, E.Y.-X. *Macromolecules* **2008**, *41*, 6353–6360.

(56) Zhang, Y.; Lay, F.; García-García, P.; List, B.; Chen, E. Y.-X. *Chem.—Eur. J.* **2010**, *16*, 10462–10473.

(57) Miyake, G. M.; Zhang, Y. -T.; Chen, E. Y. -X. *Macromolecules* **2010**, *43*, 4902–4908.

(58) Scholten, M. D.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2008**, *41*, 7399–7404.

(59) Raynaud, J.; Ciolino, A.; Baceiredo, A.; Destarac, M.; Bonnette, F.; Kato, T.; Gnanou, Y.; Taton, D. *Angew. Chem.* **2008**, *120*, 5470–5473.

(60) Raynaud, J.; Ciolino, A.; Baceiredo, A.; Destarac, M.; Bonnette, F.; Kato, T.; Gnanou, Y.; Taton, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 5390–5393.

(61) Raynaud, J.; Gnanou, Y.; Taton, D. *Macromolecules* **2009**, *42*, 5996–6005.

(62) Raynaud, J.; Liu, N.; Gnanou, Y.; Taton, D. *Macromolecules* **2010**, *43*, 8853–8861.

(63) Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019–1028.

(64) Schwesinger, R.; Schlemper, H.; Hasenfratz, C.; Willaredt, J.; Dambacher, T.; Breuer, T.; Ottaway, C.; Fletschinger, M.; Boele, J.; Fritz, H.; Putzas, D.; Rotter, H. W.; Bordwell, F. G.; Satish, A. V.; Ji, G. Z.; Peters, E. -M.; Peters, K.; von Schnering, H. G.; Walz, L. *Liebigs. Ann.* **1996**, 1055–1081.

(65) Kisanga, P. B.; Verkade, J. G.; Schwesinger, R. *J. Org. Chem.* **2000**, *65*, 5431–5432.

(66) Brittain, W.; Dicker, I. B. *Macromolecules* **1989**, *42*, 1054–1057.

(67) Schubert, W.; Sitz, H. -D.; Bandermann, F. *Makromol. Chem.* **1989**, *190*, 2193–2201.

(68) Martin, D. T.; Bywater, S. *Makromol. Chem.* **1992**, *193*, 1011.

(69) Sitz, H. -D.; Bandermann, F. In *Recent advances in mechanistic and synthetic aspects of polymerization*; Fontanille, M., Guyot, M.; Eds.; D. Reidel Publishing Company: Dordrecht, The Netherlands, 1987; p 41.

(70) Müller, A. H. E. *Macromolecules* **1994**, *27*, 1685–1690.

(71) Müller, A. H. E. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 87–104.

(72) Mai, P. M.; Müller, A. H. E. *Makromol. Rapid. Commun.* **1987**, *8*, 99–107.

(73) Mai, P. M.; Müller, A. H. E. *Makromol. Rapid. Commun.* **1987**, *8*, 247–257.

(74) Brittain, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 7440–7444.