Group Transfer Polymerization of Acrylic Monomers

Yougen Chen, Keita Fuchise, Toshifumi Satoh, and Toyoji Kakuchi

Abstract Group transfer polymerization (GTP) as one of the living polymerizations was put forward over 30 years ago by DuPont for the upscale and cost-reducing synthesis of acrylic polymers. In the GTP process, a silyl ketene acetal compound is used as an initiator and a Lewis base/acid as the catalysts, and polymerizations can be operated at advantageously moderate temperatures when compared with the conventional living anionic polymerizations of acrylic monomers. GTP using conventional catalysts, referred to as conventional GTP, had experienced a booming development during 1980–1990s. In retrospect, most of the studies in this field before 2007 had been focusing on the optimization of conventional catalysts, the exploration of applicable monomers, and the molecular design of polymeric architectures. In addition, debates on polymerization mechanisms involving associative and dissociative routes had also been discussed. In contrast to the conventional GTP, the recent progress (2007~) in this field has been mainly reflected on the significant and creative utilization of organocatalysts, such as strong organic Lewis acids/bases, which might be termed as organocatalytic GTP. This subchapter strives to provide a latest, systematic, and comprehensive summary throughout the over 30-year development, and in particular, the organocatalytic GTP will be emphatically described.

Keywords Group transfer polymerization • Silyl ketene acetal • Nucleophilicity/silicophilicity • Associative mechanism • Dissociative mechanism • Organocatalyst

1 Introduction

Group transfer polymerization (GTP) was first discovered by Webster et al. in 1983 as to find an alternative polymerization method of anionic polymerization for industrially practical and cost-reducing synthesis of acrylic polymers [1]. Immediately after the discovery, GTP had attracted great attention and was evaluated as

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"the first new approach to polymers to occur in several decades" from the academic viewpoint by polymer chemists, because of its excellent performance for "living control" under moderate polymerization conditions [2]. In principle, the initiation and propagation reactions during a GTP process are rooted on the iteration of an elementary organic reaction of the Mukaiyama-Michael reaction, which is a typical *C–C* formation reaction affording high yield and stereoselective control [3]. The term "group transfer polymerization" has been conferred based on the repetitive transfer of the silyl group from the propagating end to the incoming monomer, which becomes the new propagating end, during propagation, though it was later proven to be inappropriate according to its mechanistic studies. Except for some harsh conditions, such as superhigh pressure of thousands atms, polymerizations do not proceed at all only with silyl ketene acetals (SKAs) and without any catalysts, which strongly indicates that the Lewis base/acid plays a significant role during the polymerization process [4]. Similarly, polymerizations do not proceed only with a Lewis base/acid and without SKA, suggesting that the Lewis base/acid does not initiate any anionic/cationic polymerizations, though they are potentially an initiator or a catalyst in anionic/cationic polymerizations. Obviously, the coexistence of an SKA and a catalyst turns out to be indispensable. This finding, to some extent, supplementarily explains the concept that the polymerization proceeds through a "group transfer" mechanism. When compared with other living polymerizations, the most characteristic feature of GTP method is that the trialkylsilyl-capped end of a propagating polymer is electronically neutral. Therefore, GTP is free from recombination terminations, which is similar to an ionic polymerization. In addition, side reactions caused by impurities, such as chain transfer and termination reactions, can be suppressed to a minimum. For this reason, GTP method has been widely used to polymerize functional (meth)acrylates which bear reactive side groups such as epoxides, cyclic esters, dienes, vinyl, allylic, and styrenic groups; these functionalities are normally sensitive to the conditions of ionic and radical polymerizations [5].

Since its first discovery, GTP, which can actually be referred to as conventional GTP, had experienced a florescent development period from middle 1980s until early 1990s, basically covering all the aspects in terms of (1) the exploration of new efficient catalysts, (2) the broadening of applicable monomers, and (3) the efforts in elucidating polymerization mechanisms. During the middle 1990s–2007, the study of GTP had been a minor research field because of the emergence and rapid development of living radical polymerizations (LRPs). However, the application of organocatalysts to GTP after 2007 has made a breakthrough and significant progress in this field. Relative to the conventional one, Kakuchi et al. have proposed a new definition to the GTPs using organocatalysts as "organocatalytic GTP." Since 2007, many aspects in this field have much improved in terms of catalytic activity, applicable monomers, livingness of polymerization, and control of polymer architecture, owing to the use of organocatalysts.

This subchapter sequentially describes the introduction of catalysts and covers the contents in the following three sections:

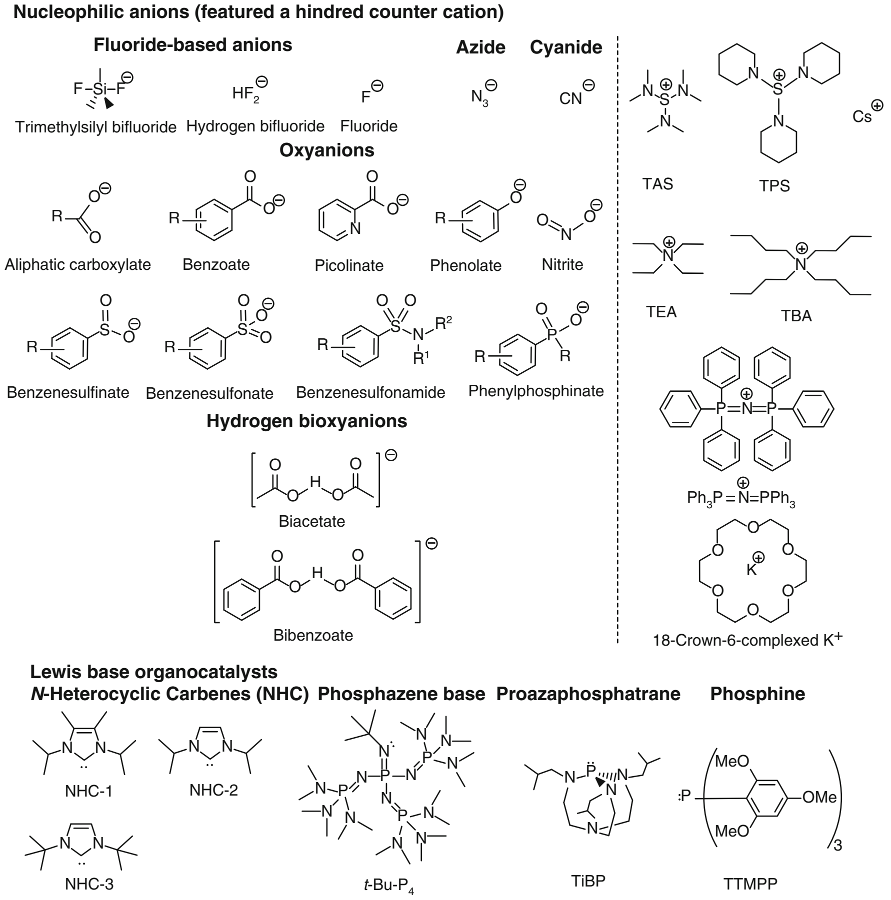
1. A comprehensive overview on the Lewis-base-catalyzed GTP, including GTPs using conventional nucleophilic anions and organic strong bases
2. A comprehensive overview on the Lewis-acid-catalyzed GTP, including GTPs using conventional metallic catalysts and organic Lewis acids
3. A recapitulative introduction on the control of polymer architectures

It is worth mentioning that an overview on the scope of applicable monomers and polymerization mechanisms is also discussed throughout this subchapter.

2 Lewis-Base-Catalyzed GTP

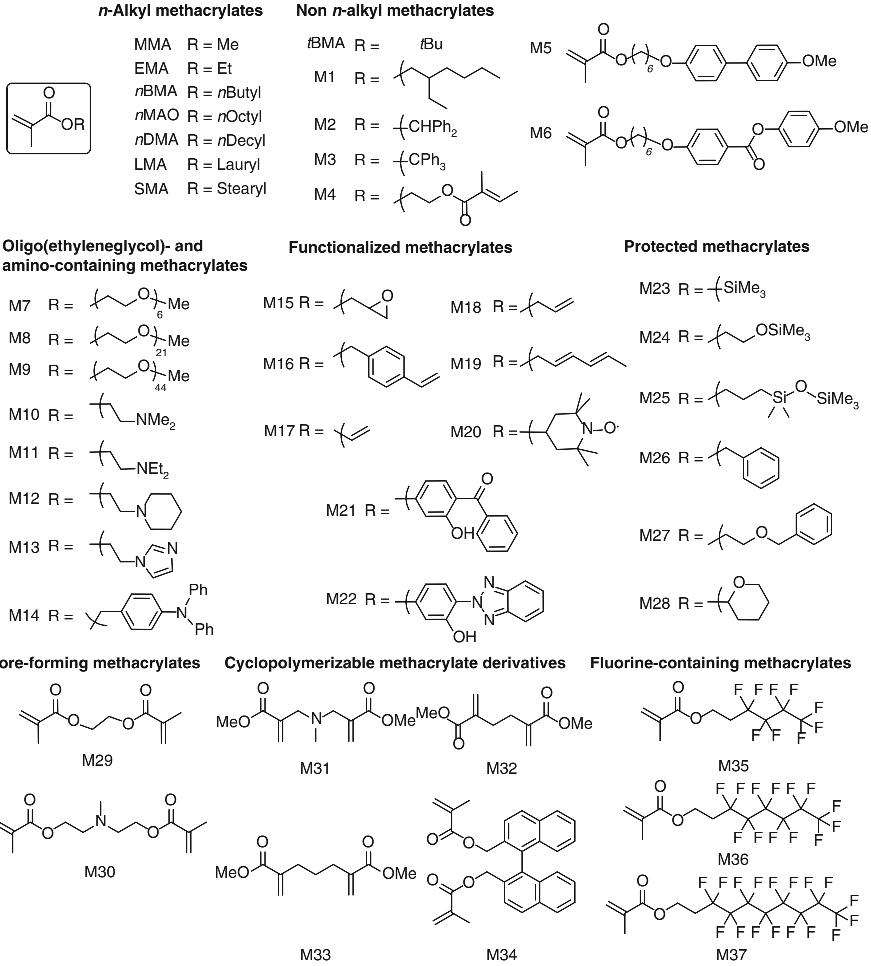
2.1 Overview

The first GTP of methyl methacrylate (MMA) was realized using tris(dialkylamino) sulfonium (TAS) salts of nucleophilic anions, such as $SiMe_3F_2^-$ [1, 6, 7], HF_2^- [1, 6–8], CN^- [1, 6, 8, 9], and N_3^- [1, 8]. The catalytic activity of these nucleophilic anions was then extensively studied and widely used as catalysts for GTP. Meanwhile, a variety of other nucleophilic anions, such as F^- [6, 8, 9], oxyanions [10, 11], and hydrogen bioxyanions [11, 12], were also used to optimize the conditions for the GTPs of (meth)acrylates. These nucleophilic anions are now referred to as conventional Lewis base catalysts. For each of them, a bulky and sterically hindered counter cation is basically required to enhance its catalytic activity and solubility in organic solvents. In addition to TASs, much cheaper and readily available tetraalkylammoniums were commonly used later. Other cations, such as cesium ion (Cs^+) [13], bis(triphenylphosphoranylidene)ammonium ($Ph_3PNPPh_3^+$) [14], and 18-crown-6-complexed K^+ [15], were also reported to be suitable for the counter cations of the catalysts. Among all the used nucleophilic anions, the fluoride-based ones exhibited the highest activity, probably due to their extremely high affinity toward silyl groups. Oxyanions and hydrogen bioxyanions are more favorable for the polymerizations above ambient temperatures. The relative order of catalytic activity is as $F^- > HF_2^- >$ oxyanions > hydrogen bioxyanions [16]. It has, for a long time, been considered that the catalytic activity of a nucleophilic anion is correlated to basicity. However, Hertler et al. found that too high basicity would cause side reactions, such as chain transfer, in the GTP of MMA [17]. In fact, the silicophilicity, rather than basicity, could be a much more suitable notion to account for the catalytic activity because Lewis base catalysts actually attack the silicon atom to activate the *Si–O* bond in an initiator or a propagating polymer end for the initiation reaction or the propagation reaction. The nucleophilic anions have been recognized to be suitable catalysts only for methacrylates because their catalytic activities are too high to control the polymerization of acrylates with much higher reactivity than methacrylates. Most of the GTPs of acrylates are out of control by nucleophilic anions.



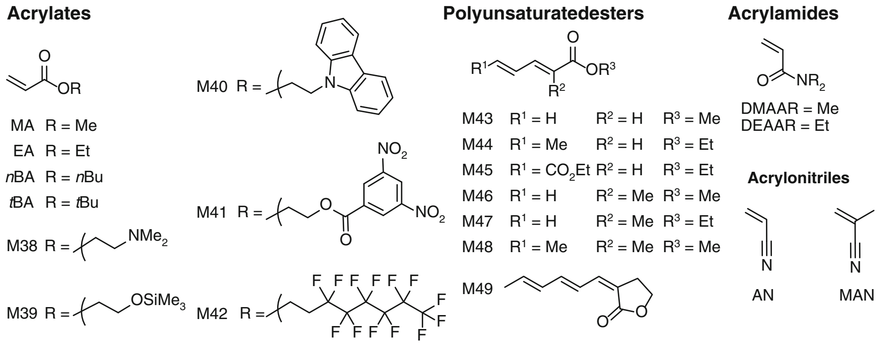
Scheme 1 Chemical structures of nucleophilic anions and Lewis base organocatalysts used in GTP

In addition to the conventionally used nucleophilic anions, the use of recently developed organocatalysts has opened a new avenue in the field of GTP. Lewis base organocatalysts, such as *N*-heterocyclic carbenes (NHCs) [18–24]; organic strong bases such as proazaphosphatranes and phosphazene bases [25–28]; and phosphines [29] have been used as catalysts for GTP since 2007. In comparison with the aforediscussed nucleophilic anions, the Lewis base organocatalysts are more advantageous because they are electronically neutral and much less nucleophilic, thus enabling to suppress side reactions between the catalyst and a monomer, a living polymer, or a solvent. Scheme 1 shows the structures of nucleophilic anions and Lewis base organocatalysts that have been used for GTP so far. The detailed discussion on each class of catalysts is separately implemented in the following sections.



Scheme 2 Structures of methacrylic monomers used in Lewis-base-catalyzed GTP

The Lewis base catalysts are widely used for (co)polymerizing most of methacrylates to produce polymers with homo, random, block, or other architectures. The polymerizable methacrylates include *n*-alkyl, non-*n*-alkyl, oligo(ethylene glycol)-, and amino-containing, functionalized, protected, core-forming, cyclopolymerizable, and some fluorine-containing methacrylates, as shown in Scheme 2. The *n*-alkyl methacrylates include methyl (MMA), ethyl (EMA) [30, 31], *n*-butyl (*n*BMA) [1, 5, 8, 32–35], *n*-octyl (*n*OMA) [36], lauryl (LMA) [8, 36, 37], and stearyl methacrylate (SMA) [26], which are widely used to synthesize homopolymers or copolymers. Other methacrylates, such as non-*n*-alkyl methacrylates (*t*BMA and M1-6) [11, 38–45], oligo(ethylene glycol)- and amino-containing methacrylates (M7-14) [27, 46–53], functionalized methacrylates (M15-20) [1, 8,



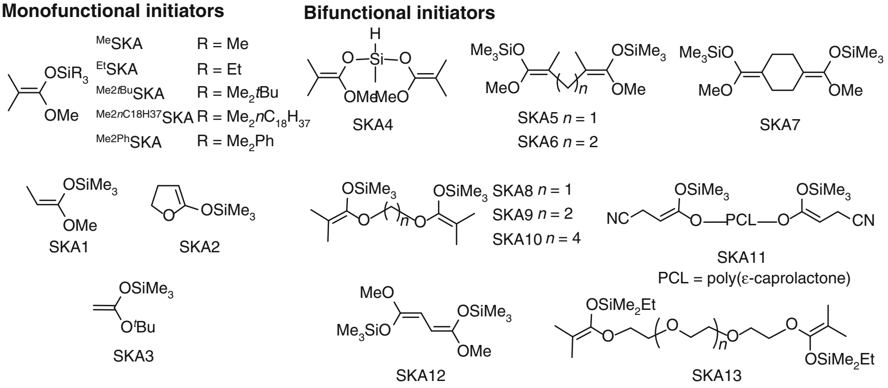
Scheme 3 Structures of acrylates and some vinyl monomers polymerized by Lewis-base-catalyzed GTP

54–59], protected methacrylates (M23-28) [36, 39, 46, 47, 55, 60–63], core-forming methacrylates (M29–30) [48–50, 52, 53, 64], cyclopolymerizable methacrylate derivatives (M31–34) [5, 35, 65, 66], and fluorine-containing methacrylates (M35–37) [67], can also be polymerized to afford corresponding (co)polymers as designed. Generally, the Lewis-base-catalyzed GTP is effective to polymerize most of methacrylates, though livingness of polymerization should be optimized by selecting an appropriate catalyst depending on the structure of a methacrylate.

In addition to methacrylates, acrylates, such as methyl (MA) [6, 7, 9], ethyl (EA) [1, 8], *n*-butyl (*n*BA) [8, 23, 26], *tert*-butyl (*t*BA) [21, 23], and functionalized (M38–42) acrylates [23, 67, 68], have been used to synthesize (co)polymers by the Lewis-base-catalyzed GTP, though most of their GTPs lack ideal control. Other vinyl monomers, such as polyunsaturated esters (M43–49) [69], some of acrylamides [1, 8, 24, 70–72], and acrylonitriles [8, 24, 73, 74], can also be polymerized by the GTP method. Their structures are shown in Scheme 3.

When it comes to GTP, initiators should be brought to discussion. It is recognized that a fast initiation can be achieved when the structure of a silyl ketene acetal has a similar structure with that of the propagating polymer chain end. Webster et al. gave a detailed summarization [75]. In order to precisely control the architectures of resulting polymers, many initiators have been designed, as shown in Scheme 4. 1-Methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene ($^{\mathrm{Me}}$SKA) is undoubtedly the most commonly used one in GTP. Other monofunctional SKAs, such as $^{\mathrm{Et}}$SKA, $^{\mathrm{Me2}t\mathrm{Bu}}$SKA, $^{\mathrm{Me2}n\mathrm{C18H37}}$SKA, $^{\mathrm{Me2Ph}}$SKA, and SKA1-3 [1, 8, 69], have also been used to synthesize homopolymers and block copolymers. The bifunctional initiators (SKA4-13) are useful initiators for the synthesis of ABA-type block copolymers [5, 8, 51, 69, 76–78]. Other SKAs, such as functionalized and star-shaped SKAs, are discussed in Sect. 4.

Table 1 summarizes the ranges of molar mass (M_n) and dispersity (M_w/M_n) reported for poly(meth)acrylates synthesized by Lewis-base-catalyzed GTP. Generally, polymethacrylates with high molar mass can be hardly synthesized using the conventional Lewis base catalysts, probably due to their high nucleophilicity which



Scheme 4 Structures of monofunctional and bifunctional silyl ketene acetals (SKA) used in Lewis-base-catalyzed GTP

leads to side reactions to terminate living polymer ends. In contrast, the use of organocatalysts can advantageously overcome these limitations in a great extent to improve the livingness of polymerization and thus afford high molar mass polymers.

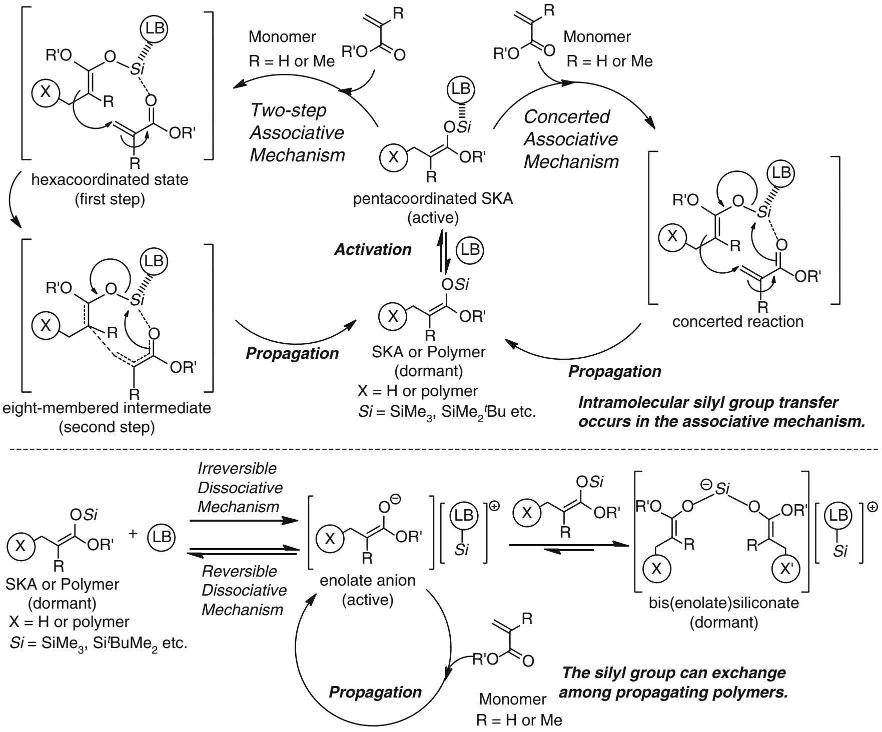
2.2 Mechanisms of Lewis-Base-Catalyzed GTP

For Lewis-base-catalyzed GTP, two mechanistic routes, i.e., associative [1, 79, 80] and dissociative mechanisms [13, 81–83], have been widely accepted so far. The associative mechanism was originally proposed by Webster et al. based on the fact that no intermolecular exchange of the silyl groups occurred between two propagating polymers labeled with an isotope of the silicon atom [1]. This mechanism involves the formation of a pentacoordinated siliconate by the addition of the catalyst to the electrophilic silyl group and a continuous intramolecular transfer of the silyl group along the same polymer chain end after each addition reaction of monomer, which was claimed to proceed in a "concerted" fashion, as shown in Scheme 5. Afterward, Müller et al. proposed a "two-step" associative mechanism based on their kinetic and stereocontrol studies, in which the formation of *C–C* bond between pentacoordinated SKA and monomer does not simply complete through a "concerted" fashion but through a two-step reaction [84, 85]. The formation of *C–C* bond first occurs via the formation of a hexacoordinated state from the pentacoordinated SKA and a monomer. The silyl group then migrates through the formation and rupture of the unstable eight-membered intermediate. However, the associative mechanism had been questioned by Quirk et al. They proposed the dissociative mechanism and believed that the dissociated enolate ions or anions, which are derived from the interaction between SKA and catalyst, are the true active species, as shown in Scheme 5 [81, 86, 87]. In the dissociative pathway,

Table 1 Ranges of M_n and M_w/M_n reported for poly(meth)acrylates synthesized by Lewis-base-catalyzed GTP

Catalyst	Monomer	Solvent	M_n(expt.) (kg mol^{-1})	M_w/M_n
TASHF$_2$	MMA	THF	≤22.1	–
TBAF	MMA	THF	≤62.3	–
TASN$_3$	MMA	MeCN	3.0	1.03
TASCN	MMA	DMF/THF (9/91)	10.5	1.14
Et$_4$NCN	MMA	DMF/THF (9/91)	11.5	1.06
Oxyanions	MMA	THF	≤17.6	1.06–1.56
TBABA	MMA	THF	≤57.9	–
TBABB	MMA	THF	≤67.6	–
NHC-1	MMA	THF	≤18.9	≤1.35
	*t*BA	THF	≤16.3	<1.20
NHC-2	MMA	THF	6.7–330	1.07–1.30
	MMA	Toluene	≤31.0	≤1.30
	*n*BA	THF	9.0–31.0	1.39–1.60
	*n*BA	Toluene	19.7	1.60
	*t*BA	THF	4.8–40.0	1.09–1.25
	*t*BA	Toluene	4.9–24.0	1.19–1.45
	M10	THF	6.5–34.0	1.10–1.15
	M38	THF	23.0	1.46
	DMAA	THF	≤42.0	≤1.15
	MAN	DMF	5.0–18.0	1.37–1.51
NHC-3	MMA	THF	2.6–110	1.10–1.30
	*n*BA	THF	≤33.0	≤1.40
	*n*BA	Toluene	21.4	1.50
	*t*BA	THF	4.8	1.30
	M10	THF	18.0	1.19
	DMAA	THF	37.0	1.17
t-Bu-P$_4$	MMA	THF	6.5–109.6	1.15–1.32
	M14	THF	6.2–34.0	1.06–1.26
TiBP	MMA	THF	6.5–55.9	1.05–1.14
TTMPP	MMA	THF	3.0–22.6	1.13–1.16
	MMA	Bulk	3.6–57.0	1.30–1.37
	*t*BA	THF	2.1–7.8	1.12–1.45

the active chain ends are true anionic species in equilibrium with dormant complexes. Due to the dissociation of silyl groups from enolates, the degenerative exchange of silyl groups between propagating polymers can readily take place. The dissociative mechanism may proceed through two possible routes, namely, the reversible dissociative mechanism and the irreversible dissociative mechanism. In the reversible dissociative mechanism, the dormant species are a propagating polymer not coordinated by a catalyst and a bis(enolate)siliconate, the adduct of an active enolate and a silyl enolate. On the contrary, the dormant species in the



Scheme 5 Proposed associative (*top*) and dissociative (*bottom*) mechanisms of Lewis-base-catalyzed GTP

irreversible dissociative mechanism should be only a bis(enolate)siliconate. Both the associative and dissociative mechanisms are respectively supported by persuasive proofs, as discussed in ref. [75].

2.3 Trimethylsilyl Bifluoride, Hydrogen Bifluoride, and Fluoride

Fluoride-based catalysts, including TAS or tetra-*n*-butylammonium (TBA) salts of trimethylsilyl bifluoride ($SiMe_3F_2^-$) [1], hydrogen bifluoride (HF_2^-) [1, 6–8], and fluoride (F^-) [6, 8, 9], are most generally used in GTP and were studied since the development of GTP. The initial use of them might be attributed to their high silicophilicity, which has been well known in Mukaiyama aldol reaction and Mukaiyama-Michael reaction. As aforediscussed, they have the highest catalytic activity to promote the GTPs of methacrylates among the catalysts for the conventional GTP. A quite low loading of $SiMe_3F_2^-$ (0.1–1 mol% relative to an SKA) is enough for the GTPs of (meth)acrylates to proceed fast. Due to its high catalytic activity, the $SiMe_3F_2^-$-catalyzed GTP is best to be implemented at low temperatures like −78 °C. Any moisture in polymerization system causes the decomposition of $SiMe_3F_2^-$ to its hydrolyzed product, HF_2^-. $SiMe_3F_2^-$ has been less used than HF_2^- and F^- perhaps because of its lower stability. The catalytic activity of HF_2^- and F^- is not so high that realizes GTPs of (meth)acrylates at room temperature. Fluorine-based catalysts are effective in the GTPs of most methacrylates to produce corresponding polymers with moderately controlled molar masses and relatively low dispersities. However, side reactions, such as chain transfer and backbiting reactions, often accompany with the chain propagation because of the high nucleophilicity of these catalysts. Therefore, these fluoride-based catalysts are usually used at a low loading relative to initiator to minimize such side reactions. The F^--catalyzed GTP of MMA could afford a hydroxyl end-functionalized PMMA with a M_n of up to 64.7 kg mol^{-1} and a M_w/M_n of 1.14. To obtain a PMMA with M_n, more than 50–60 kg mol^{-1} has been difficult by the fluoride-based catalysts.

2.4 Azide and Cyanide

N_3^- and CN^- have been also used as catalysts with 3–15 mol% relative to an initiator for the polymerizations of methacrylates and acrylates [1, 6, 8, 9]. Due to their poor solubility in apolar solvents, they required the use of polar solvents like DMF and CH_3CN.

2.5 Oxyanions and Hydrogen Bioxyanions

Oxyanions, such as carboxylates, benzoates, phenoxides, phosphinates, sulfinates, sulfonates, sulfonamides, nitrite, and corresponding bioxyanions, can effectively activate SKAs, though they are not often used [10, 11]. All the oxyanions shown in Scheme 1 can catalyze the GTP of MMA to afford moderate control over molar mass and dispersities. Sogah et al. have provided a deep insight into the oxyanion-catalyzed GTP and found that the catalytic activity of an oxyanion strongly depended on the acidity (pK_a value) of its conjugated acid [11].

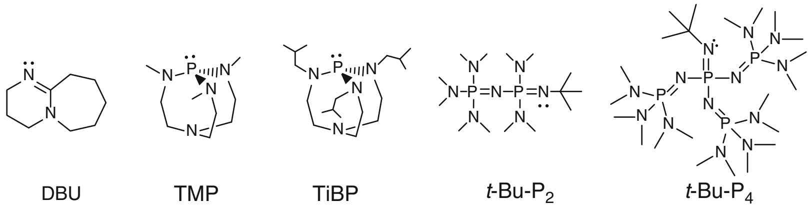
Hydrogen bioxyanions are the most effective conventional catalysts for methacrylates [11, 12]. The best examples of hydrogen bioxyanions are bibenzoates and biacetates. In most of cases, they afford better control over molar masses and dispersities than their homologous oxyanions. The reason for this phenomenon might be that the hydrogen bioxyanions have much lower nucleophilicity than corresponding oxyanions because the negative charges in hydrogen bioxyanions are more favorably delocalized than the homologous oxyanions. It has been reported that hydrogen bioxyanions could catalyze not only the GTP of MMA to produce a PMMA with a M_n of up to 67.6 kg mol^{-1} and M_w/M_n of 1.13 but also catalyze the GTPs of other methacrylates. For instance, the biacetate-catalyzed GTP of *n*BMA can produce a P*n*BMA with an M_n of up to 67.6 kg mol^{-1} and a M_w/M_n as narrow as 1.13. The biacetate- and bibenzoate-catalyzed GTPs have also been used to polymerize methacrylates, such as M1, M10, M15, M24, and M28.

2.6 N-*Heterocyclic Carbenes*

The recent development of GTP catalyzed by Lewis base organocatalysts dates back to 2007–2008 when Waymouth and Hedrick et al. and Taton et al. independently reported the GTP of (meth)acrylates using *N*-heterocyclic carbenes (NHCs). Waymouth and Hedrick reported the GTPs of MMA and *t*BA using 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (NHC-1) (0.026–3.2 mol% relative to initiator) in THF at room temperature, which afforded good control over polymerization to produce PMMAs with an M_n of up to 18.9 kg mol^{-1} and M_w/M_n narrower than 1.35 as well as P*t*BAs with an M_n of up to 16.3 kg mol^{-1} and M_w/M_n narrower than 1.20 [18, 20]. Taton et al. first reported the GTPs of MMA, *t*BA, and *n*BA using 1,3-diisopropylimidazol-2-ylidene (NHC-2) and 1,3-di-*tert*-butylimidazol-2-ylidene (NHC-3) (5–6 mol% relative to initiator for the polymerization of MMA and 1 mol% relative to initiator for the polymerization of *t*BA and *n*BA) both in THF and toluene at room temperature, which produced PMMAs with the M_n of 2.6–330 kg mol^{-1} and M_w/M_n of 1.07–1.3 as well as P*t*BAs with the M_n of 4.8–33.0 kg mol^{-1} and M_w/M_n of 1.15–1.6 [19, 21]. The polymers synthesized in toluene had relatively broader M_w/M_n than those obtained in THF. It is noteworthy that the PMMA with an M_n greater than 100 kg mol^{-1} has been obtained using NHCs, which can be hardly synthesized using a conventional catalyst. In addition to MMA, M10, *n*BA, M38, DMAA, and MAN can also be polymerized using NHC-2 and NHC-3 [21, 23].

2.7 Organic Strong Bases

Kakuchi et al. have recently used the organic strong bases, which have low nucleophilicity and high basicity, to catalyze GTP [25]. Their structures are shown in Scheme 6. Among the five bases, 2,8,9-triisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane (TiBP) and 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene) (*t*-Bu-P$_4$) are the efficient ones to catalyze GTP of MMA. The polymerization using TiBP or *t*-Bu-P$_4$ rapidly proceeded with a [TiBP or *t*-Bu-P$_4$]$_0$/[^{Me}SKA]$_0$ = 0.01, which produced PMMAs with M_n of 6.5–55.9 kg mol^{-1} and 6.5–109.6 kg mol^{-1}, while the narrow M_w/M_n was kept in a range of 1.05–1.14 and 1.15–1.32, respectively. It is worth noting that the *t*-Bu-P$_4$ can catalyze the GTP of MMA to produce a PMMA with M_n



Scheme 6 Chemical structures of organic strong bases

greater than 100 kg mol^{-1}. On the contrary, the GTPs of MMA using 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), 2,8,9-trimethyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3] undecane (TMP) and 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2Λ^5,4Λ^5-catenadi(phosphazene) (*t*-Bu-P_2) were very slow or did not proceed at all both in THF and toluene even when a large amount of the catalysts was used. Interestingly, TMP, TiBP, and *t*-Bu-P_2 showed different catalytic activity in the GTP of MMA though they have similar Brønsted basicity, indicating that ability to activate a silicon atom for the polymerization is crucially affected by the structure and silicophilicity of the strong bases, rather than by the Brønsted basicity.

2.8 Phosphines

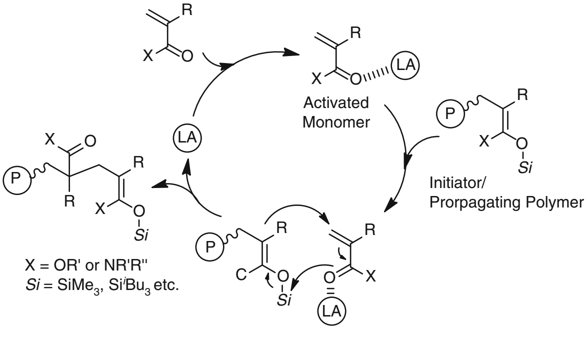
Most recently, Taton et al. attempted to use phosphines, including tri-*n*-butylphosphine (Bu_3P), tricyclohexylphosphine (Cy_3P), triphenylphosphine (Ph_3P), and tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP), as the catalysts of GTP [29]. Among these phosphines, only TTMPP showed high catalytic activity probably due to its higher Lewis basicity than others. TTMPP (10 mol% relative to initiator) promoted the GTP of MMA in THF in a living fashion to produce a PMMA with M_n of up to 22.6 kg mol^{-1} and M_w/M_n narrower than 1.16. However, in toluene or bulk, the GTP of MMA was out of control. The polymerization produced PMMAs with M_w/M_n broader than 1.3. In addition to MMA, the GTP of *t*BA has also been achieved using TTMPP. A low monomer concentration is more favorable for the GTP of *t*BA. For instance, the GTP of *t*BA in THF under the conditions of $[t\mathrm{BA}]_0/[^{\mathrm{Me}}\mathrm{SKA}]_0/[\mathrm{TTMPP}]_0 = 22/1/0.01$ and $[t\mathrm{BA}]_0 = 0.7$ mol L^{-1} produced a P*t*BA with M_n of 2.1 kg mol^{-1} and M_w/M_n of 1.12, while the same polymerization under ten times condensed condition produced a P*t*BA with an M_n of 3.1 kg mol^{-1}, and an $M_w/M_n = 1.4$. 2 h induction period has been observed in the polymerization of MMA in THF at 25 °C under the condition of $[\mathrm{MMA}]_0/[^{\mathrm{Me}}\mathrm{SKA}]_0/[\mathrm{TTMPP}]_0 = 30/1/0.1$, though the polymerization rate followed the first order of the concentration of MMA after the induction period.

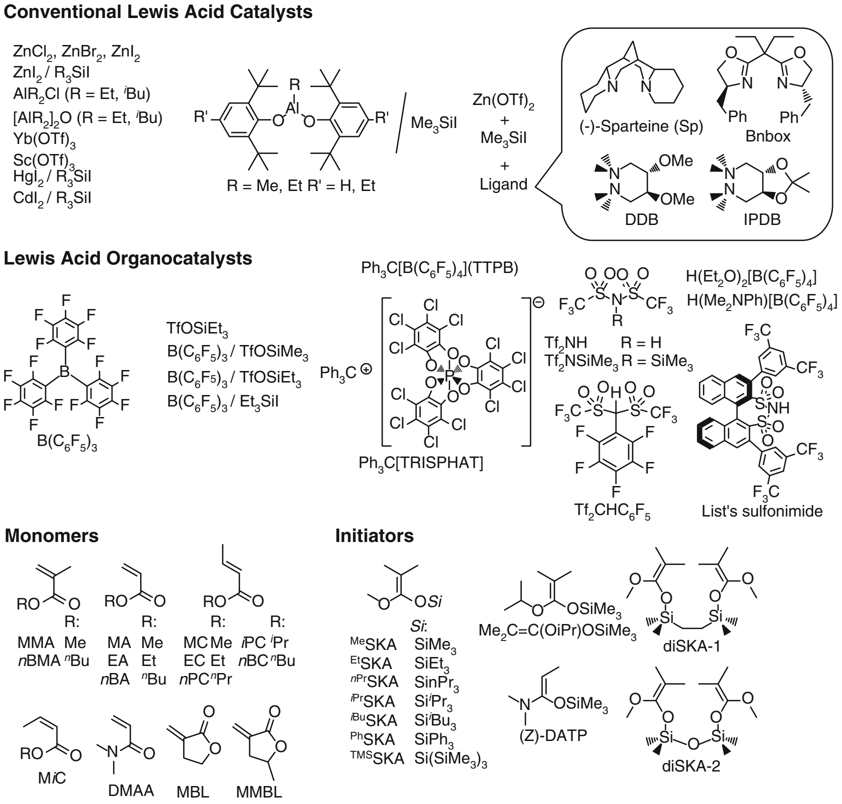
3 Lewis-Acid-Catalyzed GTP

3.1 Overview

Lewis-acid-catalyzed GTP is considered to proceed through the activation of a monomer by a Lewis acid (LA), as illustrated in Scheme 7. Scheme 8 summarizes catalysts, monomers, and initiators used in Lewis-acid-catalyzed GTP so far. Conventional Lewis acid catalysts, such as zinc halides and organoaluminums, are only suitable for the controlled polymerizations of acrylates because of the low catalytic activity, i.e., weak Lewis acidity [88]. Thus, several metallic Lewis acids with high acidity have been examined to develop controlled polymerizations of other monomers [8, 70, 89–99]. The controlled polymerization of alkyl crotonates has been achieved by the GTP catalyzed by the mixture of mercury(II) iodide (HgI_2) and trialkylsilyl iodide, even though it has been hardly achieved by radical polymerization and anionic polymerization. The emergence of highly Lewis acidic nonmetallic catalysts, namely, Lewis acid organocatalysts, has broken the limit of conventional Lewis-acid-catalyzed GTPs. The GTPs of alkyl methacrylates, DMAA, α-methylenebutyrolactone (MBL), and γ-methyl-α-methylenebutyrolactone (MMBL) have been newly achieved using Lewis acid organocatalysts, such as tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) with a silylating agent, triphenylmethyl salts, and strong organic Brønsted acids. The Lewis acid organocatalysts are regularly used at a ratio of ca. 1–50 mol% relative to the initiator to obtain polymers with M_w/M_n narrower than 1.15. Apolar solvents, such as CH_2Cl_2 and toluene and cyclohexane, are more favorable for the Lewis-acid-catalyzed GTP. Generally, the polymerization rate increases with the increasing polarity of the solvent. However, polar and donating solvents, such as THF and DMF, inhibit the polymerization. The mechanism of each polymerization is described in detail in the following sections because it slightly varies depending on the used catalyst. Table 2 summarizes the ranges of M_n and M_w/M_n for the polymers obtained from the Lewis-acid-catalyzed GTP using respective catalyst.

Scheme 7 Plausible mechanism of the Lewis-acid-catalyzed GTP





Scheme 8 Catalysts, monomers, and initiators used in the Lewis-acid-catalyzed GTP

3.2 Zinc Halides and Zinc Triflates

Hertler et al. first reported the Lewis-acid-catalyzed GTP of methacrylates and acrylates using zinc halides, such as zinc(II) iodide (ZnI_2), zinc(II) bromide ($ZnBr_2$), and zinc(II) chloride ($ZnCl_2$) [8, 88]. ZnI_2 has been the best catalyst for the polymerization of EA at ambient temperature in the conventional GTP. The GTPs of EA using 1-[2-(trimethylsiloxy)ethoxy]-1-(trimethylsiloxy)-2-methylprop-1-ene (SKA14) and ZnI_2 in CH_2Cl_2 or ethylene dichloride produced PEAs with M_n of 1.25–3.30 kg mol^{-1} and M_w/M_n of 1.03–1.10. The GTP of MMA using ^{Me}SKA and $ZnBr_2$ in ethylene dichloride produced a PMMA with M_n of 6.02 kg mol^{-1} and M_w/M_n of 1.20, though the M_n was almost 1.8 times greater than the calculated M_n. 10–20 mol% of the catalyst is required for the controlled polymerization of both EA and MMA. $ZnBr_2$ has been used for the GTP of 2-methacryloxyethyl acrylate and DEAA using ^{Me}SKA. In the former polymerization, the acryloyl group in the monomer was selectively polymerized to produce a polyacrylate-bearing methacryloyl groups on the side-chain [8]. The latter

Table 2 M_n and M_w/M_n scopes of Lewis-acid-catalyzed GTP

Catalyst	Monomer	Solvent	M_n(expt.) (kg mol^{-1})	M_w/M_n
ZnI_2	EA	CH_2Cl_2	1.25–3.30	1.03–1.10
	DEAA	CH_2Cl_2	–[a]	–[a]
$ZnBr_2$	MMA	CH_2Cl_2	6.02	1.20
Organoaluminums	EA or *n*BA	CH_2Cl_2	1.98–2.37	1.06–1.17
$(^iBuO)_2Al$	EA	Toluene	1.33	1.19
$HgI_2 + R_3SiI$	*n*BA	Toluene	≤3.7	1.08–1.15
	MC	CH_2Cl_2	5.2–13	1.12–1.22
	M*i*C	CH_2Cl_2	9.0	1.20
$CdI_2 + Et_3SiI$	MC	CH_2Cl_2	1.3–7.7	1.06–1.19
$B(C_6F_5)_3$ + silylating agents	MMA	CH_2Cl_2	12.1	1.06
	EA	CH_2Cl_2	5.3–21.7	1.14–1.26
	EA	Toluene	17.4	1.12
TTPB	MMA	CH_2Cl_2	20.8	1.07
	MMA	Toluene	21.6	1.07
	*n*BMA	CH_2Cl_2	42.1	1.07
	*n*BMA	Toluene	49.1	1.08
	*n*BA	Toluene	24.3	1.07
	MMBL	CH_2Cl_2	18.8–548	1.01–1.06
$[Ph_3C][TRISPHAT]$	MMA	–[b]	–[b]	–[b]
	MMBL	CH_2Cl_2	36.2	1.01
Tf_2NH	MMA	CH_2Cl_2	3.86–17.0	1.04–1.08
	DMAA	CH_2Cl_2	12.7	1.08
	DMAA	Toluene	3.24–53.9	1.06–1.16
Tf_2NSiMe_3	MMA	CH_2Cl_2	4.1–8.6	1.07–1.11
$Tf_2CHC_6F_5$	MA	Toluene	2.9–108	1.03–1.07
	DMAA	CH_2Cl_2	2.8–10.4	1.04–1.07
$H(Et_2O)_2[B(C_6F_5)_4]$	MMA	CH_2Cl_2	11.3-74.1	1.07–1.12
	MMA	Toluene	20.0	1.08
	BMA	CH_2Cl_2	44.3	1.07
	*n*BA	Toluene	23.2	1.08
	DMAA	CH_2Cl_2	102	1.09
	MMBL	CH_2Cl_2	40.0	1.07
$H(Me_2NPh)[B(C_6F_5)_4]$	MMA	CH_2Cl_2	18.5	1.07
List's sulfonimide	MMA	CH_2Cl_2	–[a]	–[a]
	DMAA	CH_2Cl_2	30.2	1.13

[a] Not polymerized

[b] Not mentioned in the original article [100]

polymerization in CH_2Cl_2 did not proceed [70]. The combined use of ZnI_2 and trialkylsilyl iodide has been found to be as effective as the catalytic system of HgI_2 and trialkylsilyl iodide for the controlled polymerization of methyl crotonate (MC) (see Sect. 3.4) [95].

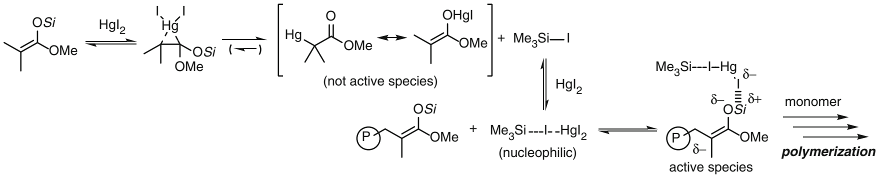
3.3 Organoaluminums

The GTPs of EA and *n*BA using ^{Me}SKA and organoaluminum, such as chlorodiethylaluminum, chlorodiisobutylaluminum, and oxybis(diisobutylaluminum), in CH_2Cl_2 or a mixture of CH_2Cl_2 and acetonitrile (1/2, v/v) produced corresponding polyacrylates with M_n of 1.98–2.37 kg mol^{-1} and M_w/M_n of 1.06–1.17, though it required low polymerization temperature as −78 °C. On the contrary, the GTP of EA using oxybis(diisobutylaluminum) and ^{Me}SKA in toluene quantitatively proceeded at ambient or higher temperatures (20–58 °C) to produce PEA with M_n of 1.33 kg mol^{-1} and M_w/M_n of 1.19 [8, 70]. The polymerization of MMA using chlorodiisobutylaluminum and ^{Me}SKA in CH_2Cl_2 was uncontrolled, which produced a PMMA with M_n of 3.0 kg mol^{-1} and M_w/M_n of 2.43. In contrast to zinc halides, the aluminum catalysts were used at 10 mol% relative to an initiator.

The combination of alkylaluminum bis(2,6-di-*tert*-butylphenoxide) and trimethylsilyl iodide was effective for the synthesis of highly syndiotactic PMMA using ^{Me}SKA in CH_2Cl_2 at 0 °C under the condition of $[M]_0/[I]_0/[Al]_0/[Si]_0 = 50/1/0.75/0.5$, though the resulting PMMA had bimodal and dispersity [89]. The high molar mass part was highly syndiotactic (*rr* = 95.6–98.7 %) and insoluble in acetone, THF, and toluene, while the solubility of the low molar mass part (*rr* = 78.9–88.6 %) was the same as conventional PMMA.

3.4 Mercury(II) Iodide with Trialkylsilyl Iodide

Conventionally, the most efficient catalytic system consisting of Lewis acids is a mixture of HgI_2 and trialkylsilyl iodide, which was effective for the controlled polymerization of acrylates in toluene, with 5.2 mol% of HgI_2 and 2.1 mol% of trimethylsilyl iodide relative to the initiator [90–93], as well as crotonates in CH_2Cl_2, with 8 mol% of HgI_2 and 24 mol% of triethylsilyl iodide relative to the initiator [94, 95]. Müller et al. proposed the mechanism of the GTP catalyzed by HgI_2 and trialkylsilyl iodide, as shown in Scheme 9, in order to elucidate the high catalytic activity of this catalytic system [92, 93]. The polymerization of *n*BA using HgI_2 itself as a catalyst required a maximum of 200 min of induction period, though the polymerization eventually proceeded with a first-order kinetics on monomer concentration [92]. Trimethylsilyl iodide (Me_3SiI) itself did not show any catalytic



Scheme 9 Plausible mechanism of the GTP catalyzed by HgI_2 and trialkylsilyl iodide

activity for the polymerization. Thus, they proposed that Me_3SiI is generated from the reaction of a trimethylsilyl enolate and HgI_2 as a byproduct in the formation of α-mercuroester or *O*-mercuric enolate. The generated Me_3SiI forms a nucleophilic adduct with HgI_2, Me_3SiI-HgI_2, which can activate a silyl enolate of an initiator or the propagating end to catalyze the initiation/propagation reaction. The isolated mixture of α-mercuroester or *O*-mercuric enolate has been recognized to be not the active species in the polymerization, because they produced only a mixture of oligomer of *n*BA.

The controlled polymerization of alkyl crotonates has been achieved with the GTP catalyzed by HgI_2 and trialkylsilyl iodide for the first time [94–97]. The polymerization of methyl crotonate (MC) at −20 °C using ^{Et}SKA/Et_3SiI, ^{nPr}SKA/$^{n}Pr_3SiI$, or ^{Me2tBu}SKA/Me_2tBuSiI in CH_2Cl_2 produced poly(methyl crotonate) (PMC) with M_n of 5.2–13 kg mol^{-1} and M_w/M_n of 1.12–1.22 [95, 97]. The PMC obtained using ^{Me2tBu}SKA/Me_2tBuSiI had the highest disyndiotacticity up to 94 % among them. The polymerizations of *n*-propyl crotonate (*n*PC), isopropyl crotonate (*i*PC), and *n*-butyl crotonate (*n*BC) using ^{Et}SKA and HgI_2/Et_3SiI were also controlled to produce corresponding polymers with M_n of 71–90 kg mol^{-1}, M_w/M_n of 1.07–1.16, and predominant disyndiotacticity [96]. In addition, the controlled polymerization of methyl isocrotonate (M*i*C) has been for the first time achieved by the GTP using ^{Me}SKA, HgI_2, and Me_3SiI at −40 °C in CH_2Cl_2 to produce a poly(methyl isocrotonate), which has the same primary structure as PMC, with M_n of 9.0 kg mol^{-1} and M_w/M_n of 1.20. Interestingly, the stereoregularity of the resulting polymer was similar to the PMC obtained by the same polymerization condition, though the structures of the monomers are geometrically different. The unique mechanism of the GTP using HgI_2/trialkylsilyl iodide might be the reason why the controlled polymerizations of alkyl crotonates and methyl isocrotonate have been achieved.

3.5 Other Metallic Catalysts

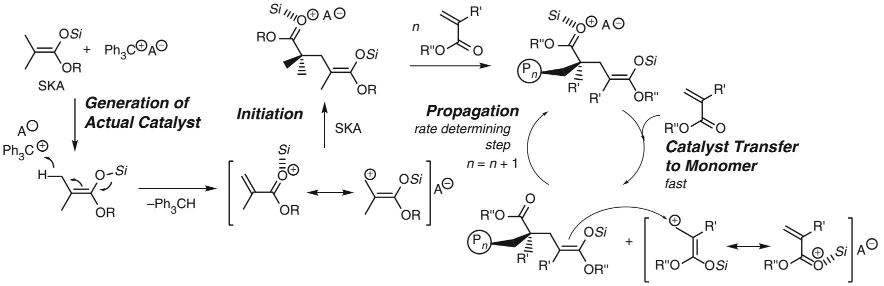
Matyjaszewski et al. once reported that tris(trifluoromethanesulfonyl) lanthanides, such as $Yb(OTf)_3$ and $Sc(OTf)_3$, were effective for the GTP of acrylates [98]. Oishi et al. attempted the GTP of *N*-cyclohexylmaleimide catalyzed by the complexes of zinc(II) trifluoromethanesulfonate ($Zn(OTf)_2$) and chiral diamine ligands [99]. Kitayama et al. found that a catalytic system of cadmium(II) iodide and trialkylsilyl iodide was also effective for the polymerization of MC, which produced PMC with M_n of 1.3–7.7 kg mol^{-1} and M_w/M_n of 1.06–1.19 [95].

3.6 $B(C_6F_5)_3$ with Silylating Agents

The first example of the GTP catalyzed by a nonmetallic Lewis acid is the GTP of EA catalyzed by $B(C_6F_5)_3$ [101, 102] or triethylsilyl trifluoromethanesulfonimide ($TfOSiEt_3$) [103] reported in 2000, though it was not originally reported as an organocatalytic polymerization [104]. The former polymerization was carried out with ^{Et}SKA in CH_2Cl_2 at 20 °C for 1 h under the conditions of $[EA]_0/[^{Et}SKA]_0/[B(C_6F_5)_3]_0 = 100/1/0.1$ and $[EA]_0 = 2.5$ mol L^{-1} to produce a PEA with an M_n of 7.5–12.6 kg mol^{-1} and an M_w/M_n of 1.13–1.52. The latter polymerization was carried out in CH_2Cl_2 at 0 °C for 24 h under the conditions of $[EA]_0/[^{Et}SKA]_0/[TfOSiEt_3]_0 = 50/1/0.5$ and $[EA]_0 = 2.5$ mol L^{-1} to produce a PEA with an M_n of 3.2 kg mol^{-1} and an M_w/M_n of 2.35. However, the combined use of $B(C_6F_5)_3$ and $TfOSiEt_3$ improved the control of the polymerization; the GTP of EA catalyzed by $B(C_6F_5)_3$ and $TfOSiEt_3$ under the conditions of $[^{Et}SKA]_0/[B(C_6F_5)_3]_0/[TfOSiEt_3]_0 = 5–20/1/0.01$ produced PEAs with M_n of 5.3–21.7 kg mol^{-1} and M_w/M_n of 1.14–1.18. The same catalytic system allowed the controlled block copolymerization of EA and *n*BA. It is noteworthy that the controlled polymerization of MMA by the GTP catalyzed by a Lewis acid has been for the first time achieved by the combined use of $B(C_6F_5)_3$ and Et_3SiI in the same report. The polymerization was carried out in CH_2Cl_2 at 0 °C under the conditions of $[MMA]_0/[^{Et}SKA]_0/[B(C_6F_5)_3]_0/[Et_3SiI]_0 = 100/1/2/0.5$ and $[MMA]_0 = 2.5$ mol L^{-1} to produce PMMA with an M_n of 12.1 kg mol^{-1} and M_w/M_n of 1.06, though it required two equivalents of $B(C_6F_5)_3$ relative to the initiator. The triethylsilyl cation generated from $B(C_6F_5)_3/TfOSiEt_3$ and $B(C_6F_5)_3/Et_3SiI$ was presumed to be the true catalyst in the polymerization, though a detailed mechanism of the polymerization had not been experimentally investigated.

3.7 Triphenylmethyl Salts

Since 2008, Chen et al. proposed and demonstrated the oxidative GTP catalyzed by triphenylmethyl salts, especially triphenylmethyl tetrakis(pentafluorophenyl)borate (TTPB), which can lead to the living polymerization of alkyl (meth)acrylates as well as MMBL [100, 105–107]. The controlled polymerization of MMA has been achieved by adding TTPB to a solution of MMA and ^{Me}SKA at ambient temperature both in CH_2Cl_2 and toluene, which produced PMMAs with an M_n greater than 100 kg mol^{-1} and narrow M_w/M_ns of 1.04–1.12 [105]. However, donating solvents, such as tetrahydrofuran (THF), inhibited the polymerization. The same initiating system consisting of ^{Me}SKA and TTPB allowed the quantitative polymerization of *n*BMA at room temperature (~25 °C) within 60 min to give poly(*n*-butyl methacrylate) (P*n*BMA) with an M_n of 54.4 kg mol^{-1}, an M_w/M_n of 1.06, and a high syndiotacticity ($rr = 80$ %). Scheme 10 depicts the proposed mechanism of the oxidative GTP promoted by triphenylmethyl salts, which postulates that in situ



Scheme 10 Presumed mechanism of the GTP promoted by a triphenylmethyl salt

generated silylium cation is the actual catalyst for the polymerization. The triphenylmethyl cation abstracts a hydrogen atom from a SKA to generate a triphenylmethane and an alkyl methacrylate coordinated by a silylium cation, which has been proven from a ^{1}H NMR measurement at low temperature. Another silyl enolate reacts with the activated methacrylate to produce an adduct coordinated by the silylium cation. The catalyst transfer from the propagating polymer to the incoming monomer is much faster than the *C–C* bond formation by intermolecular Michael addition between the propagating polymer and the monomer activated by the silylium cation because the kinetics of the polymerization is zero order on monomer concentration and first order on the concentrations of SKA and TTPB regardless of the $[M]_0/[SKA]_0/[TTPB]_0$ ratio. It has not been investigated whether the silyl groups of the propagating end and the catalyst exchanged through the propagation reaction.

The silyl group in the silyl enolate significantly affects the reactivity and stability of the propagating polymer [100]. This result is rational because the silyl group has been involved in whole polymerization step as the propagating end and the catalyst. For example, in the polymerization of MMA, the reactivity of the propagating PMMA decreased as the increasing bulkiness of the silyl group, which caused the deceleration of polymerization rate of MMA. The polymerization of MMA under the condition of $[\mathrm{MMA}]_0/[^{\mathrm{Me}}\mathrm{SKA}]_0/[\mathrm{TTPB}]_0 = 400/2/1$ at 25 °C in CH_2Cl_2 could complete within 25 min. Under the same condition, the polymerizations using $^{i\mathrm{Bu}}$SKA with a triisobutylsilyl group and 1-tris(trimethylsilyl)siloxy-1-methoxy-2-methyl-1-propene ($^{\mathrm{TMS}}$SKA) with a tris(trimethylsilyl)silyl group became 5 times and 175 times slower than that using $^{\mathrm{Me}}$SKA. Instead, the syndiotacticity of the resulting PMMA increased with the increasing bulkiness of the silyl group; the polymerization using $^{\mathrm{Me}}$SKA, $^{i\mathrm{Bu}}$SKA, 1-triphenylsilyl-1-methoxy-2-methyl-1-propene ($^{\mathrm{Ph}}$SKA), and $^{\mathrm{TMS}}$SKA produced PMMAs with *rr* triad content of 70 %, 73 %, 73 %, and 77 %, respectively. The stability of the propagating polymer also increased with the increasing bulkiness of the silyl group. Rapid and controlled polymerization of *n*BA has been achieved with $^{i\mathrm{Bu}}$SKA in toluene at room temperature (~25 °C) under the condition of $[n\mathrm{BA}]_0/[^{\mathrm{Me}}\mathrm{SKA}]_0/[\mathrm{TTPB}]_0 = 200/1.1/0.1$ to produce a P*n*BA with an M_n of 24.3 kg mol^{-1} and an $M_\mathrm{w}/M_\mathrm{n}$ of 1.06, though the polymerization with $^{\mathrm{Me}}$SKA under the condition of $[n\mathrm{BA}]_0/[^{\mathrm{Me}}\mathrm{SKA}]_0/$

$[TTPB]_0 = 400/2/1$ at 25 °C in CH_2Cl_2 was terminated within 6 h at a conversion of 24.6 % to give a P*n*BA with an M_n of 15.5 kg mol^{-1} and a broad M_w/M_n of 1.63. The M_n of P*n*BA was controlled in a range of 23.1–73.1 kg mol^{-1} while keeping M_w/M_n narrower than 1.17, though attempts to synthesize P*n*BAs with M_n more than 100 kg mol^{-1} resulted in the formation of P*n*BA with M_w/M_n broader than 1.5. Even cyclohexane as a less polar solvent than toluene was available for the polymerization of *n*BA to give P*n*BA with an M_w/M_n of 1.06. In addition, ^{TMS}SKA was also effective for the polymerization of *n*BA.

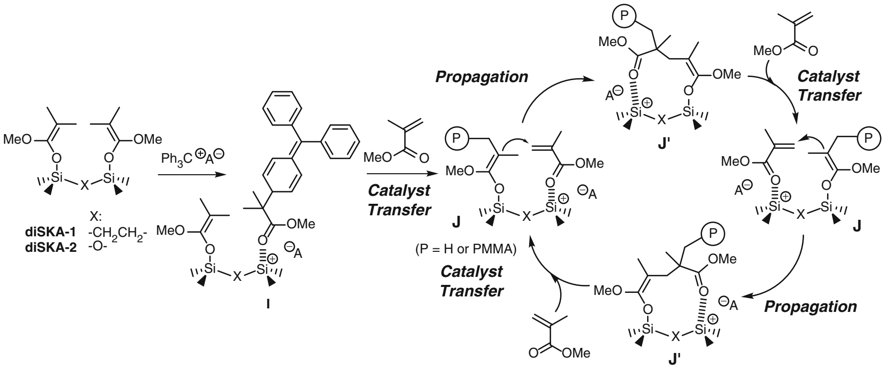
For the TTPB-promoted GTP, the effectiveness of other dimethyl ketene group 14 (alkyl, germyl, and stannyl) acetals has been investigated [100]. Dialkyl dimethylketene acetal did not act as an initiator for the polymerization, though the oligomerization occurred in the presence of TTPB. The synthesis of germyl and stannyl dimethyl ketene acetal was unsuccessful because of exclusive formation of *C*-germyl/stannyl compounds, which was ineffective for the polymerization, in the reaction of lithium enolate and germyl/stannyl chlorides. On the contrary to the large effect of the silyl group on the polymerization behavior, the alkoxy group of the initiator did not show any appreciable effects on entire polymerization characteristics because the difference in the alkoxy group only affected the initiation reaction, which was similar to the result in the conventional GTP [8, 100].

The effect of the counter anion of triphenylmethyl salt on the polymerization was also reported [100]. $Ph_3C[BF_4]$ and $Ph_3C[(C_6F_5)_3Al\text{-}F\text{-}Al(C_6F_5)_3]$ led to the addition of the triphenylmethyl group to ^{Me}SKA rather than the polymerization of MMA because the silylium cation, which was supposed to be generated from the reaction between the triphenylmethyl salts and ^{Me}SKA, was trapped by the fluoride anion released from the counter anions. On the other hand, $[Ph_3C]$[*rac*-TRISPHAT] promoted the polymerization of MMA in CH_2Cl_2 at 25 °C to produce PMMA with *rr* triad content of 73 %, though the polymerization rate was three times slower than the polymerization using TTPB.

Applicable monomers for the TTPB-promoted GTP have been expanded to MMBL [106]. The GTP of MBL using either ^{Me}SKA or ^{iBu}SKA in CH_2Cl_2 was uncontrolled to produce poly(α-methylenebutyrolactone) (PMBL) with bimodal molar mass distribution due to the low solubility of resulting polymer. The polymerization in DMF was totally inhibited probably due to the exclusive coordination of the silylium cation to the solvent, even though a polar solvent was favorable for PMBL. On the other hand, the GTP of MMBL using ^{iBu}SKA and TTPB in CH_2Cl_2 at ~25 °C under the condition of $[MMBL]_0/[^{iBu}SKA]_0 = 200$ homogeneously proceeded within 10 min with a quantitative monomer conversion. The obtained poly(γ-methyl-α-methylenebutyrolactone) (PMMBL) had an M_n of 30.4 kg mol^{-1} and an M_w/M_n of 1.02 as determined by size exclusion chromatography (SEC) combined with a light-scattering detector. Kinetics of the polymerization in CH_2Cl_2 at ambient temperature (25 °C) showed zero-order dependence on monomer concentration regardless of the ratio of $[MMBL]_0/[^{iBu}SKA]_0/[TTPB]_0$, which implied that the polymerization mechanism of MMBL could be also expressed by Scheme 10. The M_n of the resulting PMMBL increased with the increasing monomer conversion while keeping M_w/M_n narrower than 1.09. $[Ph_3C]$[TRISPHAT] was also effective for the polymerization, though the polymerization rate was slightly slower than that using TTPB. The resulting PMMBL had almost similar stereoregularity, *mm*/*mr*/*rr* = 11.3/43.0/45.7, in comparison with that obtained using TTPB, *mm*/*mr*/*rr* = 14.3/39.9/45.8.

Furthermore, the TTPB-promoted GTP of MMA was investigated using difunctional silyl enolates (diSKA), namely, 1,2-bis([(1-methoxy-2-methyl-1-propenyl) oxy](dimethyl)silyl)ethane (diSKA-1) and 1,3-bis([(1-methoxy-2-methyl-1-propenyl)oxy])-1,1,3,3-tetramethyldisiloxane (diSKA-2), to increase activity of the silylium catalyst and stereoregularity of the resulting PMMA [107]. The polymerization of MMA using diSKA-1 and TTPB in CH_2Cl_2 at ambient temperature (~25 °C) under the condition of $[MMA]_0 = 0.935$ mol L^{-1} and $[MMA]_0/[diSKA\text{-}1]_0/[TTPB]_0 = 400/1/1$ was 12 times more rapid than that using ^{Me}SKA in the early stage of the polymerization. However, a resulting PMMA had an M_n around 1.5 times smaller than M_n calculated from the polymerization condition and a broad M_w/M_n of 1.2–1.7, which indicated occurrence of side reactions, such as chain-transfer reaction. The polymerization of MMA using diSKA-2 under similar conditions reached completion within 1 min to give a PMMA with an M_n of 47.4 kg mol^{-1} and an M_w/M_n of 1.28, which was 3.7 times faster than that using diSKA-1 though the M_w/M_n was still broad. The presence of oxygen atom between two silicon atoms in diSKA-2 might have caused the increased reactivity of the silyl enolate. The polymerization with tenfold smaller amount of TTPB ($[MMA]_0/[diSKA\text{-}1]_0/[TTPB]_0 = 400/1/0.1$) produced PMMA with a broad M_w/M_n of 1.28, though the rate of polymerization significantly decreased (42.1 % conversion in 31 h). Opposite to the expectation of Chen et al., the stereoregularity of the PMMA synthesized with diSKAs was similar to that synthesized with ^{Me}SKA regardless of the polymerization condition and the employed triphenylmethyl salts, i.e., TTPB and [Ph_3C][TRISPHAT]; the polymerization in CH_2Cl_2 at 25 °C and −78 °C produced PMMA with *mm*/*mr*/*rr* of 2/28/70 and 1/7/92.

Unlike the GTP using ^{Me}SKA and TTPB, the kinetics of the polymerization using diSKA-2 in CH_2Cl_2 at 25 °C under the condition of $[diSKA\text{-}2]_0/[TTPB]_0 = 1/1$ showed first-order dependence on monomer concentration, which implied that the mechanism of the propagation reaction differs in respective polymerizations. The mechanism of the polymerization using a diSKA was presumed as illustrated in Scheme 11. The reaction of TTPB and diSKA generates mono cationic adducts of the triphenylmethyl cation, which was proven by ^{1}H NMR measurements in deuterated CH_2Cl_2 at −78 °C. The propagation reaction proceeds with intramolecular Michael addition through the formation of the propagating polymer coordinating to MMA (**J**) as an intermediate, which was considered plausible because the polymerization rate must show second-order dependence on catalyst concentration and zero-order dependence on monomer concentration when two propagating polymers are involved in the reaction. The first-order dependence of the polymerization rate on monomer concentration also implied that the transfer of the silylium cation from the propagating polymer, i.e., intermediate **J′**, to the incoming monomer was the rate-determining step.



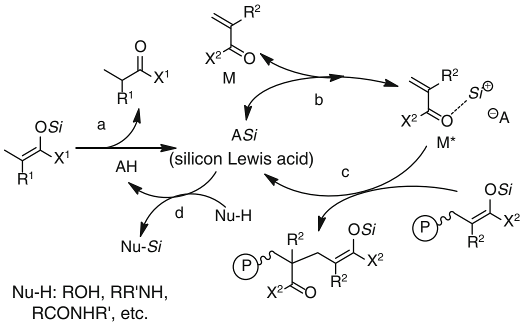
Scheme 11 Proposed mechanism for the GTP of MMA using a difunctional silyl enolate (diSKA)

The GTPs of MBL and MMBL were also examined with diSKAs and TTPB, though they were less controlled than the polymerization using ${}^{i\mathrm{Bu}}$SKA. The polymerization of MBL using TTPB in CH_2Cl_2 was uncontrolled because the resulting PMBL was insoluble in CH_2Cl_2. The polymerization in DMF did not proceed because the silylium cation dominantly coordinated to DMF rather than to the monomer. The polymerization of MMBL using diSKA-1 and TTPB terminated before reaching perfect monomer conversion and only produced PMMBLs with broad M_w/M_ns of around 1.4–1.5. The GTP of MMBL using diSKA-2 and TTPB was about 6.7 times faster than that using diSKA-1. The resulting PMMBL had broad M_w/M_ns of 1.64–2.07 regardless of the polymerization condition, though monomer conversion reached 78–98 %.

3.8 Organic Strong Acids

Not only triphenylmethyl salts but also Brønsted acids have been found to be effective for GTP. Kakuchi et al. first paid attention to the potential of strong Brønsted acids and applied them to GTP [108]. In advance of the series of study, Yamamoto et al. have reported that trifluoromethanesulfonimide (Tf_2NH), one of the strong Brønsted acids, can efficiently promote Mukaiyama aldol reaction of which reaction mechanism is similar to the propagation reaction of GTP [109, 110]. List et al. achieved the asymmetric Mukaiyama aldol reaction promoted by a chiral strong Brønsted, which showed a high reactivity and high enantioselectivity [111]. In these reactions, a strong Brønsted acid (A-H) was considered to first react with a silyl enolate to form silicon Lewis acid ($A\text{-}SiR_3$) as an actual catalyst with extremely high Lewis acidity.

The GTP of MMA was carried out using Tf_2NH and ${}^{\mathrm{Me}}$SKA in CH_2Cl_2 at 27 °C under the condition of $[\mathrm{MMA}]_0/[{}^{\mathrm{Me}}\mathrm{SKA}]_0/[\mathrm{Tf_2NH}]_0 = 100/1/0.05$ to produce PMMA with an M_n of 13.5 kg mol^{-1} and an M_w/M_n of 1.04 within 24 h of the



a. Generation of a silicon Lewis acid as the actual catalyst

b. Coordination of the actual catalyst to a monomer for activation

c. Initiation/Propagation reaction

d. Decomposition of A*Si* by protic contaminants

Fig. 1 Plausible mechanism of the GTP promoted by a strong Brønsted acid (AH)

polymerization time [108]. The kinetics of the polymerization showed first-order dependence between polymerization time and monomer conversion. The M_n of the resulting PMMA linearly increased with the increasing monomer conversion while retaining low M_w/M_n. The postpolymerization experiment directly proved the living nature of the polymerization. The matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) spectrum of the resulting PMMA showed only one population of molecular ion peaks, which corresponded to the molar mass of PMMA bearing terminal structure originated from ^{Me}SKA. The polymerization allowed to synthesize PMMAs with various M_ns of 3.86–17.0 kg mol^{-1} and M_w/M_ns of 1.04–1.08 by changing initial feed ratio of MMA and ^{Me}SKA, $[MMA]_0/[^{Me}SKA]_0$. Another feature of the polymerization was simultaneous control of molar mass and stereoregularity; the polymerization of MMA in CH_2Cl_2 at −55 °C afforded PMMA with M_n of 14.0 kg mol^{-1}, M_w/M_n of 1.04, and *mm*/*mr*/*rr* of 0/10/90 after the 168 h of polymerization.

The polymerization mechanism was presumed based on an analogy with the mechanism of the strong Brønsted-acid-promoted Mukaiyama aldol reaction, as shown in Fig. 1 [111–113]. Five possible elemental reactions were considered as following: (a) the generation of the silicon Lewis acid (A*Si*) as the actual catalyst from the irreversible reaction between a strong Brønsted acid (AH) and the silyl enolate, (b) the reversible coordination of A*Si* to the monomer for the formation of an activated monomer (M*), (c and d) the initiation/propagation reaction between M* and the silyl enolate or the propagating polymer, and (e) the decomposition of A*Si* with protic impurities (Nu-H) accompanied by the regeneration of AH as a side reaction. Thus, the polymerization was considered to proceed through a similar mechanism to the conventional Lewis-acid-catalyzed GTP, though the generation and decomposition of A*Si* additionally occurred [88]. It has not been investigated whether the silyl groups of the propagating end and the catalyst exchange through the propagation reaction. Figure 2 depicts plausible structure of the reaction center on the propagation reaction for the formation of *r* diad and *m* diad. Highly selective formation of *r* diad in the polymerization of MMA was described by the fact that the structure on the left for the formation of *r* diad was considered more favorable

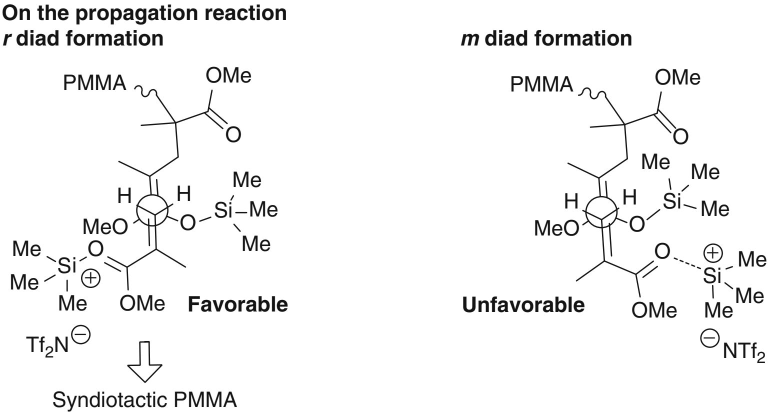


Fig. 2 Speculation of the syndiotactic control of the strong Brønsted acid-promoted GTP of MMA

because of the low steric repulsion between the propagating end and the MMA coordinated by Tf_2NSiMe_3.

Kakuchi et al. later investigated the GTP of MMA using the isolated Tf_2NSiMe_3 itself as the catalyst [114]. The polymerization in CH_2Cl_2 at 25 °C under the condition of $[MMA]_0/[^{Me}SKA]_0/[Tf_2NSiMe_3]_0 = 80/1/0.05$ and $[MMA]_0 = 2.0$ mol L^{-1} produced a PMMA with M_n of 8.6 kg mol^{-1} and M_w/M_n of 1.07 within 9 h. The initiation efficiency of the polymerization using Tf_2NSiMe_3 (94–100 %) improved from that using Tf_2NH (71–75 %). The kinetics of the polymerization using Tf_2NSiMe_3 also showed first-order relationship between polymerization time and monomer conversion. The M_n of the resulting PMMA linearly increased with increasing monomer conversion while retaining low M_w/M_n. The MALDI-TOF MS measurement proved that the product is PMMA-bearing terminal structure originated from ^{Me}SKA. The consumption of a silyl enolate can be avoided by the direct use of a silicon Lewis acid instead of a strong Brønsted acid. However, one must still be aware that contamination of protic impurities causes the decomposition of the silicon Lewis acid and the consumption of a silyl enolate by the regeneration of the silicon Lewis acid from the strong Brønsted acid.

Living polymerization of MA was achieved by the GTP using $^{i\mathrm{Pr}}$SKA as the initiator and 2,3,4,5,6-pentafluorophenyl-1,1-bis(trifluoromethanesulfonyl)methane ($Tf_2CHC_6F_5$) [115, 116] as the catalyst [117]. On analogy to the TTPB-promoted GTP of *n*BA, a silyl enolate with bulky silyl group was favorable for the polymerization. A PMA with an M_n of 108 kg mol^{-1} and an M_w/M_n of 1.07 was obtained from the polymerization in toluene at room temperature (23 °C ± 5 °C) under the condition of $[MA]_0/[^{i\mathrm{Pr}}SKA]_0/[Tf_2CHC_6F_5]_0 = 1000/1/0.02$ and $[MA]_0 = 1.0$ mol L^{-1} within 1 h of the polymerization time. Polymerization kinetics showed first-order relationship between monomer conversion and polymerization time. Unlike the polymerization of MMA, the stereoregularity of the resulting PMA was poor.

The Tf_2NH-promoted GTP of *N*,*N*-dimethylacrylamide (DMAA) initiated by (*Z*)-1-(dimethylamino)-1-trimethylsiloxyprop-1-ene ((Z)-DATP), an amino silyl enolate, proceeded in a living fashion, which is the first success for the controlled/living polymerization of acrylamide monomers in the chemistry of GTP [118]. The polymerization using ^{Me}SKA was uncontrolled and produced PDMAA with broad M_w/M_ns of 1.24–1.76 due to the slower initiation rate than the propagation rate. The analogous structure of (*Z*)-DATP to the propagating end of PDMAA was considered to increase the initiation rate, which led to the living nature of the polymerization. The Tf_2NH-promoted GTP of DMAA in CH_2Cl_2 was faster than that in toluene. The M_n of the resulting PDMAA was controlled in a range of 3.24–53.9 kg mol^{-1} while retaining narrow M_w/M_ns of 1.06–1.16. The MALDI-TOF MS analysis revealed that the resulting PDMAA had a terminal structure originated from (*Z*)-DATP initiator residue and desialylated propagating end, indicating that the Tf_2NH-catalyzed GTP of DMAA proceeded without any side reactions. Although the polymerization kinetics was originally regarded as first order of the monomer concentration [118], it was later revealed to be intermediate of zero order and first order by analytically deriving the polymerization rate equation and numerically analyzing the experimental polymerization rate [119]. The stereoregularity of the resulting PDMAA was moderately syndiotactic and controlled in a range of 56–73 % of *r* diad contents depending on the polymerization solvent and polymerization temperature. Only strong Brønsted acids, such as Tf_2NH and $Tf_2CHC_6F_5$, were effective for the GTP using (*Z*)-DATP; the polymerizations using other conventional catalysts, such as TAS-HF_2, tetra-*n*-butylammonium acetate (TBA-AcO), and ZnI_2, did not proceed or was uncontrolled.

Chen et al. have employed Brønsted acids, such as $H(Et_2O)_2[B(C_6F_5)_4]$, $H(Me_2NPh)[B(C_6F_5)_4]$, and (*R*)-3,3′-Bis[3,5-bis(trifluoromethyl)phenyl]-1,1binaphthyl-2,2′-disulfonimide (List's sulfonimide), for GTP [106, 107, 120]. Formation of silicon Lewis acids from the reaction of the Brønsted acids and ^{Me}SKA was carefully investigated by ^{1}H, ^{19}F, and ^{29}Si NMR measurements in CD_2Cl_2 [120]. The reaction of ^{Me}SKA and $H(Et_2O)_2[B(C_6F_5)_4]$ generated both trimethylsilyl cation coordinated by methyl isobutyrate and diethyl ether. On the other hand, the reaction of ^{Me}SKA with $H(Me_2NPh)[B(C_6F_5)_4]$ or the List's sulfonimide generated only trimethylsilyl cation coordinated by *N*,*N*-dimethylaniline or the sulfonimido group, which indicated coordinating nature of the nitrogen atom to the silylium cation. The GTP of MMA promoted by $H(Et_2O)_2[B(C_6F_5)_4]$ in CH_2Cl_2 at 25 °C under the conditions of $[MMA]_0 = 0.935$ mol L^{-1} and $[MMA]_0/[^{Me}SKA]_0/[H(Et_2O)_2[B(C_6F_5)_4]]_0 = 100/1/0.05$, 133/1/0.067, 200/1/0.10, 400/1/0.20, and 800/1/0.40 reached perfect monomer conversion within 3 h and produced PMMAs with M_ns of 11.3–74.7 kg mol^{-1}, M_w/M_ns of 1.07–1.12, and *mm*/*mr*/*rr*s of 2/26/72. Unlike the GTP of MMA promoted by Tf_2NH, the kinetics of the polymerization showed zero-order dependence on the monomer concentration, which was explained by the difference in coordinating nature of the counter anions, namely, Tf_2N^- and $B(C_6F_5)_4^-$ (*vide infra*). The polymerization rate was first order with respect to the concentration of both $H(Et_2O)_2[B(C_6F_5)_4]$ and ^{Me}SKA. The M_n of the resulting PMMA linearly increased with monomer conversion while keeping low M_w/M_n. The GTP of MMA promoted by $H(Me_2NPh)[B(C_6F_5)_4]$ in

CH_2Cl_2 at 25 °C under the condition of $[MMA]_0/[^{Me}SKA]_0/[H(Me_2NPh)[B(C_6F_5)_4]]_0 = 200/1/0.10$ reached only 97.6 % of monomer conversion after 15 h of polymerization, while the polymerization using $H(Et_2O)_2[B(C_6F_5)_4]$ completed within 40 min under the similar polymerization condition. The GTP of MMA using the List's sulfonimide did not proceed due to exclusive coordination of the silylium cation to the sulfonamide as the counter anion. The result indicated that the presence of a nucleophilic counter anion or a nucleophilic compound inhibits the catalytic activity of the silicon Lewis acid. Chen et al. proposed that the polymerization mechanism for the GTP promoted by a strong Brønsted acid in a manner slightly differed from that shown in Fig. 1, in which the silicon Lewis acid was considered to always coordinate to a propagating polymer or a monomer as well as the mechanism shown in Scheme 10.

The controlled polymerization of DMAA, which has higher Lewis basicity than MMA, was also achieved by the GTP using ^{Me}SKA as the initiator and both $H(Et_2O)_2[B(C_6F_5)_4]$ and List's sulfonimide as the precatalyst, which produced PDMAAs with M_ns of 30.2–102 kg mol^{-1} and M_w/M_ns of 1.09–1.13. The stereoregularity of the resulting PDMAA was atactic ($mm/(mr + rr) = 38.5/61.5$) in the latter polymerization even though the chiral catalyst was utilized. $H(Et_2O)_2[B(C_6F_5)_4]$ was also effective for the polymerization of *n*BMA using ^{Me}SKA [120] as well as that of *n*BA and MMBL using ^{iBu}SKA [106, 120] to give corresponding polymers with narrow M_w/M_ns of 1.07–1.08. However, the polymerization rate of MMBL was four times slower than the polymerization using TTPB. Similarly, $H(Et_2O)_2[B(C_6F_5)_4]$ was less effective than TTPB in the polymerization of MMA using diSKAs; the initiation efficiency was only 27 % [107].

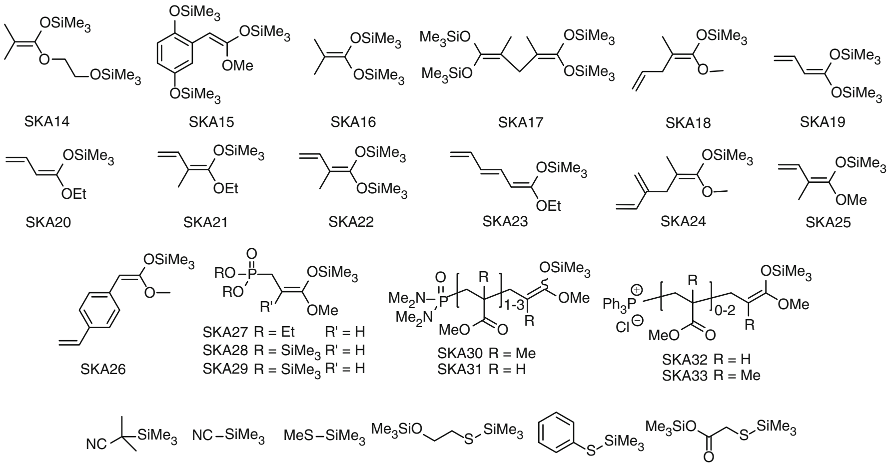
4 Precise Synthesis of Polymer Architectures

4.1 *End-Functionalized Polymers*

Living/controlled polymerization methods have been utilized for the synthesis of end-functionalized polymers as precursors for intelligent materials and diverse polymer architectures, such as end-functionalized, block, star-shaped, dendritic, and cyclic polymers [121]. Synthesis of end-functionalized polymers has been attempted with GTP using both functional initiators [8, 69, 78, 122–126] and terminating agents [8, 127–129].

4.1.1 GTP Using Functional Initiators

Scheme 12 summarizes the functional initiators. SKA14 bearing a silylated hydroxyl group was used for the synthesis of hydroxyl end-functionalized polymers [8, 78]. SKA15 was used for the synthesis of 2,5-dihydroxyphenyl



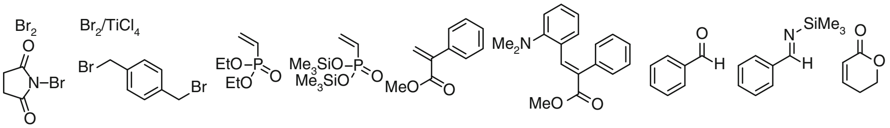
Scheme 12 Functional initiators used in the GTP

end-functionalized polymers, which were subsequently used for the polycondensation [126]. SKA16 and SKA17 were used for the synthesis of PMMA end functionalized with a carboxylic acid [4, 78]. For example, the polymerization of MMA using SKA17 produced PMMA end functionalized with a carboxylic acid with a M_n of 2.1 kg mol^{-1} and an M_w/M_n of 1.29. The polymerizations using SKA18-22 and SKA23-24 produced vinyl and dienyl end-functionalized polymers, respectively [69, 125]. The GTPs of MMA using SKA19 and SKA20 exclusively produced vinyl end-functionalized polymers, while the similar polymerizations using SKA21 and SKA22 produced 71–72 % of vinyl end-functionalized PMMA and 28–29 % of internal olefin end-functionalized polymers. Bandermann et al. later investigated the polymerization of MMA using other vinyl- and dienyl-functionalized initiators [124]. For example, The GTP using SKA25 produced vinyl end-functionalized PMMA with M_ns of 11.2–91.8 kg mol^{-1} and M_w/M_ns of 1.41–1.69. The polymerization of MMA using SKA26 produced 4-vinylphenyl end-functionalized PMMA with M_ns of 6.9–35.5 kg mol^{-1} and M_w/M_ns of 1.27–1.55. Silyl enolates bearing a phosphonate group (SKA27-31) were used to prepare phosphonate end-functionalized polymers. For instance, SKA27 and SKA29-30 were effective for the synthesis of narrowdispersed phosphonate end-functionalized PMMAs, though the M_n of the product when using SKA30 was 2–3 times higher than the calculated M_n. In contrast, the GTP of MMA using SKA28 and SKA31 was uncontrolled and produced PMMAs with broad M_w/M_ns. Shen et al. reported the GTP of MMA using triphenylphosphine and chlorotrimethylsilane [123]. In this case, trimethylsilyl chloride is the potential initiator and can add to a monomer to form a silyl enolate (SKA32-33) in accordance with the formation of a Wittig reagent. The triphenylmonoalkyl phosphonium cation is stable under the condition of GTP to produce a Wittig reagent end-functionalized polymer.

In addition, α-cyanosilyl compounds and silylated thiols were also applied for the GTP to develop stable initiator than silyl enolates, which eventually produced cyano end-functionalized polymers and sulfide end-functionalized polymers. Sogah et al. carried out the polymerization of MMA using α-trimethylsilylisobutyronitrile and TAS-HF_2 in THF, which resulted in an uncontrolled polymerization to produce a PMMA with a M_n of 47.5 kg mol^{-1} and an M_w/M_n of 3.96 [8]. Trimethylsilyl cyanide was also used for the polymerization of MMA in acetonitrile catalyzed by tetraethylammonium cyanide (TEACN) to produce a PMMA with a M_n of 6.91 kg mol^{-1} and an M_w/M_n of 1.49 [8]. Some of the silylated thiol initiators were designed to have a protected functional group and used for the synthesis of hydroxyl or carboxylic acid end-functionalized polymers [122]. Webster et al. carried out the polymerization of MMA using methyl trimethylsilyl sulfide and that of EA using phenyl trimethylsilyl sulfide catalyzed by TEACN in acetonitrile, which produced a PMMA with an M_n of 11.8 kg mol^{-1} and an M_w/M_n of 1.64 and a PEA with an M_n of 2.27 kg mol^{-1} and an M_w/M_n of 1.83 [8]. Reetz et al. carried out the polymerization of MA and *n*BA using four silylated thiol initiators [122]. The polymerization of *n*BA using methyl trimethylsilyl sulfide or 2-(trimethylsiloxy)ethyl trimethylsilyl sulfide catalyzed by $TASHF_2$ in THF or acetonitrile was uncontrolled and produced P*n*BAs with M_ns of 1.1–1.5 kg mol^{-1} and M_w/M_ns of 1.44–2.0. Lewis acids, such as ZnI_2 and chlorodiisobutylaluminum, were effective for the polymerization of MA and *n*BA using trimethylsilyl methyl sulfide and 2-(trimethylsiloxy)ethyl trimethylsilyl sulfide in toluene or CH_2Cl_2 to produce corresponding polymers with M_ns of 6.9–14.2 and M_w/M_ns of 1.08–1.16.

4.1.2 GTP Using Terminating Agents

The end-functionalization using terminating agents is based on the termination reaction of the silyl enolate in the propagating polymer. Scheme 13 summarizes the terminating agents employed so far. Sogah et al. synthesized bromine end-functionalized PMMA by the termination reaction of a living PMMA using molecular bromine or *N*-bromosuccinimide [78]. Difunctional alkylating and acylating agents were used for the coupling reaction of two propagating polymers. Sogah et al. synthesized α,ω-end-functionalized polymers by the termination reaction of α-end-functionalized polymers synthesized using functional initiators, such as SKA14 and SKA15, and difunctional alkylating and acylating agents, which required equimolar fluoride anion relative to the propagating polymer [8, 78]. 4-Vinylphenyl end-functionalized PMMA was synthesized in the same



Scheme 13 Terminating agents used in the GTP

manner using 4-(bromomethyl)styrene [130, 131]. These reactions required equimolar fluoride anion [8]. The mixture of molecular bromine and titanium (IV) chloride was used for the direct coupling reaction of two living PMMAs based on the bromination of the living PMMA and the coupling reaction between the PMMA end functionalized with tertiary alkyl bromide and the PMMA bearing a silyl enolate, which was also used for the synthesis of α,ω-dihydroxyl and α,-ω-carboxylic acid PMMA [78]. Diethyl vinylphosphonate and bis(trimethylsilyl) vinylphosphonate were used as a terminating agent for the synthesis of phosphonate end-functionalized PMMAs synthesized using TAS-HF_2 in THF [127]. The phosphonic acid end-functionalized PMMA was obtained by treating the diethyl phosphonate end-functionalized PMMA with bromotrimethylsilane and the bis (trimethylsilyl) phosphonate end-functionalized PMMA with aqueous THF in the presence of catalytic amount of *p*-toluenesulfonic acid. Quirk et al. reported end-functionalization reaction using a monomer with high ceiling temperature, such as methyl 2-phenylmethacrylate and methyl (*E*)-3-(2-(dimethylamino)phenyl)-2-phenylacrylate [128]. The Mukaiyama-Michael reaction as the termination reaction using both of the terminating agent quantitatively proceeded in the presence of TAS-HF_2 to give corresponding end-functionalized PMMAs. The latter terminating agent produced the dimethylamino end-functionalized PMMA. Sivaram et al. performed the termination reaction of the PMMA synthesized using TBABB by treating with benzaldehyde, *N*-trimethylsilylbenzylideneimine, and 5,6-dihydro-2*H*-pyran-2-one to synthesize hydroxyl, amino, and *δ*-valerolactone end-functionalized PMMA, though the number-average degree of functionalization was in the range of 0.70–0.85 [129]. The termination reaction using *N*-trimethylsilylbenzylideneimine was carried out with additional ZnI_2 as a catalyst, which is only one method to synthesize primary amine end-functionalized polymer with GTP method.

4.2 Block Copolymers

Before the emergence of LRPs, conventional GTP was a universally used means to prepare block copolymers consisting of polymethacrylate and polyacrylate segments due to the living nature of the polymerization. The syntheses of block copolymers by GTP can be readily achieved by a sequential addition of monomer. For instance, an AB-type diblock copolymer with the simplest structure can be prepared by the following procedures: the synthesis of the first block possessing a living chain end with a quantitative consumption of the first monomer and the addition and polymerization of a second monomer. Similarly, a multiblock copolymer like ABC type can also be easily prepared by this method. In addition to AB- and ABC-type block copolymers, the syntheses of ABA-type block copolymers have been also reported by using difunctional initiators. The block copolymers consisting of similar sort of monomer units, such as two different alkyl methacrylates, generally have controlled molar masses (up to 204 kg mol^{-1}) and dispersities

Table 3 Ranges of M_n and M_w/M_n for star-shaped poly(meth)acrylates synthesized by GTP

Star-shaped polymer	SKA	Catalyst	Arm number	M_n(expt) (kg mol^{-1})	M_w/M_n
PEA[a]	SKA34	$(i\text{-Bu}_2\text{Al})_2\text{O}$	3	2.19	1.39
	SKA35	$(i\text{-Bu}_2\text{Al})_2\text{O}$	4	2.40	1.24
PMMA[b]	SKA36	TBA-OAc	4	6.3–50.9	1.21–1.30
P(M14)[b]	SKA37	$t\text{-Bu-P}_4$	3	11.1–41.6	1.09–1.10
PMMA[b]	SKA38	$t\text{-Bu-P}_4$	3	3.9–132.0[c]	1.07–1.14
PMMA[b]	SKA39	$t\text{-Bu-P}_4$	4	5.5–130.3[c]	1.07–1.17
P(M18)[b]	SKA39	$t\text{-Bu-P}_4$	4	13.6–21.2[c]	1.11–1.16
P(M10)[b]	SKA39	$t\text{-Bu-P}_4$	4	15.5–23.3[c]	1.10–1.16
PSMA[b]	SKA39	$t\text{-Bu-P}_4$	4	34.5–65.2[c]	1.06–1.08
PMMA[b]	SKA40	$t\text{-Bu-P}_4$	6	7.5–131.6[c]	1.06–1.15
PMMA[a]	SKA38	$\text{Tf}_2\text{NSiMe}_3$	3	12.9[c]	1.04
PMMA[a]	SKA39	$\text{Tf}_2\text{NSiMe}_3$	4	12.9[c]	1.04
PMMA[a]	SKA40	$\text{Tf}_2\text{NSiMe}_3$	6	13.4[c]	1.04

[a] The polymerizations were carried out in CH_2Cl_2
[b] The polymerizations were carried out in THF
[c] The molar masses are absolute molar masses determined by multi-angle laser light scattering (MALS) in THF

(lower than 1.64) by conventional GTP [1, 8, 30, 36, 40, 42, 45, 46, 61, 76, 132, 133]. On the other hand, the synthesis of (polymethacrylate-*b*-polyacrylate)-type block copolymers is proven to be difficult due to the big difference in the reactivities of methacrylate and acrylate as well as the lack of a suitable catalyst for both monomers [1, 76, 134–136]. Therefore, the conventional GTP has been actually unsuitable to prepare block copolymers consisting of different polymer segments. It is restricted to synthesize either all acrylic or all methacrylic block copolymers.

Fortunately, the organocatalytic GTP has realized the block copolymerization of structurally different monomers in some extent. As described before, NHCs are known to catalyze the GTP of (meth)acrylates, DMAA, and MAN under similar polymerization conditions, which has opened new doors for the synthesis of block copolymers consisting of different sort of polymer segments. The sequential block copolymerization of MMA and *t*BA was first achieved via the GTPs using NHC-1 by Waymouth et al. and using NHC-2 by Taton and Gnanou et al. [19, 20]. Taton and Gnanou et al. further succeeded in the synthesis of various di- and triblock copolymers by the sequential GTP of MMA, M10, *n*BA, *t*BA, M38, DMAA, and MAN catalyzed by NHC-2 or NHC-3 regardless of the addition order of monomers, as summarized in Table 3, though some of them had rather broad M_w/M_n [21, 24]. Notably, the synthesized PMMA-*b*-P*t*BA-*b*-PDMAA might have partially gradient structure because the monomer conversion in the second polymerization of *t*BA and the third polymerization of DMAA were not quantitative. They explained that the feature of the GTP catalyzed by NHC-2 or NHC-3, which plausibly proceeds with the associative mechanism, realized the synthesis of various block copolymers by the sequential polymerization. The GTP catalyzed by

TTMPP was also effective for the block copolymerization of MMA and *t*BA, which produced PMMA-*b*-P*t*BA with an M_n of 22.0 kg mol^{-1} and an M_w/M_n of 1.19 with quantitative conversions of monomers on both steps [29].

In contrast to the success in the Lewis-base-catalyzed GTP, the block copolymerization with the Lewis-acid-catalyzed GTP is still limited to the synthesis of polymethacrylate-*b*-polyacrylate and polymethacrylate-*b*-poly(-α-methylenebutyrolactone) because of the difference in the reactivity of monomers. Chen et al. have investigated the block copolymerization by the GTP promoted by triphenylmethyl salts and strong Brønsted acids. Sequential block copolymerization of MMA and *n*BA was attempted by the GTP using TTPB starting from both MMA and *n*BA [100]. The former polymerization produced a PMMA-*b*-P*n*BA with an M_n of 45 kg mol^{-1} and an M_w/M_n of 1.1 both in CH_2Cl_2 and toluene, while the latter polymerization only produced homo P*n*BA. Interestingly, statistical copolymerization of MMA and *n*BA also turned out to be a selective polymerization of *n*BA to produce only homo P*n*BA. There are two possible reasons: (1) the nucleophilicity of the propagating end derived from *n*BA is insufficient to attack MMA; (2) the silyl cation does not coordinate to the carbonyl group of MMA due to steric hindrance. More future work is needed for this interesting issue. Sequential GTP of MMA and MBL as well as MMA and MMBL using TTPB in CH_2Cl_2 successfully produced PMMA-*b*-PMBL and PMMA-*b*-PMMBL, even though the solubility of the PMBL segment in CH_2Cl_2 is low [106]. These block copolymerizations did not proceed when the polymerization was started from MBL or MMBL probably due to the similar reasons in the block copolymerization of *n*BA and MMA (*vide supra*). The block copolymerization of MMBL and MBL successfully produced well-defined diblock copolymer, PMMBL-*b*-PMBL ($M_n = 117$ kg mol^{-1} and $M_w/M_n = 1.02$), when the polymerization was initiated from MMBL. Unlike the statistical copolymerization of MMA and *n*BA, the statistical copolymerization of MBL and MMBL proceeded to give statistical copolymer, PMMBL-*co*-PMBL ($M_n = 123$ kg mol^{-1} and $M_w/M_n = 1.01$). The GTP using ^{iBu}SKA and $H(Et_2O)_2[B(C_6F_5)_4]$ also allowed the block copolymerization of MMA and *n*BA in toluene in a controlled fashion to produce a PMMA-*b*-P*n*BA with an M_n of 42.5 kg mol^{-1} and an M_w/M_n of 1.08 [120].

4.3 Star-Shaped Polymers

A propagating end of polymer in GTP is stable and electronically neutral, which is advantageous for core-first synthesis of a star-shaped polymer in comparison with other living/controlled polymerizations. Unlike the LRPs, GTP is free from intermolecular termination reaction involved by two propagating polymers. In addition, the high solubility of multivalent initiator/propagating polymer in solvents assists the homogeneous growth of arm polymers, which is hard to achieve in anionic/cationic polymerizations. Several attempts to synthesize star-shaped polymers using the GTP have been revealed by several groups so far, as summarized in

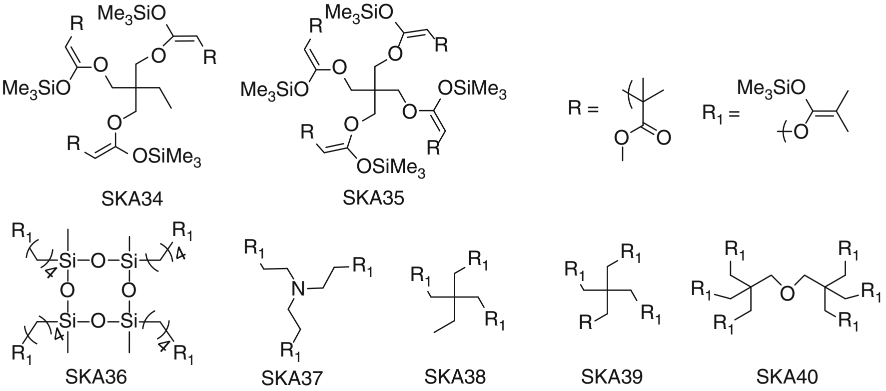
Table 4 Block copolymers synthesized by sequential GTP using organocatalysts

Catalyst	Initiator	Solvent	Block copolymer	M_n (expt.)[a] (kg mol^{-1})	M_w/M_n[a]	Ref.
NHC-1	^{Me}SKA	THF	PMMA-*b*-P*t*BA	11.8	1.14	[20]
NHC-2	^{Me}SKA	Toluene	PMMA-*b*-P*t*BA	21.9	1.3	[19]
		THF	PMMA-*b*-P*t*BA-*b*-PMMA	12.6	1.4	[19]
		THF	PMMA-*b*-P(M38)	11.0[b]	1.3	[24]
		THF	PMMA-*b*-P(M10)	22.0[b]	1.1	[24]
		THF	PMMA-*b*-PDMAA	16.9[b]	1.09	[24]
		THF	PMMA-*b*-PMAN	71.0[b]	1.18	[24]
		THF	PMMA-*b*-P*t*BA-*b*-PDMAA	5.3[b]	1.09	[24]
		THF	P(M10)-*b*-PDMAA	13.0[b]	1.29	[24]
		THF	P(M10)-*b*-P(M38)	4.8[b]	1.21	[24]
		THF	P*t*BA-*b*-PMMA	12.0[b]	1.27	[24]
		THF	P*t*BA-*b*-PDMAA	21.3[b]	1.2	[24]
		THF	P*t*BA-*b*-P(M10)	36.7[b]	1.23	[24]
		THF	PDMAA-*b*-P(M10)	17.6[b]	1.4	[24]
		THF	PDMAA-*b*-PMMA	23.9[b]	1.3	[24]
NHC-3	^{Me}SKA	THF	PMMA-*b*-P*n*BA	16.0	1.5	[21]
		Toluene	PMMA-*b*-P*n*BA	18.2	1.6	[21]
		THF	P*n*BA-*b*-PMMA	10.5[b]	1.4	[24]
		THF	PMMA-*b*-P*n*BA-*b*-PMMA	130	1.6	[21]
TTMPP	^{Me}SKA	THF	PMMA-*b*-P*t*BA	22.0	1.19	[29]
TTPB	^{iBu}SKA	CH_2Cl_2	PMMA-*b*-P*n*BA	44.8	1.09	[100]
		Toluene	PMMA-*b*-P*n*BA	45.3	1.13	[100]
		CH_2Cl_2	PMMA-*b*-PMBL	68.4[c]	1.01[c]	[106]
		CH_2Cl_2	PMMA-*b*-PMMBL	68.1[c]	1.03[c]	[106]
		CH_2Cl_2	PMMBL-*b*-PMBL	117[c]	1.02[c]	[106]
$H(Et_2O)_2$ [B $(C_6F_5)_4$]	^{iBu}SKA	Toluene	PMMA-*b*-P*n*BA	42.5	1.08	[120]

[a] Determined with SEC measurements
[b] Determined by NMR measurements
[c] Determined by multi-angle laser light scattering (MALS)

Table 4. Webster and Sogah first reported the core-first synthesis of three- and four-armed star-shaped PEA through an in situ GTP using a conventional Lewis acid catalyst of $(i\text{-}Bu_2Al)_2O$. They first synthesized tri- and tetra-functional initiators (SKA34-35) by the Michael addition of trimethylolpropane triacrylate and pentaerythritol tetraacrylate with ^{Me}SKA, respectively. After a consequent addition of EA to the initiator solution, the $(i\text{-}Bu_2Al)_2O$-catalyzed GTP of EA proceeded with quantitative conversion to produce three- and four-armed star-shaped PEAs without cross-linking. The obtained star-shaped PEAs however had only low M_ns ($\leq$2.4 kg mol^{-1}) and broad dispersities above 1.24 [8]. Wnek et al. then reported the

core-first synthesis of the four-armed star-shaped PMMAs with M_n of 6.3–50.9 kg mol^{-1} and M_w/M_n of 1.21–1.30 using SKA36 and a Lewis base catalyst of TBAOAc [137]. Patrickios et al. reported the arm-first synthesis of various star-shaped poly(methacrylate)s or copolymers with undefined arm number using monofunctional monomers and bifunctional linking agents like M29-31 [44, 48–50, 53]. Most recently, our group first achieved the core-first synthesis of star-shaped polymers by organocatalytic GTP using star-shaped initiators with multiple SKA groups (SKA37-40) and either a Lewis base organocatalyst (t-Bu-P_4) or a Lewis acid organocatalyst (Tf_2NSiMe_3) [26–28, 114]. The t-Bu-P_4-catalyzed GTP favored in producing star-shaped polymers with high molar mass, while Tf_2NSiMe_3-catalyzed GTP was advantageous in producing star-shaped polymers with high stereoregularity. The t-Bu-P_4-catalyzed GTP of MMA using the SKA38-40 homogeneously proceeded to give the well-defined three-, four-, and six-armed star-shaped PMMAs with M_n of 3.6–118.0 kg mol^{-1} and M_w/M_n of 1.06–1.17. The homogeneous growth of each arm polymer was proven by cleavage experiments of the core linkage. It is noteworthy that the star-shaped PMMAs with definite arm number, high M_n, and narrow M_w/M_n were obtained with easy procedures under moderate conditions, which was absolutely different from the core-first synthesis of star-shaped PMMAs by LRPs and ionic polymerizations. In addition to MMA, t-Bu-P_4-catalyzed GTP was also suitable for other methacrylates, such as M10, M14, M18, and SMA. The t-Bu-P_4-catalyzed GTPs of M10, M18, and SMA using SKA39 in THF quantitatively produced corresponding four-armed star-shaped polymers with predetermined M_ns and M_w/M_ns narrower than 1.16 within 1 h. The polymerization of M14 using SKA37 produced three-armed polymers with M_ns of 11.1–41.6 kg mol^{-1} and M_w/M_ns of ~1.10 within 30 min. On the other hand, Tf_2NSiMe_3-catalyzed GTP of MMA using SKA38-40 could produce well-defined syndiotactic-rich star-shaped PMMAs (rr up to 89 %). The star-shaped SKAs are shown in Scheme 14.

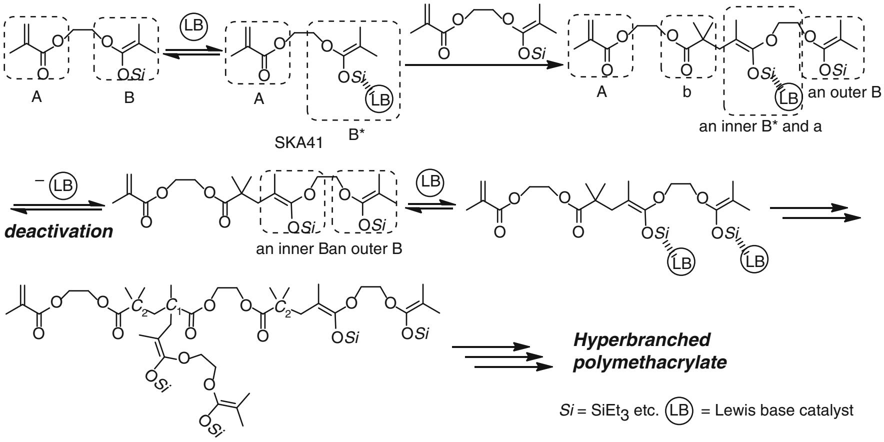


Scheme 14 Structures of star-shaped initiators used in GTP (SKA34-40)

4.4 Hyperbranched Polymers

The one-pot synthesis of hyperbranched polymethacrylates has been attempted by a creative design of an inimer composed of a methacrylate (A) and a SKA (B). B in a polymer is a latent propagating site. It becomes active (B*) when activated by a Lewis base catalyst. B* then intermolecularly reacts with A in another inimer to produce an adduct consisting of a reacted A (a), a reacted B (b), an inner B*, and an outer B, as shown in Scheme 15. After the first addition of an inimer, the inner B* may be deactivated due to the detachment of the catalyst in the associate mechanism or the silylation of the active enolate anion in the dissociate mechanism. Therefore, if the deactivation rate of the inner B* is much slower than that of its propagation, the polymerization will occur predominantly at the inner B*. A perfect hyperbranched polymethacrylate can be ideally obtained when the inner B*s are completely deactivated before propagation, and the reaction rates of the inner and outer B*s with the methacryloyl group are the same. Since propagations from the inner B* and the outer B* generate methyl- and dimethyl-substituted quaternary carbons (C_1 and C_2, respectively), the degree of branching (DB) can be estimated by ^{13}C NMR analyses.

Both Sakamoto et al. and Müller et al. reported the self-condensing GTP of 2-(2-methyl-1-triethylsiloxy-1-propenyloxy)ethyl methacrylate (SKA41). The self-condensing GTP of SKA41 using Lewis base catalyst of $TASMe_3SiF_2$ or TBABB by Sakamoto et al. produced hyperbranched polymers with M_ns of 5.7–11.0 kg mol^{-1} and M_w/M_ns of 1.10–1.70 within 5 min. In their studies, the extent of branching was evaluated by the ratio of C_1 and C_2 (C_1/C_2). A perfect hyperbranched polymethacrylate has a C_1/C_2 value of 1. The higher the C_1/C_2 value is, the more defective the hyperbranched polymethacrylate is. It has been



Scheme 15 One-pot synthesis of hyperbranched polymethacrylate by GTP catalyzed by a Lewis base catalyst

found that a less active catalyst tends to decrease the C_1/C_2 value because the deactivation of the inner active sites seemed to much easily take place [138]. The self-condensing GTP of SKA41 by Müller et al. produced hyperbranched polymethacrylates with an M_w up to 38.0 kg mol^{-1} at a dispersity of ca. 3.6. The resulting hyperbranched polymethacrylates in their study had a maximum *DB* of ≈ 0.4 on the basis of a standard calculation. In addition, they also reported the self-condensing group transfer copolymerization of SKA41 and MMA to afford highly branched polymethacrylates, the M_w of which could reach a maximum of 240 kg mol^{-1} at a dispersity of ca. 3.0. When MMA was replaced by *t*BMA, the self-condensing group transfer copolymerization of SKA41 and *t*BMA was also achieved, from which a water-soluble highly branched poly(methacrylic acid) was obtained by acid-catalyzed hydrolysis of the *tert*-butyl groups [139–143].

5 Conclusion and Outlook

The field of GTP is divided into two branches, i.e., the conventional and organocatalytic GTPs, on the basis of the employed catalysts. The conventional GTP catalyzed by traditional nucleophilic anions or metallic Lewis acids has been extensively studied, and their polymerization behavior and mechanisms were well understood though many debates have been lasting so far. On the contrary, the organocatalytic GTP has been flourishing since 2007. It is more advantageous than the conventional one and has made great progress in many aspects such as catalytic activity, applicable monomers, molar mass control, and control of polymer structures. In short, much more work should be conducted in this field. The future development in GTP is expected to achieve the following goals: (1) to realize controlled/living polymerizations of other vinyl monomers, such as α- or β-substituted acrylates, α- or β-substituted acrylamides, acrylonitrile, and vinylphosphonate; (2) to further develop chemically stable initiators as to greatly enhance the practical application of GTP because silyl enolates used nowadays are rather expensive and unstable; (3) to achieve new organocatalytic aldol GTP, which should further expand the scope of applicable monomer; (4) to design and synthesize polymers with functional groups and/or complicated architectures by GTP or by the combination of GTP and other controlled/living polymerization procedures; (5) to prepare stereospecific polymers, and so on. In conclusion, the GTP method still has much potential to bring about further development in polymer chemistry. The authors firmly believe that the aforementioned introduction would lead the readers to a comprehensive understanding on the methodology of GTP.

Abbreviations

AN	Acrylonitrile
*n*BA	*n*-Butyl acrylate
*t*BA	*t*-Butyl acrylate
*n*BMA	*n*-Butyl methacrylate
*t*BMA	*t*-Butyl methacrylate
t-Bu-P_4	1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene)
(*Z*)-DATP	(*Z*)-1-(Dimethylamino)-1-trimethylsiloxy-1-propene
DEAA	*N*,*N*-Diethyl acrylamide
*n*DMA	*n*-Dodecyl methacrylate
DMAA	*N*,*N*-Dimethyl acrylamide
EA	Ethyl acrylate
EMA	Ethyl methacrylate
LMA	Lauryl methacrylate
LRP	Living radical polymerization
MA	Methyl acrylate
MAN	Methacrylonitrile
MBL	α-Methylenebutyrolactone
MMA	Methyl methacrylate
MMBL	γ-Methyl-α-methylenebutyrolactone
M_n	Number average molar mass
M_w	Weight average molar mass
M_w/M_n	Dispersity
NHC	*N*-heterocyclic carbene
NHC-1	1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene
NHC-2	1,3-Diisopropylimidazol-2-ylidene
NHC-3	1,3-Di-*tert*-butylimidazol-2-ylidene
*n*OMA	*n*-Octyl methacrylate
^{Me}SKA	1-Methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene
^{Et}SKA	1-Methoxy-1-(triethylsiloxy)-2-methylprop-1-ene
^{iBu}SKA	1-Methoxy-1-[tri(*iso*-butyl)siloxy]-2-methylprop-1-ene
^{iPr}SKA	1-Methoxy-1-[tri(*iso*-propyl)siloxy]-2-methylprop-1-ene
^{nPr}SKA	1-Methoxy-1-[tri(*n*-propyl)siloxy]-2-methylprop-1-ene
^{Ph}SKA	1-Methoxy-1-(triphenylsiloxy)-1-methylprop-1-ene
^{TMS}SKA	1-Methoxy-1-[tri(trimethylsilyl)siloxy]-2-methylprop-1-ene
SKA	Silyl ketene acetal
SMA	Stearyl methacrylate
TAS	Tris(dialkylamino)sulfonium
TBA	Tetra-*n*-butylammonium
TBABA	Tetra-*n*-butylammonium biacetate
TBABB	Tetra-*n*-butylammonium bibenzoate
TBAF	Tetra-*n*-butylammonium fluoride

$Tf_2CHC_6F_5$	2,3,4,5,6-Pentafluorophenyl-1,1-bis(trifluoromethanesulfonyl) methane
Tf_2NH	Trifluoromethanesulfonimide
TiBP	2,8,9-Triisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane
TTMPP	Tris(2,4,6-trimethoxyphenyl)phosphine
TTPB	Triphenylmethyl tetrakis(pentafluorophenyl)borate

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