Synthesis of Well-Defined Acrylate Polymer Architectures by Organocatalyzed Group Transfer Polymerization

A Dissertation for the Degree of Doctor of Philosophy

Kenji Takada

Hokkaido University

March, 2015

Acknowledgement

The study presented in this dissertation has been performed under the direction of Professor Toyoji Kakuchi and Professor Toshifumi Satoh, Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, from 2010 to 2015. The author wishes to express his sincere appreciation to Professor Toyoji Kakuchi for his kind instruction, helpful advice, and unstinting encouragement during the course of this work.

The author is deeply grateful to Professor Toshifumi Satoh for his helpful and valuable suggestions with continuous encouragement throughout this work. In addition, the author feel sincere grateful to Dr. Keita Fuchise for his patient teaching, fruitful daily discussion and spiritual care.

The author enjoyed working with colleagues because the friendship and good humor of the members in the laboratory created a pleasant and stimulating environment in which to work. The author thanks all of members of Professor Kakuchi's and Professor Satoh's groups, especially, Messrs. Dr. Hideki Misaka, Dr. Takuya Isono, Dr. Naoya Sakai, Dr. Kosuke Makiguchi, Atsushi Nagai, Seiya Kikuchi, Yusuke Satoh, Kana Miyachi, Tatsuya Saitoh, Takuhiko Matsuno, Kouhei Yoshida, Mingoo Jin, Megumi Tanefuji, and Kaori Matsuda. Especially, he appreciates and respects Shigeki Ohta, Yoshitaka Ogasawara, Kensuke Kamoshida, Toshimitsu Takaoka, and Naoki Nishikawa with their friendship.

The author would like to give his special thanks to Messrs. Keita Fuchise, Yougen Chen, Junsuke Kitakado, Naoya Kubota, Shinji Tsuchida, Yu Takagi, Takahiro Ito, and Kodai Kitano for their fine contributions to this dissertation work.

The author is also grateful to the "Research Fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists" during 2013-2015.

Finally, the author to express his deep gratitude to him family for their understanding, support, and encouragement throughout him study.

March, 2015

Contents

Chapter 1

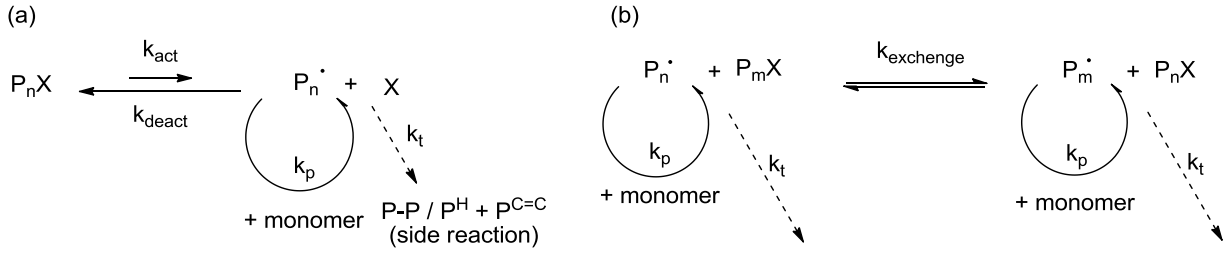
General Introduction

1.1 Controlled/Living Polymerization of Acrylate Monomers

1.1.1 Living Radical Polymerization

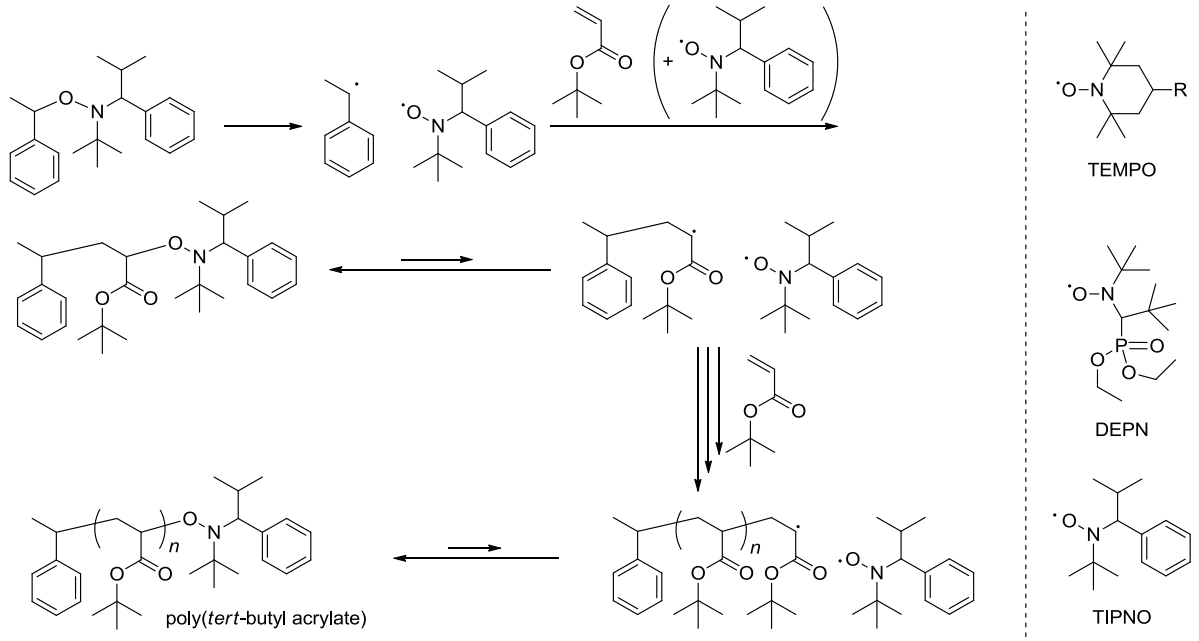
Controlled/living polymerization is one of the important methods in the chemistry of polymer synthesis, which is defined as a chain growth process without any chain-breaking reactions, such as termination and transfer reactions, affording precisely synthesized polymers with controlled molecular weights, dispersities, and architectures.[1] The controlled/living radical polymerization (CRP) is one of the efficient method for the synthesis of acrylate polymers, which is classified according to its mechanism. Nitroxide-mediated radical polymerization (NMP) and atom transfer radical polymerization (ATRP) proceed through a "reversible termination mechanism", which the newly genetrated radicals (P_n^*) were rapidly trapped in a deactivation process by X, nitroxide or organometallic species, as shown in Scheme 1-1(a). The other one is the reversible addition-fragmentation chain transfer (RAFT) polymerization through a "chain transfer dominated mechanism", which involves the conventional free radical polymerization of a substituted monomer in the presence of a suitable chain transfer agent (CTA) as shown in Scheme 1-1(b).

Scheme 1-1. Mechanism of the Controlled/living Radical Polymerization



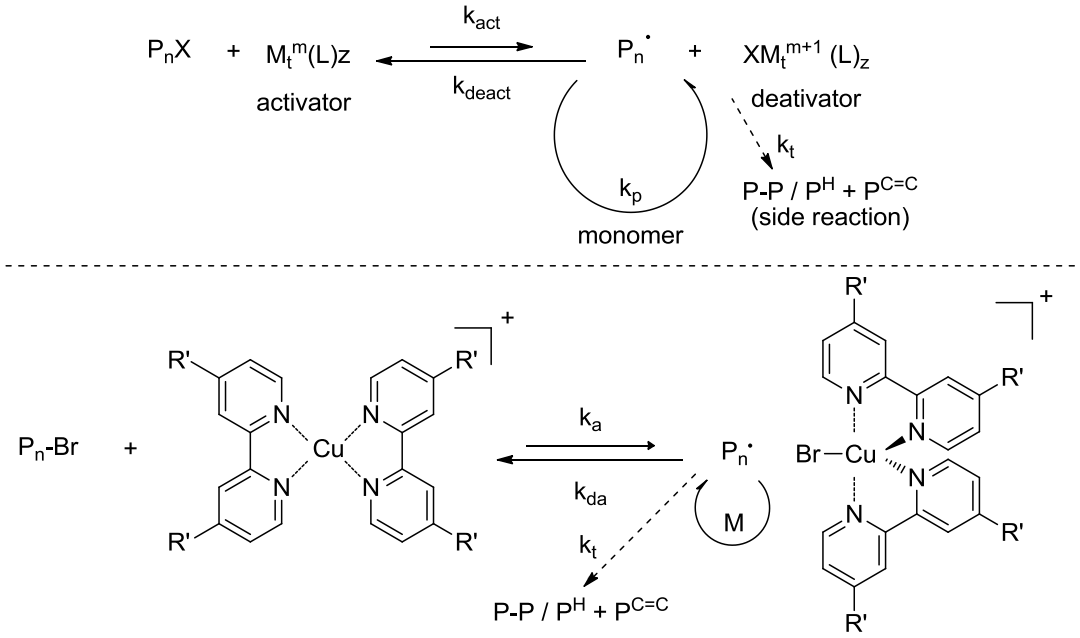
The NMP system relies on the reversible homolytic cleavage of a relatively weak bond in a covalent species to generate a growing radical and a less reactive species (usually the persistent radical, but can also be species with an even number of electrons).[2,3] This species should reversibly react only with growing radicals and should not react amongst themselves or with monomers to initiate the growth of new chains, and they should not participate in side reactions such as the absorption of β-H atoms. The nitroxides were originally employed as stable free radicals in the polymerization of (meth)acrylates. TEMPO, DEPN, and TIPNO derivatives form relatively strong covalent bonds in alkoxyamines (Scheme 1-2).[4-6] Especially, the stabilities of the DEPN and TIPNO derivatives are sufficient to control the polymerization of a wide range of monomers including the (meth)acrylate monomers.

Scheme 1-2. The General Mechanism of NMP using TIPNO-type Nitroxide as an Initiator



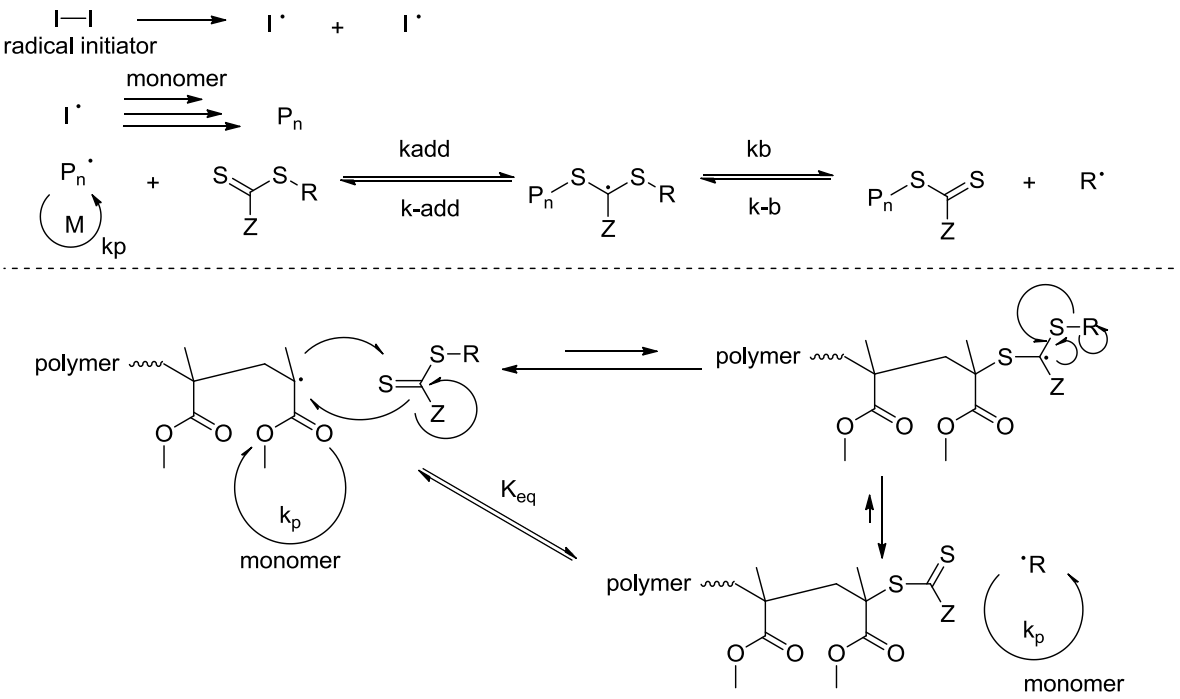
ATRP is currently the most widely used CRP technique. [7-12] This originates from the commercial availability of all the necessary ATRP reagents, including the transition metal compounds and ligands used as catalysts, as well as alkyl halide initiators, and also from the large range of monomers polymerizable by this technique under the wide range of conditions. The basic working mechanism of ATRP involves hemolytic cleavage of an alkyl halide bond R-X (or macroinitiator of P_n-X) by a transition metal complex. This reaction reversibly generates the corresponding higher oxidation state metal halide complex such as $CuBr/bpy_2$ and an alkyl radical (Scheme 1-3).[8,13] The monomers homopolymerized by ATRP is quite extensive and includes various substituted styrenes,[14] (meth)acrylate,[15-17] (meth)acrylamide,[18,19] vinyl pyridine,[20] acrylonitrile,[21] vinyl acetate,[22] vinyl chloride,[23] and more.[8] It has been considered that the ATRP has been successfully used to control the topology (linear, stars, cyclic, comb, brushes, network, dendritic, and hyperbranched), composition, and functionalities.[24-26]

Scheme 1-3. The General Mechanism of ATRP



Conventional free radical initiators are used in the degenerative transfer process, and control is assured by the presence of transfer agents which exchange a group/atom X between the all growing chains. This thermodynamically neutral transfer reaction should be fast in comparison to propagation. At any instant, the concentration of the dormant species P_n-X is much higher than that of the active species P_n*. The degrees of polymerization are defined by the ratio of the concentration of the consumed monomer to the sum of the concentrations of the consumed transfer agent and the decomposed initiator. The RAFT polymerization is among the most successful deactivated transfer processes.[27-31] While addition-fragmentation chemistry was originally applied to the polymerization of unsaturated methacrylate monomers, the RAFT polymerization employs various dithioesters, dithiocarbamates, trithiocarbonates, and xanthates as CTAs leading to polymers with a low dispersity of polymers and various controlled architectures for a broad range of monomers.[32] In this system, there will always be a small propagation of continuously generated chains (Scheme 1-4). They will terminate faster than the long propagating chains. This will also make the formation of pure block copolymers via CRP techniques impossible as low molecular weight products will always generate new homopolymer chains during the polymerization of the second monomer.

Scheme 1-4. General Mechanism of RAFT Polymerization



As already mentioned, the polymerization of vinyl monomers, especially acrylate monomers, was generally synthesized by those CRP methods. In fact, approximately 50% of all synthetic polymers are currently made via the radical polymerization processes.[1] However, serious problems with the CRP methods also remained not only involving the toxicity of the catalyst, and the time-consuming polymerization, but also biradical coupling and a chain transfer reaction during the polymerization reaction. Thus, it had been required to develop a methodology for the precise polymerization of acrylate monomers by living polymerization techniques.

1.1.2 Living Anionic Polymerization

The living anionic polymerization method is the most suitable method to synthesize well-defined polymers as the state-of-the-art technique.[1] Since Michael Szwarc described the

anionic polymerization process of styrene initiated by electron transfer in tetrahydrofuran,[33,34] a variety of α-olefins substituted with an electron withdrawing group, such as styrene, butadiene, (meth)acrylates, acrylamides, acrylonitrile, and their derivatives, have been subjected to anionic polymerization (Scheme 1-5).[35] Several substituted monomers can be polymerized via anionic polymerization exept for those bearing acidic protons for the obvious reactions that electrophiles react with active species and quench the initiator or terminate the anionic propagating chain end (Chart 1-1).

Scheme 1-5. General Mechanism of Anionic Polymerization Initiated by *sec*-Butyllithium

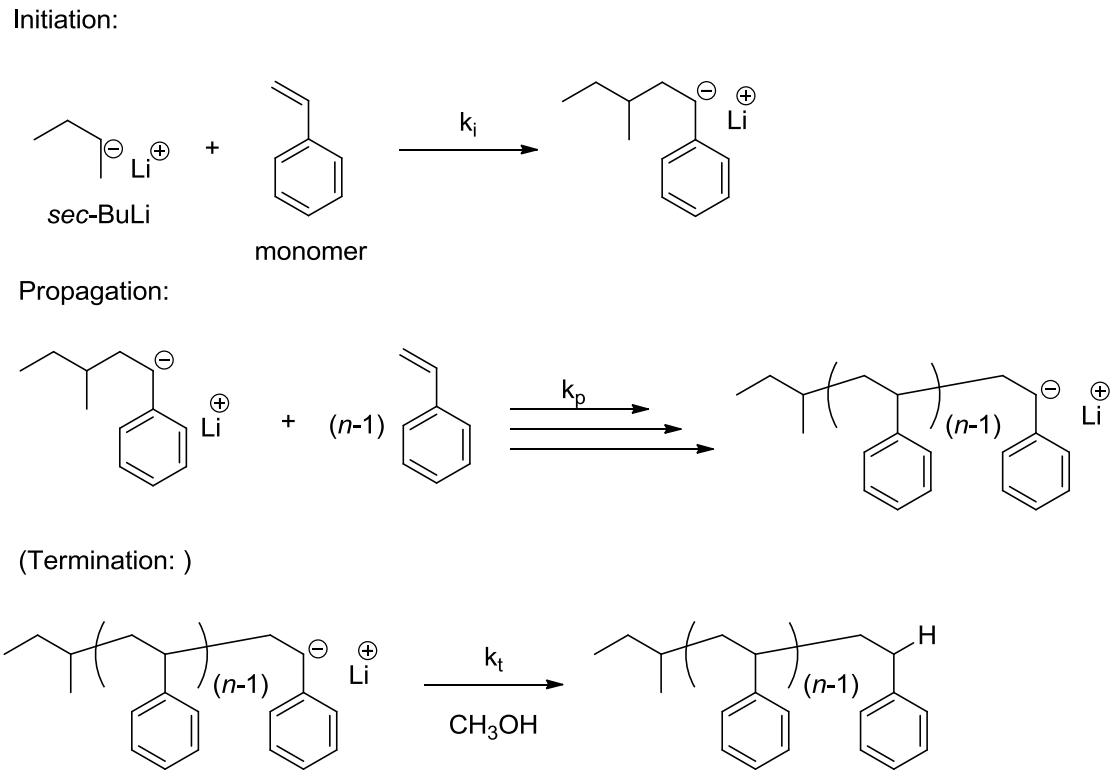
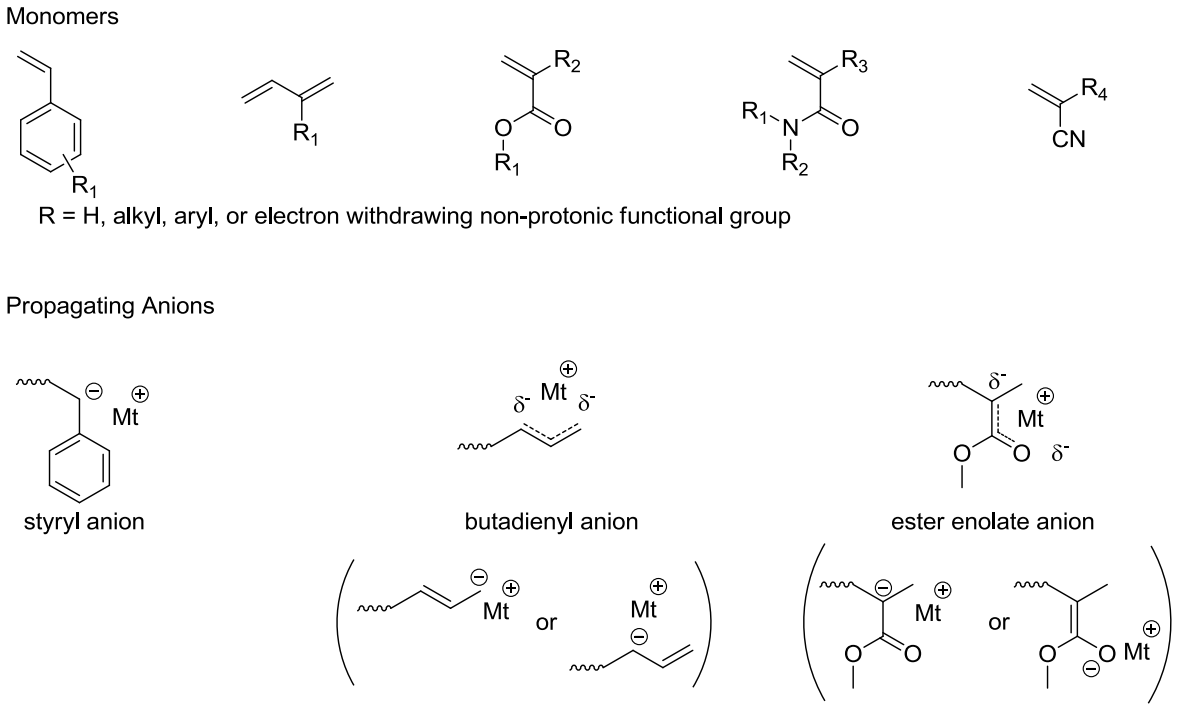
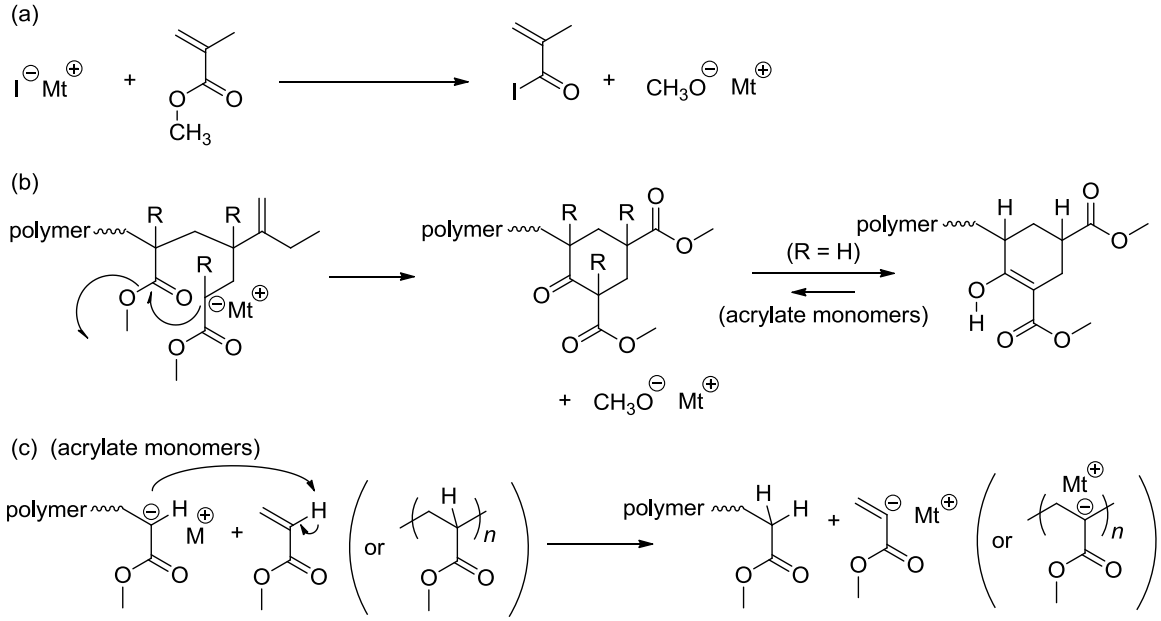


Chart 1-1. Applicable Monomers for Anionic Polymerization and Propagating Anions of Corresponding Monomers



The polymerization of acrylic monomers is the one of important fields involving the anionic polymerization methods. The initiation of alkyl (meth)acrylates with classical initiators like butyllithium is difficult and proceeds with several side reactions, yielding polymers with a broad molecular weight distribution and the low conversion (Scheme 1-6).[36-38] The nonideal behavior of alkyl (meth)acrylate monomers is due to following two facts: 1) side reactions by the nucleophilic attack of the initiator or the active chain end onto the monomer or polymer ester group and intramolecular backbiting reaction[39,40] ; 2) aggregation of the active chain ends having an ester enolate structure; and 3) abstruction reaction of α-hydrogen in the acrylate monomer or polymer.

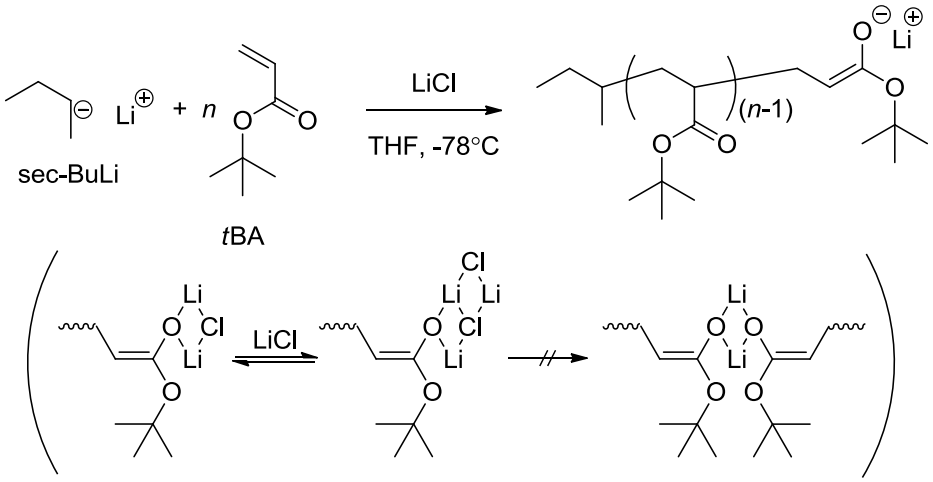
Scheme 1-6. Side Reactions in the Anionic Polymerization of Methyl Methacrylate: (a) Initiator Attack onto the Monomer Ester Group, (b) Backbiting Reaction of Propagating Enolate Anion, and (c) Abstruction Reaction of α-Hydrogen in the Monomers/Polymers



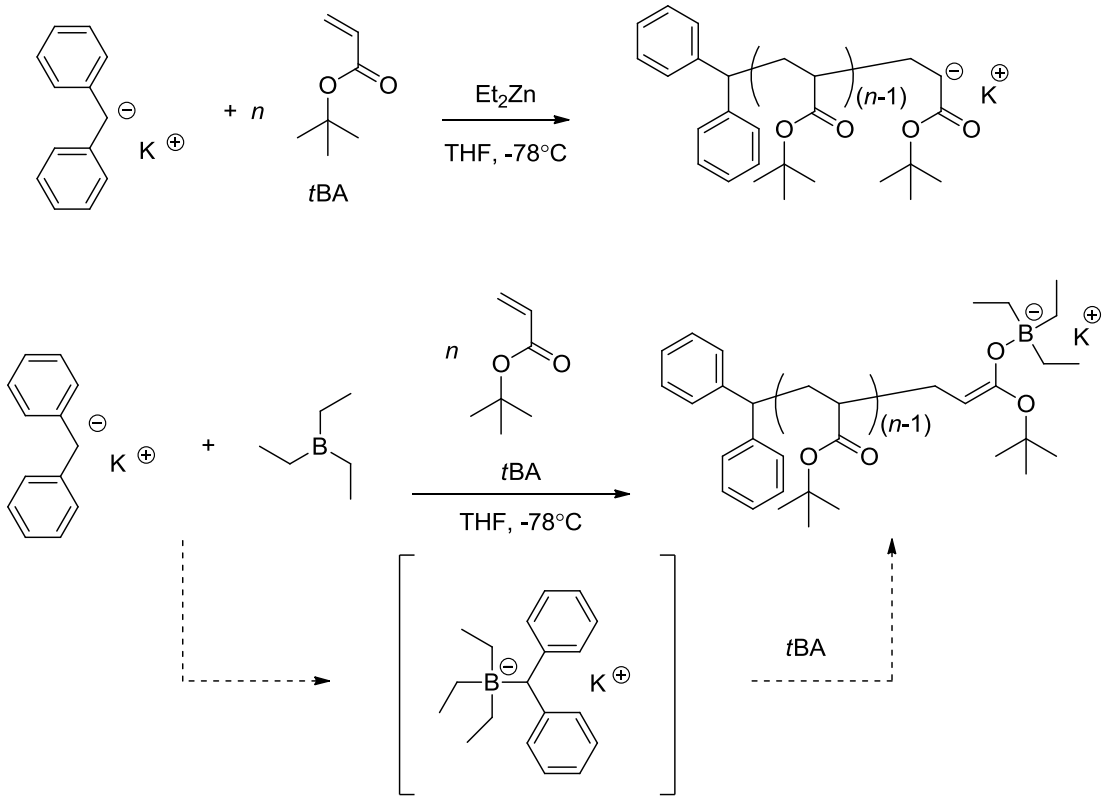
The living polymerization of acrylate monomers is still challenging in comparison to those of methacrylates and acrylamides because the anionic polymerization and GTP, as described later, of *n*-alkyl acrylates are generally hard to control and are usually disturbed by inherent side reactions of the ester carbonyl group and the labile α-hydrogen of the monomer units in the polymer with the anionic initiators and the active chain ends.[41] Based on these results, the controlled/living polymerization of alkyl acrylates has not been possible due to incomplete polymerizations and broad molecular weight distribution until the late 1980s. In 1987, Teyssie et al. reported for the first time the living anionic polymerization of *tert*-butyl acrylate (*t*BA) in THF in the presence of an excess of lithium chloride, leading to a well-defined poly(*t*BA) (Scheme 1-7).[42,43] Furthermore, Müller et al. reported that the anionic

polymerization of *t*BA using lithium *tert*-butoxide in the presence of lithium chloride was sufficiently controlled to produce the poly(*t*BA)s,[44,45] Ishizone et al. reported the controlled polymerization of *t*BA using the diphenylmethyl anion in the presence of dialkylzinc or triethylborane (Scheme 1-8).[46,47] It was assumed that the beneficial effect of lithium chloride and coodinative compounds are due to complexation with the chain end (anionic species), which suppresses the side reaction of backbiting. However, the anionic polymerization of acrylates still has been so far difficult. Therefore, the living polymerization of acrylate monomers still remains a challenging task in polymer chemistry.

Scheme 1-7. Anionic Polymerization of *tert*-Butyl Acrylate (*t*BA) Initiated by *sec*-Butyllithium (*sec*-BuLi) in the Presence of Lithium Chloride (LiCl) in THF



Scheme 1-8. Anionic Polymerizattion of *t*BA Initiated by Diphenylmethylanion in the presence of dialkylzinc or triethylborane

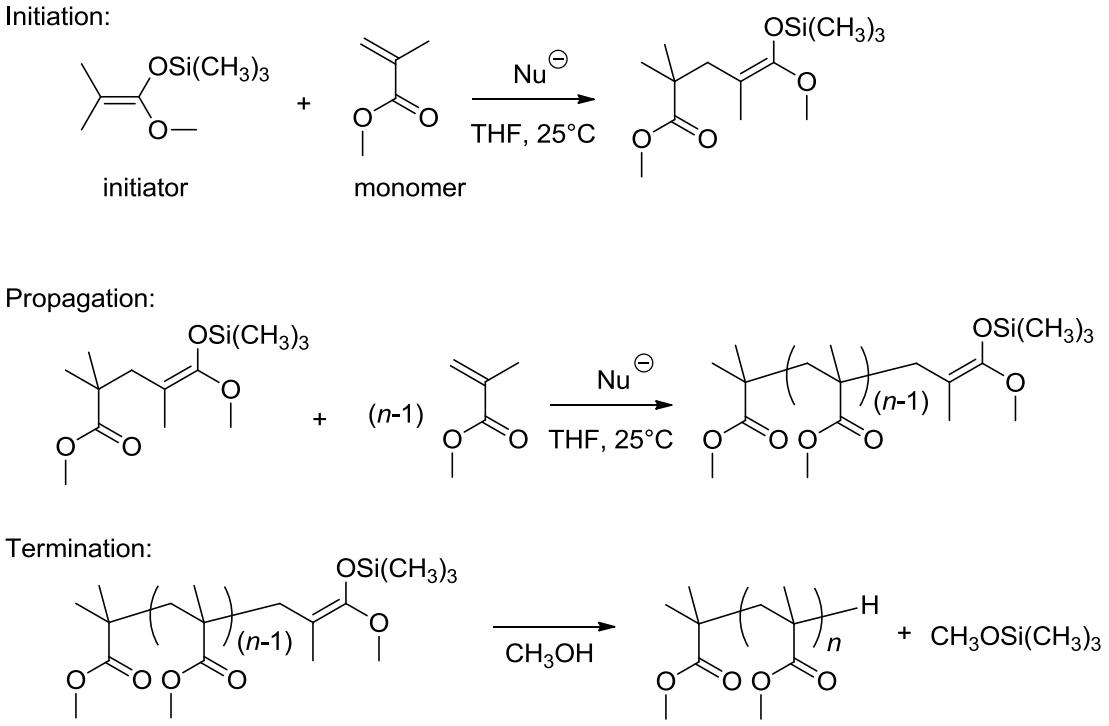


1.2 Group Transfer Polymerization

1.2.1 The Birth of Group Transfer Polymerization

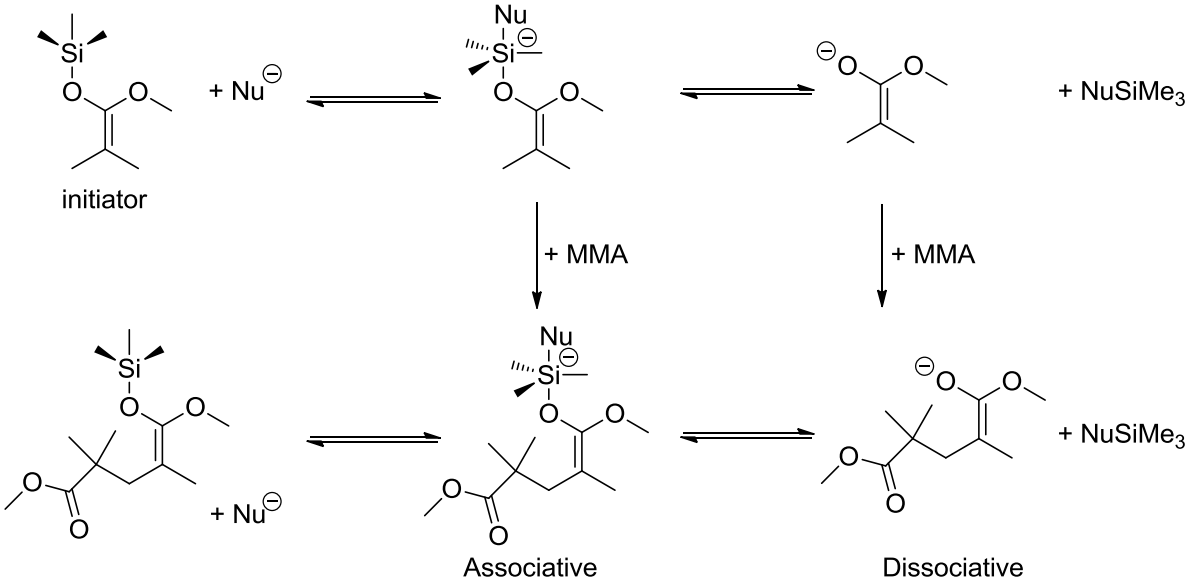
In 1983, Webster et al. demonstrated for the first time that a silyl ketene acetal (silyl ester enolate) was an initiator for the controlled polymerization of alkyl (meth)acrylate at room temperature leading to poly(alkyl methacrylate) with a narrow molecular weight distribution in the presence of a small amount of nucleophilic catalysts.[48] They proposed and claimed that the polymerization process based on the Mukaiyama-Michael reaction mechanism was called the group transfer polymerization (GTP), in which the trimethylsilyl group coordinated with a nucleophlic catalyst transferred from the initiator or propagating chain end to the carbonyl oxygen of the incoming monomer, as shown in Scheme 1-9.

Scheme 1-9. GTP of MMA with Nucleophilic Catalysts



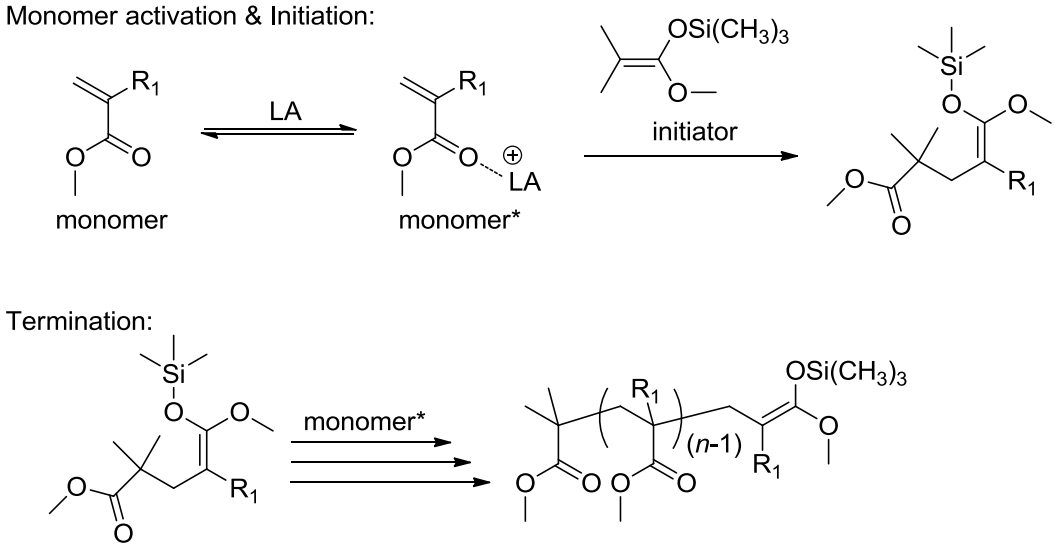
There has been a long discussion on the GTP mechanism, which seems to depend on the type of catalyst used for the polymerization.[49-57] This was originally proposed by Webster and Sogah in which the double labeling experiments supported the direct transfer of the pentacoordinated siliconate from the chain end to the incoming monomer's carbonyl group, called the "associative mechanism",[58] though several questions related to this mechanism remained unanswered.[59-64] Quirk et al. proposed a "dissociative mechanism" in which the pentacoodinated siliconate dissociates into an ester enolate anion and the corresponding trimethylsilyl-nucleophile compound (Scheme 1-10).[60,65] The two equilibria ensure the necessary exchange of activity between the dormant silyl ketene acetal and active enolate chain ends, leading to control of the molecular weight and distribution.

Scheme 1-10. Associative and Dissociative Mechanism of GTP of MMA in the Presence of Nucleophilic Catalyst



On the other hand, the Lewis acid was also considered as an "associative mechanism" when the GTP was first reported by Webster and coworkers. However, with recent progress in the Lewis-acid-catalyzed GTP, it was proposed that the "oxidative activation mechanism" proceeds by coordination with the carbonyl oxygen of acrylates as indicated by the large amount of Lewis acid necessary (10 to 20% based on monomer) for the controlled polymerization (Scheme 1-11).[66-69]

Scheme 1-11. Mechanism of the Lewis Acid (LA)-Catalyzed GTP

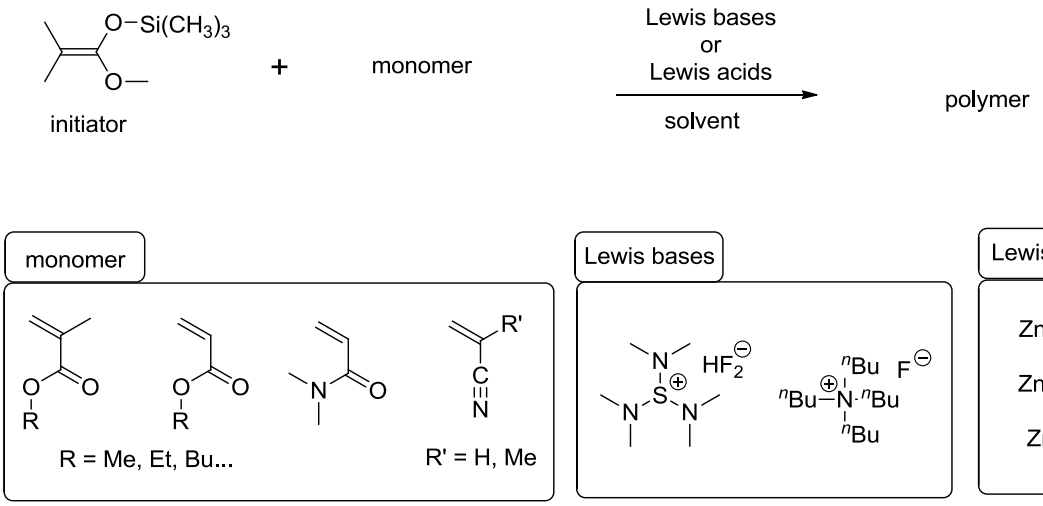


The participation of enolate anions as the intermediate during the propagation proceeds along with the backbiting side reaction similar to the classical anionic polymerization.[70] Based on these results, the GTP has been attractive for not only the mechanism, but also the differential of the polymerization ability based on the catalytic activity, applicable monomers, synthesis of polymer architecture, and availability of GTP for development in the field of precise polymer synthesis.

1.2.2 Organocatalyzed Group Transfer Polymerization

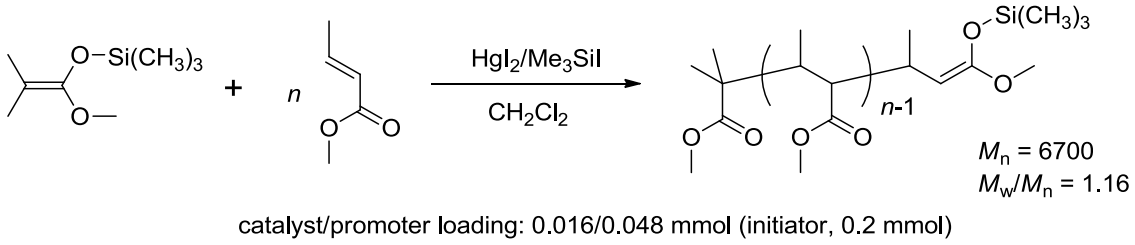
As mentioned in the previous section, GTP is the one of the important living polymerization methods for (meth)acrylate monomers, which proceeds through numerous iterations of the Mukaiyama-Michael reaction.[48,71] Since Webster and coworkers established the concept of GTP, there have been many efforts to precisely control the polymerizations of (meth)acrylates,[72,73] acrylamides,[74] and (meth)acrylonitrile,[75] leading to the corresponded polymers. In general, methacrylate monomers were the most suitable among the polar monomers. 1-Methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS^{Me}) has been used as the conventional initiator, and both Lewis bases and Lewis acids have been employed as catalysts, as shown in Scheme 1-12.[76]

Scheme 1-12. General Schematic of Group Transfer Polymerization (GTP) with Applicable Monomers and Lewis Bases/Acids as Catalysts



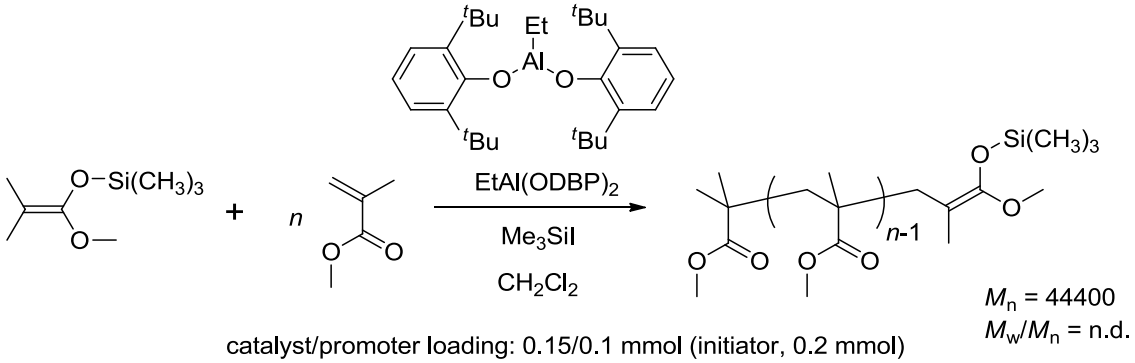
The catalytic efficiency of Lewis acids, such as zinc halides and organic aluminums, is extremely low so that a 10-20% catalyst loading based on the monomer concentration was required,[67,71] while $HgI_2/(CH_3)_3SiI$,[77,78] $RAl(OAr)_2/(CH_3)_3SiI$,[79] and $B(C_6F_5)_3/(C_2H_5)_3SiOSO_2CF_3$[80] have an exceptionally high catalytic activity, as shown in Schemes 1-13, 1-14, and 1-15. On the other hand, typical Lewis bases, such as F_2^-,[48] HF_2^-,[48] CN^-,[81,82] N_3^-,[72] and RCO_2^-,[49,83] are the most efficient catalyst for GTP, which are normally used at the catalyst loading of 0.1-1.0% based on the initiator.

Scheme 1-13. GTP of Methyl Crotonate using $HgI_2/(CH_3)_3SiI$ as Catalyst and Promoter



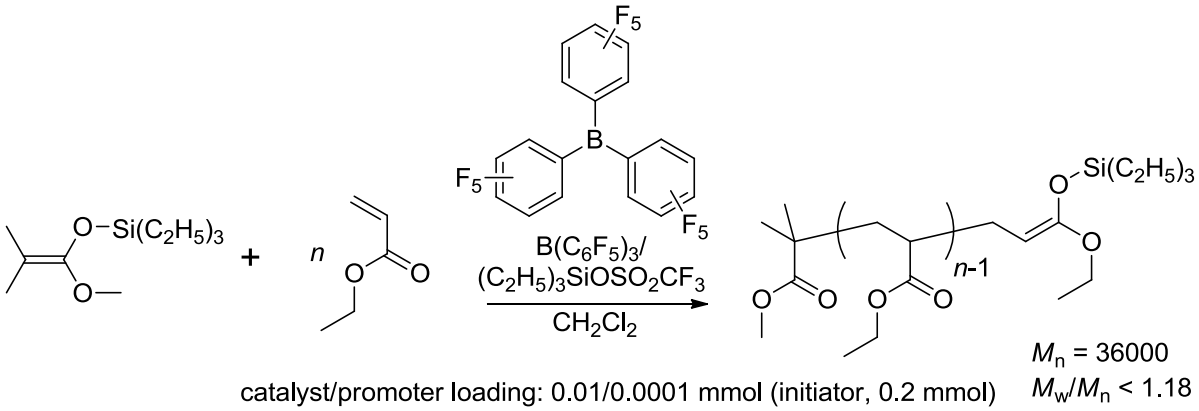
catalyst/promoter loading: 0.016/0.048 mmol (initiator, 0.2 mmol)

Scheme 1-14. Stereospecific GTP of Methyl Methacrylate using $RAl(OAr)_2/(CH_3)_3SiI$ as Catalyst/Promoter



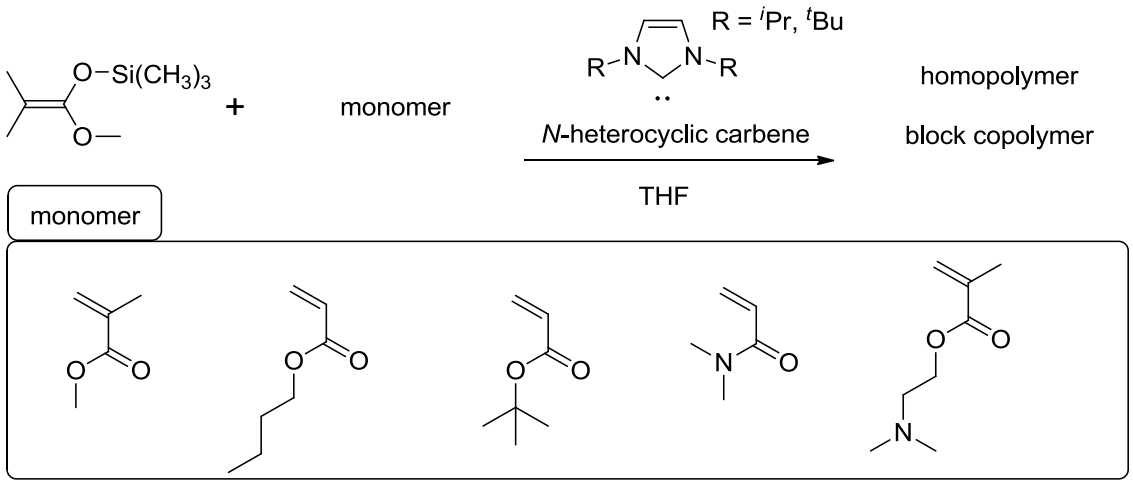
catalyst/promoter loading: 0.15/0.1 mmol (initiator, 0.2 mmol)

Scheme 1-15. GTP of Ethyl Acrylate using $B(C_6F_5)_3/(C_2H_5)_3SiOSO_2CF_3$ as Catalyst/Promoter



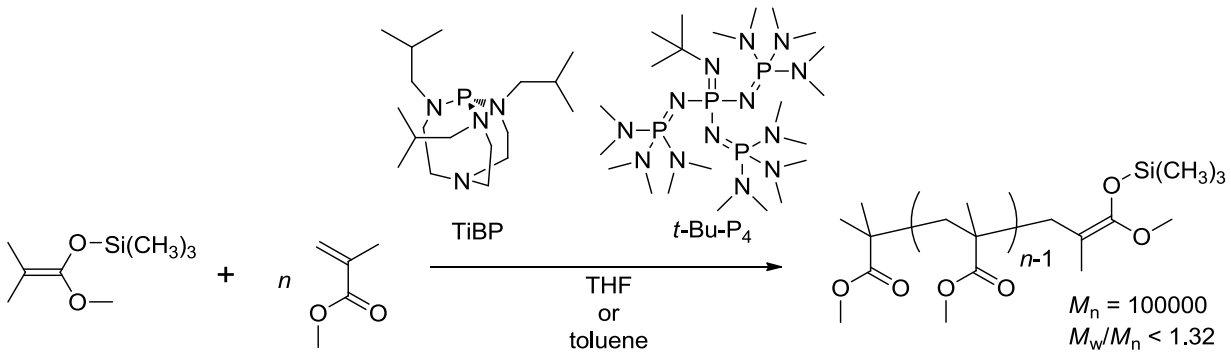
Organocatalysts have been developed and were found to be new and useful catalysts for the GTP. Taton et al. and Waymouth et al. first reported the *N*-heterocyclic carbene-catalyzed GTPs of methyl methacrylate (MMA) and *t*BA using MTS^{Me}, which produced well-defined homopolymers and block copolymers, as shown in Scheme 1-16.[73,74]

Scheme 1-16. Synthesis of Various Homopolymers and Block Copolymers using *N*-Heterocyclic Carbene-catalyzed GTP

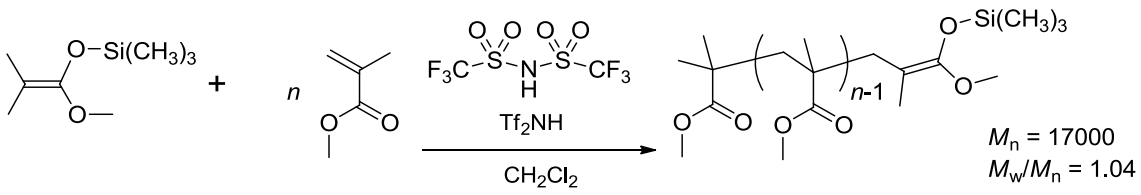


Kakuchi and coworkers reported that the phosphazene base, 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-2 Λ^5,4Λ^5-catenadi(phosphazene) (*t*-Bu-P_4), a very strong organic base, was extremely efficient for the syntheses of the poly(methyl methacrylate)s (PMMAs) as shown in Scheme 1-17.[86] Furthermore, Kakuchi et al. found that trifluoromethanesulfonimide (Tf_2NH), a very strong Brønsted acid, could promote the GTP of MMA using MTS^{Me} to afford the syndiotactic PMMA without any obvious side reactions, as shown in Scheme 1-18.[87] Thus, of great interest is to further elucidate the scope and limits of organocatalysts, monomers, and initiators applicable to polymer synthesis in the chemistry of organocatalyzed GTP.

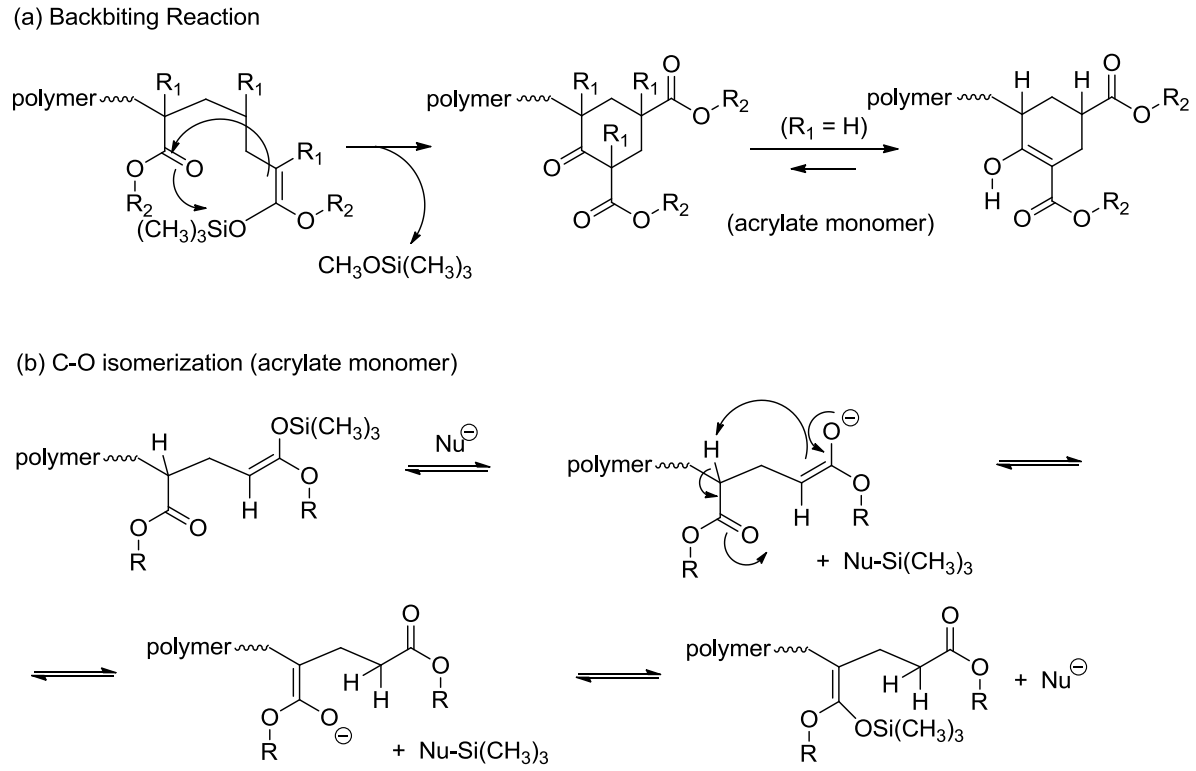
Scheme 1-17. Phosphazene Base-Catalyzed GTP of Methyl Methacrylate



Scheme 1-18. Trifluoromethanesulfonimide (Tf_2NH)-Promoted GTP of Methyl Methacrylate

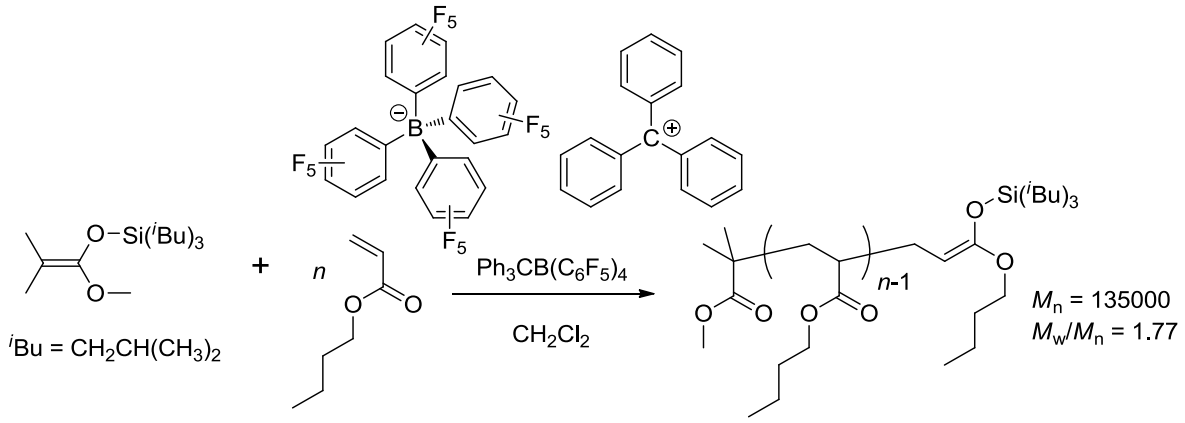


Scheme 1-19. Side Reactions during GTP of (Meth)acrylate Monomers



The living polymerization of *n*-alkyl acrylate by the GTP was also more difficult than those of *t*BA due to the frequent occurrence of a side reaction similar to the anionic polymerization and further isomerization, as shown in Scheme 1-19. Especially, Chen et al. and Kitayama et al. reported that the GTP of *n*-alkyl acrylate proceeded in a living fashion using $Ph_3CB(C_6F_5)_4$[84,85] or $B(C_6F_5)_3/(C_2H_5)_3SiOSO_2CF_3$[80] combined with trialkylsilyl ketene acetals, as shown in Scheme 1-15 and Scheme 1-20.

Scheme 1-20. GTP of *n*-Butyl Acrylate using $Ph_3CB(C_6F_5)_4$ as a Catalyst and Triisobutylsilyl Ketene Acetal as an Initiator



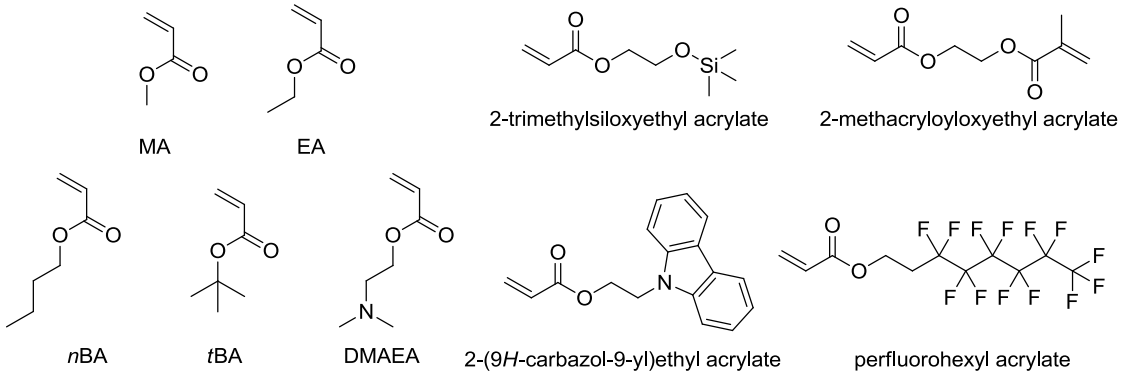
1.2.3 Applicable Acrylate Monomers for Group Transfer Polymerization Leading to Block Polymers

As mentioned above, the field of organocatalyzed GTP has been developed with growth of organocatalyst chemistry, which was the validated polymerization method for the synthesis of (meth)acrylate polymers. Furthermore, it is important to clarify the scope and limits of applicable monomers for the organocatalyzed GTP. Chart 1-2 shows the applicable monomers for GTP, for instance, methyl acrylate (MA),[88-90] ethyl acrylate (EA),[66,72,91] *n*-butyl acrylate (*n*BA),[72,75,92,93] *t*BA,[92,93] *N*,*N*-dimethylaminoethyl acrylate (DMAEA),[93] 2-trimethylsiloxyethyl acrylate,[94] 2-methacryloyloxyethyl acrylate,[72,91] 2-(9*H*-carbazol-9-yl)ethyl acrylate,[94] and perfluorohexyl acrylate.[95] Especially, Taton et al. reported the synthesis of homo, diblock, and triblock polymers consisting of the MMA, *N*,*N*-dimethylacrylamide (DMAA), and *t*BA using *N*-heterocyclic carbenes (NHCs) with controlled molecular weights and low dispersities.[73,75,92] Furthermore, the Tf_2NH-promoted GTP of DMAA using the specially designed initiator,

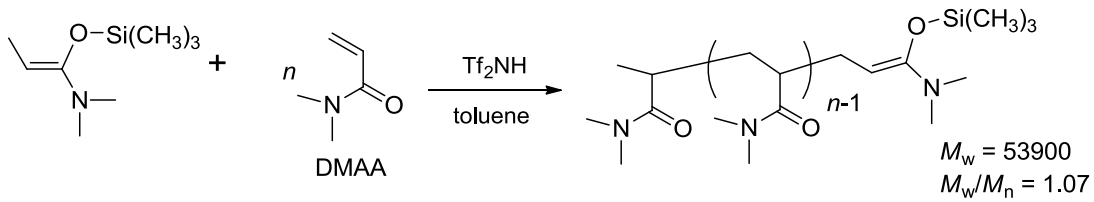
(*Z*)-1-(dimethylamino)-1-trimethylsiloxy-1-propene, produced the well-defined poly(*N*,*N*-dimethylacrylamide) with a low polydispersity (M_w/M_n), which was the first reliable demonstration for the living polymerization of the acrylamide monomer through the GTP process, as shown in Scheme 1-21.[96]

Although there are many reports for the synthesis of acrylate homopolymers, the applicable monomers were still few compared to the methacrylate monomers. In addition, the block polymerization of the applicable acrylate monomers is a challenging issue because of the limited research in GTP chemistry.

Chart 1-2. Applicable Acrylate Monomers for GTP



Scheme 1-21. Precise Synthesis of Poly(*N*,*N*-dimethylacrylamide)s by Tf_2NH-Promoted GTP using Specially Designed Initiator



1.3 Synthesis of Specially-Structured Acrylate Polymers by Living Polymerization

1.3.1 End-Functionalized Acrylate Polymers

The end-functionalized polymers were synthesized by the controlled/living polymerizations using appropriate functional initiators, chain transfer agents, and terminating agents, which were utilized to produce intelligent materials and diverse polymer architectures, such as block copolymers, graft copolymers, star-shaped polymers, dendritic polymers, and cyclic polymers, as shown in Figure1-1.[97] Several techniques of controlled polymerizations, namely, living anionic polymerization,[98] GTP,[67,83] and controlled radical polymerization, such as ATRP,[99,100] NMP,[101] and RAFT polymerization,[102,103] can be used for the synthesis of end-functionalized polymers with two approaches; i. e., the use of functional initiators or the termination of the living chain by a suitable electrophile (or radical precursor) bearing the functional group. The nature of the polymer and the functional group to be introduced will determine the specific choice of the synthesis method. GTP also could synthesize end-functionalized polymethacrylates (Scheme 1-22). Webster and coworkers reported the preparation of α-end-functionalized polymers based on the conventional GTP, in which ethyl acrylate was only investigated as an acrylate monomer using a silyl ketene acetal with a functional group for the homopolymerization and copolymerization with MMA, leading to an α-hydroxyl-functionalized homopolymer with a low molecular weight and an α-hydroxyl-functionalized copolymer with a high polydispersity.[104] In addition, Quirk et al. and Sivaram et al. reported the termination reaction of the conventional GTP using benzaldehyde and methyl 2-phenylacrylate, in which their derivatives were used as the functional terminators for the GTP leading to ω-end-functionalized polymers with hydroxyl

and amino groups though MMA was only investigated and the efficiency of the end-functionalizations was poor.[83,105] Thus, the precise synthesis of end-functionalized acrylate polymers is still challenging from the viewpoint of the living anionic polymerization involving the GTP method.

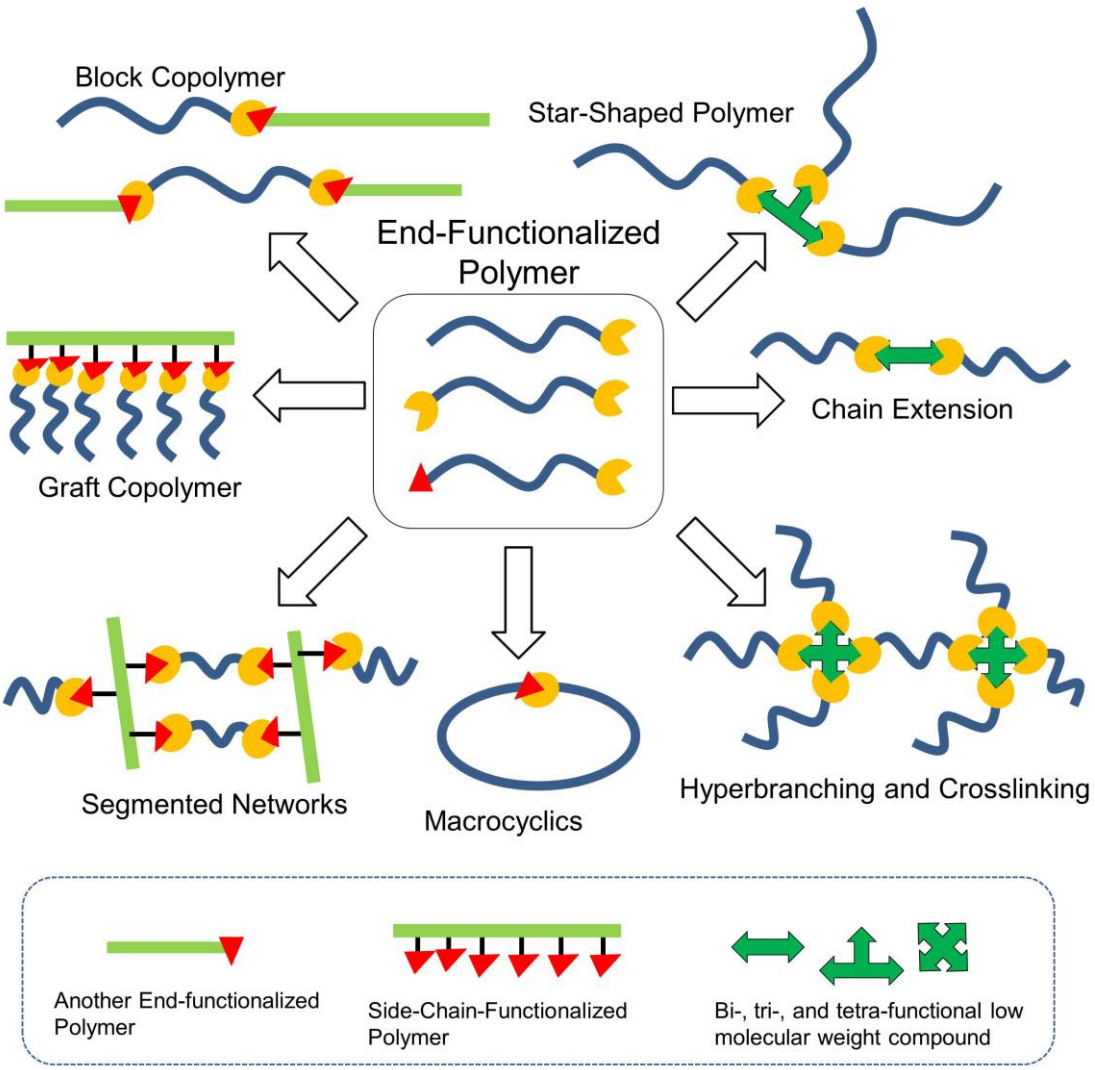
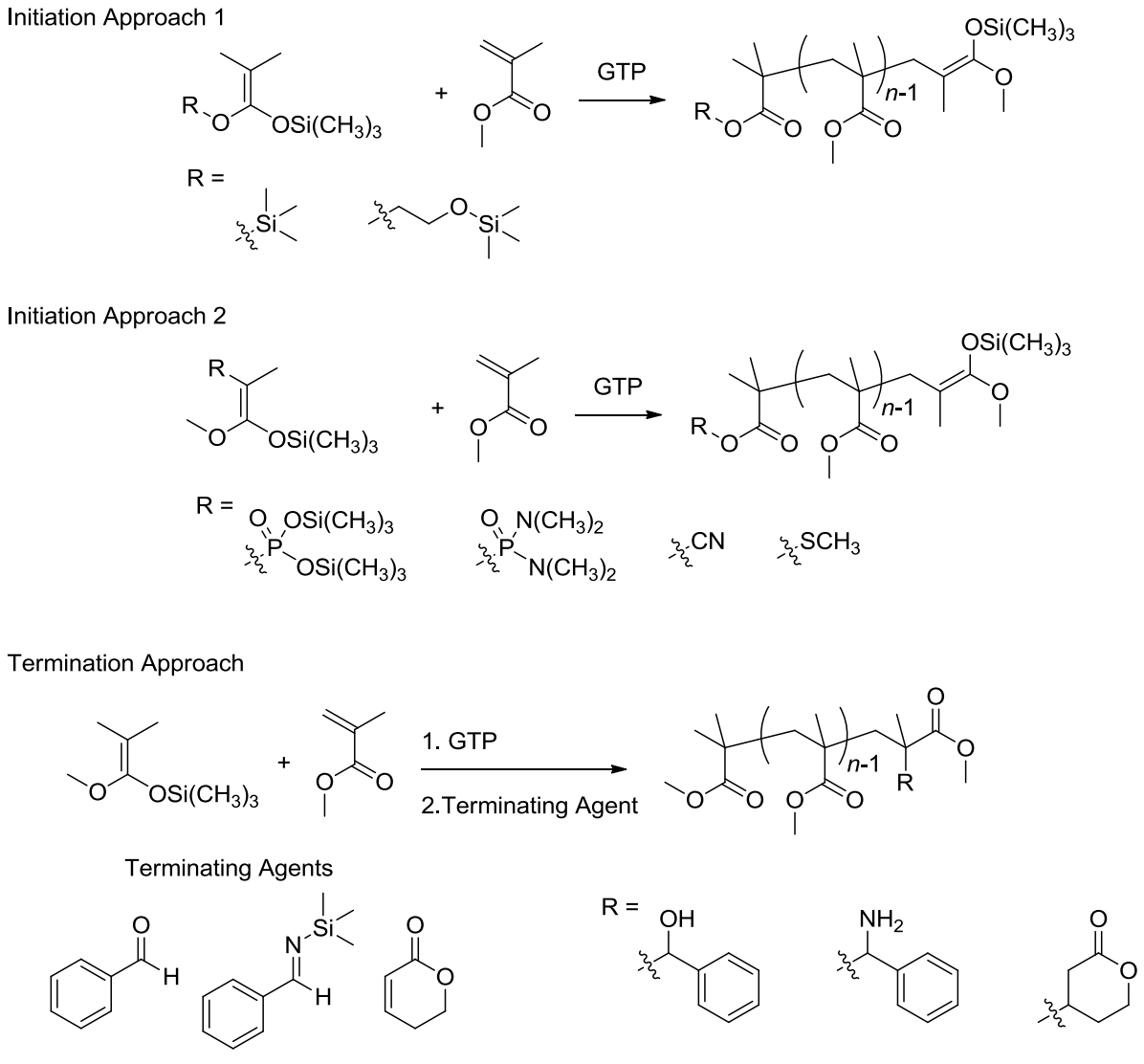


Figure 1-1. Various Architectures Obtained by the Reactions of End-Functionalized Polymers.[97]

Scheme 1-22. Synthesis of End-Functionalized Poly(methyl methacrylate) by GTP using Initiation and Termination Approaches



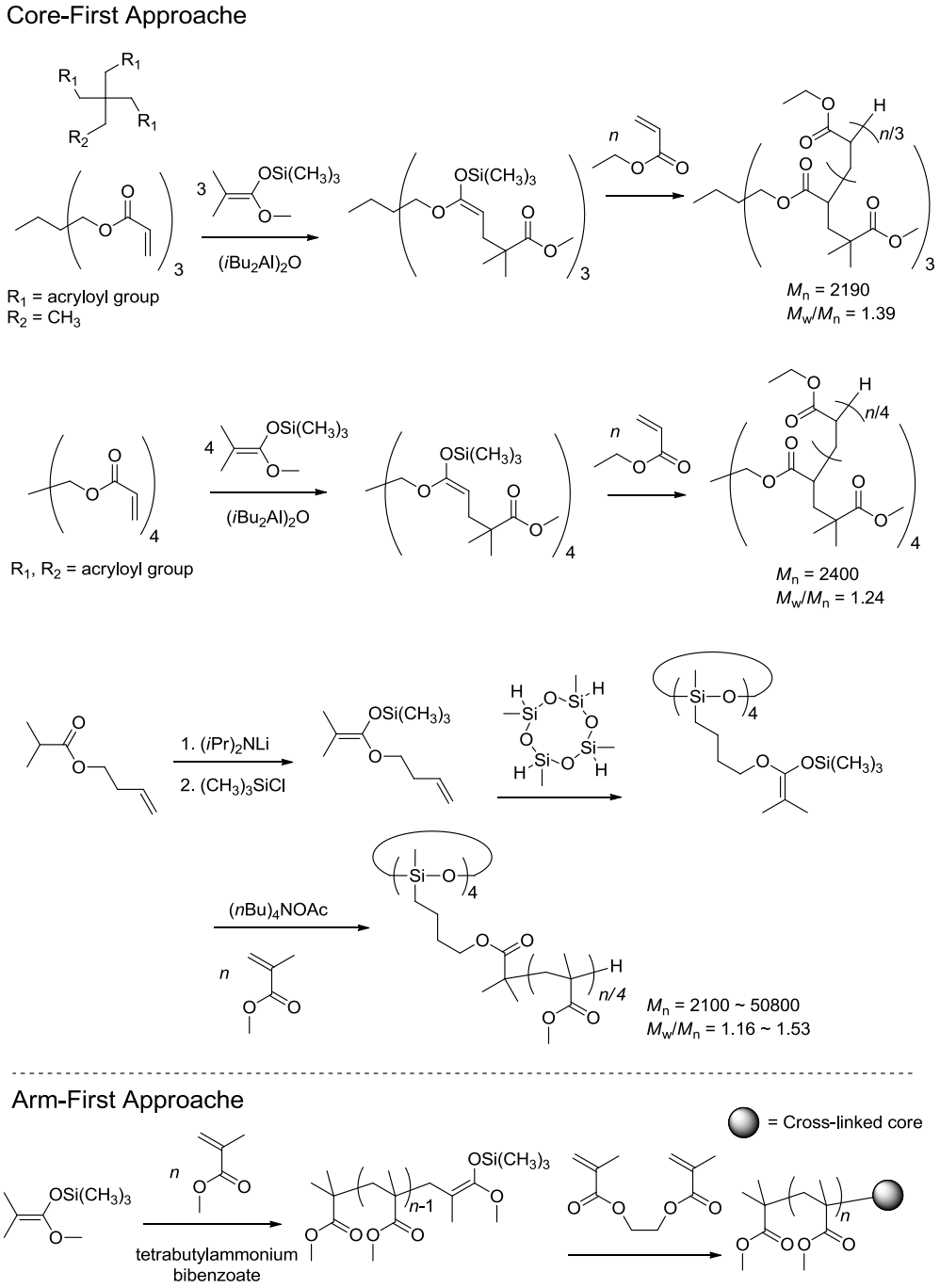
1.3.2 Star-Shaped Acrylate Polymers

Star-shaped, dendritic, and hyperbranched polymers are well-known to display unique properties, such as a low hydrodynamic volume and low viscosity in solution.[1] For example, the recent development in the controlled/living radical and anionic polymerization has enabled the preparation of the star-shaped polymers consisting of several identical linear chains linked to a central core.[106-108] The well-defined star-shaped polymers have been

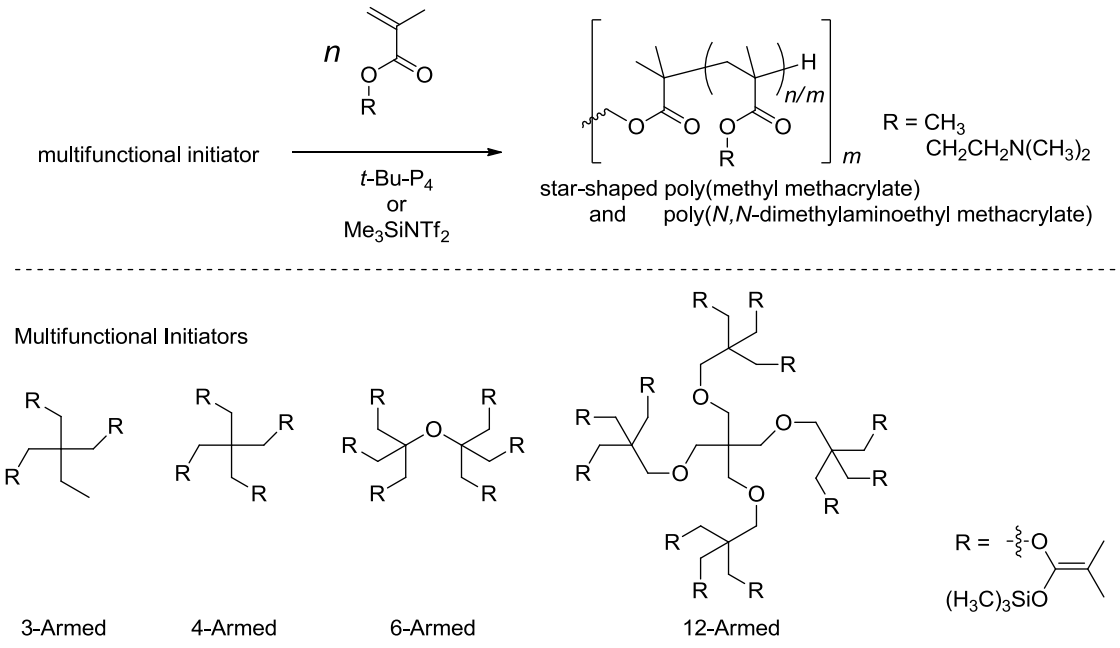
generally synthesized using three methods, such as 1) the core-first method, 2) the arm-first method, and 3) the coupling onto method. However, the anionic polymerization processes require severe reaction conditions and complicated purification processes to prevent the interaction of each active chain end, backbiting reaction, and more. In addition, the synthesis of the star-shaped polymers by CRP was disturbed by the coupling reaction of the inter/intra molecules based on the radical species of the propagating chain ends. Thus, it is necessary to establish a method for the precise synthesis of star-shaped polymers by controlled/living polymerization.

The synthesis of star-shaped/branched methacrylate polymers was reported by several researchers (Scheme 1-23).[109] For instance, Webster and Sogah et al. reported the star-shaped poly(ethyl acrylate) using three and four-armed initiators,[72] Wnek et al. investigated the core-first synthesis of the four-armed star-shaped poly(methyl methacrylates),[110] Patrickios et al. reported the arm-first synthesis of various star-shaped methacrylate polymers using a bifunctional monomer, diacryloyl compound, as the linking agent,[111-115] and Kakuchi et al. reported the core-first synthesis of poly(methyl methacrylate) and poly(*N*,*N*-dimethylaminoethyl methacrylate) by organic superbases and acids (Scheme 1-24).[116-118] However, the precise synthesis of the star-shaped acrylate polymer had never been reported using the GTP method. Thus, the precise synthesis of the star-shaped acrylate polymers is the remaining task from the viewpoint of the living anionic polymerization involving the GTP method.

Scheme 1-23. Synthesis of Star-Shaped (Meth)acrylate Polymers by GTP with Core-First and Arm-First Approaches



Scheme 1-24. Synthesis of Three-, Four-, Six-, and Twelve-armed Star-Shaped Methacrylate Polymers by the *t*-Bu-P_4- or Me_3SiNTf_2-Catalyzed GTP with Core-First Method



1.4 Objectives and Outline of the Thesis

Acrylate polymers are important plastic materials possessing a notable transparency, flexibility, and extension and are primarily utilized in paints and other surface coatings, adhesives, and textiles. In general, acrylate polymers involving their copolymers are produced in industry using radical polymerization methods. The recent progress in the chemistry of the controlled/living polymerizations has enabled the preparation of well-defined polymers including block copolymers, end-functionalized polymers, and various macromolecular architectures, such as cyclic, star-shaped, dendritic, and hyper-branched polymers. However, these methods have been included the defects of the polymer structure by the side reactions as described in the previous section (Section 1.1). Thus, it is important to develop controlled/living polymerization systems for precisely preparing well-defined acrylate polymers.

Group transfer polymerization (GTP), one of the anionic polymerizations, is well known as the polymerization method for (meth)acrylates monomers using conventional Lewis acids and bases. Recently, organoctalysts were founded to sufficiently control the GTP leading to well-defined methacrylate polymers with predicted molecular weights and narrow molecular weight distribution. In addition, the organocatalyzed GTP is an efficient method for the methacrylate and acrylamide monomers (Section 1.2). Of great interest for the GTP is to further elucidate the scope and limits of the applicable monomers and initiators for the polymer synthesis. In addition, the precise synthesis of the multiblock, end-functionalized, and star-shaped acrylate polymers is also a challenging task due to the difficult synthesis of well-defined polymers using the living polymerization techniques. Based on this information, the objective of this thesis is the development of a synthetic method of well-defined acrylate polymers with a high-molecular-weight, multiblock structure, α-, ω-, and α,ω-end-functional

structures, and star-shaped structures through the organocatalyzed GTP. The molecular-design of silyl ketene acetals of the initiators is the key point to control not only the polymerization, but also the sttucture of the obtained polymers.

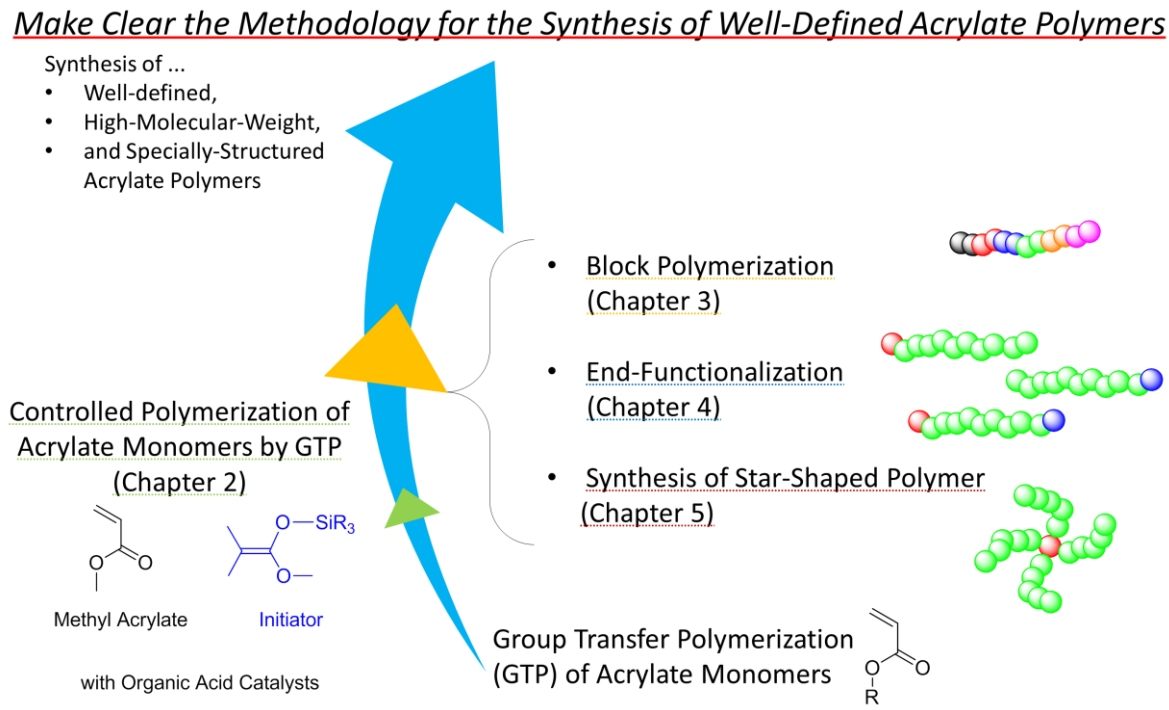


Figure 1-2. Objectives and outline for the research of the organocatalyzed group transfer polymerization of acrylates to synthesize the well-defined acrylate polymer architectures.

The outline of this thesis is as follows:

Chapter 2 describes the synthesis of the high-molecular-weight acrylate polymers by GTP using pentafluorophenylbis(triflyl)methane ($C_6F_5CHTf_2$) as the organocatalyst and 1-trimethylsiloxy-, 1-triethylsiloxy-, and 1-triisopropylsiloxy-1-methoxy-2-methyl-1-propenes (MTS^{Me}, MTS^{Et}, and MTS^{iPr},

respectively) as the initiators, as shown in Figure 1-3. The $C_6F_5CHTf_2$-promoted GTP of methyl acrylate (MA) using MTS^{iPr} proceeded in a living nature to produce poly(methyl acrylate)s (PMAs) with controlled molecular weights and narrow molecular weight distributions, which allowed the synthesis of high-molecular-weight PMA and poly(*n*-butyl acrylate)s (P*n*BA) with the number average molecular weight ($M_{n,SEC}$) of up to 100 000 and the dispersity (M_w/M_n) as low as 1.10. The matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF MS) measurement revealed that the obtained PMA possessed the chain end structure that originated from MTS^{iPr}, showing that the $C_6F_5CHTf_2$-promoted GTP of MA proceeded without any side reactions. In addition, the kinetic study and the post-polymerization experiment supported the living manner of the polymerization. Moreover, the block copolymerization of MA and *n*-butyl acrylate (*n*BA) smoothly proceeded to afford the well-defined PMA-*block*- P*n*BA.

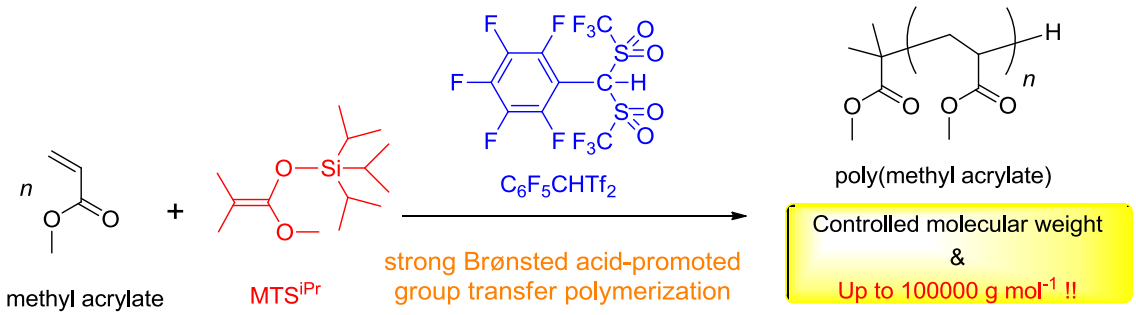


Figure 1-3. Synthesis of high-molecular-weight acrylate polymers by strong Brønsted acid-promoted GTP.

Chapter 3 describes that the GTP with *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNTf_2) and

1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene (MTS^{iPr}) has been studied using MA, ethyl acrylate (EA), *n*BA, 2-ethylhexyl acrylate (EHA), cyclohexyl acrylate (*c*HA), dicyclopentanyl acrylate (d*c*PA), *tert*-butyl acrylate (*t*BA), 2-methoxyethyl acrylate (MEA), 2-(2-ethoxyethoxy)ethyl acrylate (EEA), 2-(dimethylamino)ethyl acrylate (DMAEA), allyl acrylate (AlA), propargyl acrylate (PgA), 2-(triisopropylsiloxy)ethyl acrylate (TIPS-HEA), and triisopropylsilyl acrylate (TIPSA), as shown in Figure 1-4. Except for *t*BA and DMAEA, the GTPs of all the other monomers described above rapidly proceeded in a living manner and produced well-defined homo acrylate polymers. The living nature of the GTPs of such acrylate monomers was further applied to the postpolymerizations of MA, EA, *n*BA and MEA and also to the sequential GTPs of the diverse acrylate monomers for preparing di- and multiblock acrylate polymers. In greater detail, the AB and BA diblock copolymers, $(ABC)_4$ dodecablock terpolymer, $(ABCD)_3$ dodecablock quaterpolymer, and ABCDEF hexablock sestopolymer were synthesized by sequential GTP methods using various acrylate monomers.

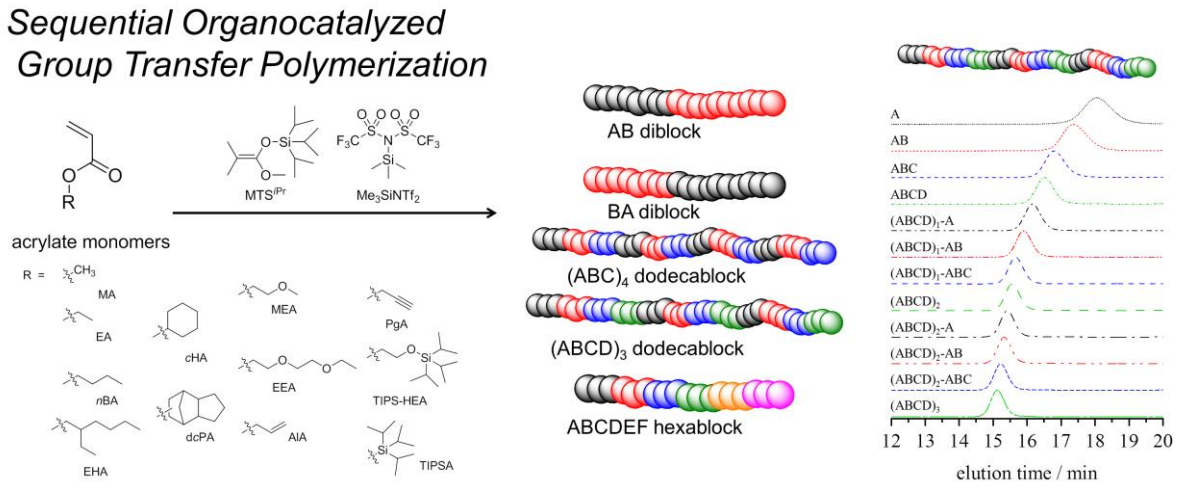


Figure 1-4. Synthesis of AB/BA diblock, $(ABC)_4$ dodecablock, $(ABCD)_3$ dodecablock, and ABCDEF hexablock polymers by organocatalyzed GTP using MTS^{iPr} as an initiator.

Chapter 4 describes that the α-functionalized (hydroxyl, ethynyl, vinyl, and norbornenyl), ω-functionalized (ethynyl, vinyl, hydroxyl, and bromo), and α,ω-functionalized polyacrylates were precisely synthesized by the Me_3SiNTf_2-catalyzed GTP of *n*BA as shown in Figure 1-5. The α-functionalization and ω-functionalization were carried out using the functional triisopropylsilyl ketene acetal as the initiator (initiation approach) and 2-phenylacrylate derivatives as the terminator (termination approach) for the organocatalyzed GTP, respectively. All the polymerizations precisely occurred and produced well-defined end-functionalized poly(*n*-butyl acrylate)s which had predictable molecular weights and narrow molecular weight distributions. High-molecular-weight polyacrylates were easily synthesized using both approaches. In addition, the α,ω-functionalized (hetero)telechelic polyacrylates were synthesized by the combination of the initiation and termination approaches. The structure of the obtained polyacrylates and degree of functionalization were confirmed by the ^{1}H NMR and the MALDI-TOF MS measurements. The spectra of the ^{1}H NMR and MALDI-TOF MS showed that the end-functionalization quantitatively proceeded without any side reactions.

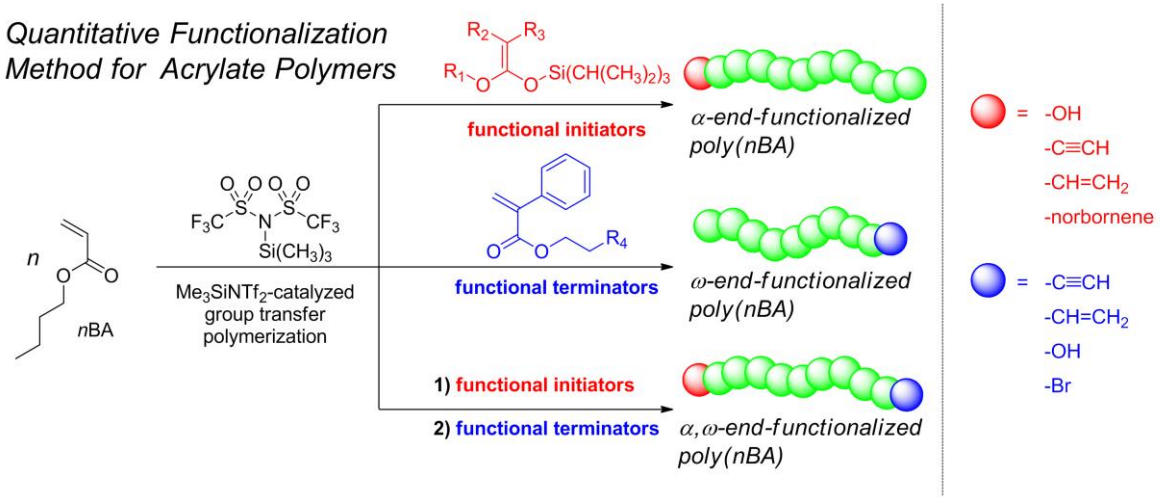


Figure 1-5. Synthesis of α-, ω-, and α,ω-end-functionalized acrylate polymers by organocatalyzed GTP through the initiation and termination approaches using functional initiators and terminators.

Chapter 5 describes the synthesis of star-shaped acrylate polymers using the core-first approaches based on the organocatalyzed GTP through the molecular design and synthesis of multifunctional initiators, such as $MTS^{Ph}{}_3$, $MTS^{Ph}{}_4$, and $MTS^{Ph}{}_8$, as shown in Figure 1-6. The three-, four-, and eight-armed star-shaped P*n*BAs and various acrylate polymers were synthesized by the GTP of acrylates using polyvalent triphenylsilyl ketene acetals as multifunctional initiators, in which Me_3SiNTf_2 is used as the organocatalyst, as shown in Figure 1-6. The living natures for GTP using the multifunctional initiator, $MTS^{Ph}{}_4$, were confirmed by a kinetic experiment and controlled the molecular weight of the four-armed star-shaped P*n*BAs. Furthermore, the high-molecular-weight star-shaped P*n*BA was obtained in this study which had predicted the $M_{w,MALS}$ (M_w/M_n) of 425 100 (1.25). The star-block copolymers were synthesized by the sequential GTP method to produce the P*n*BA-*b*-PMA and P*n*BA-*b*-PEHA. In addition, PTIPS-*b*-P*n*BA, which could produce polyacrylate-*b*-P*n*BA, and P*n*BA-*b*-PMEA, amphiphilic block copolymers, was also synthesized by a similar

procedure. The formations of star-shaped homo and copolymers were determined by size exclusion chromatography measurement using THF. The obtained star-shaped polymer structures are confirmed based on the ^{1}H NMR measurements.

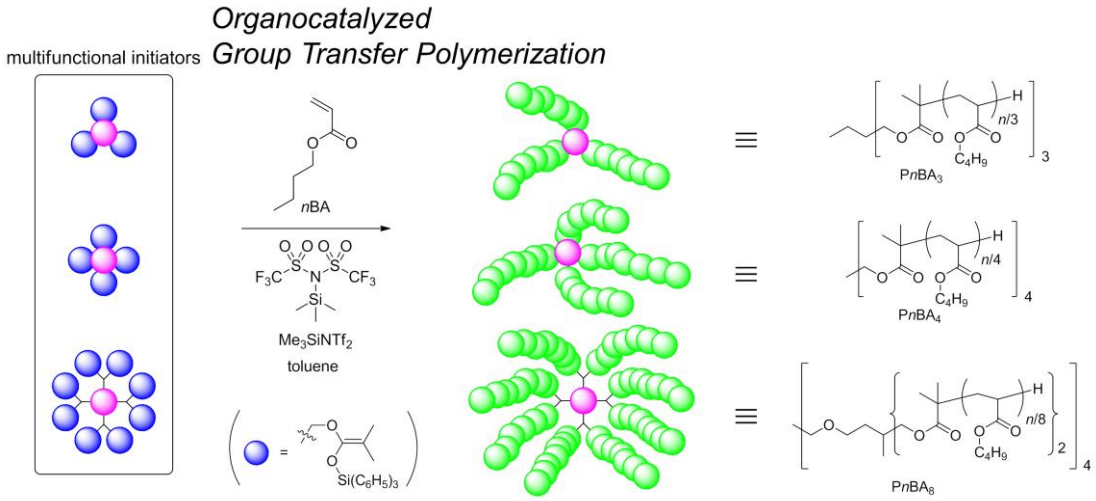


Figure 1-6. Synthesis of three-, four-, and eight-armed star-shaped poly(*n*-butyl acrylate), P*n*BA$_3$, P*n*BA$_4$, and P*n*BA$_8$, by Me_3SiNTf_2-catalyzed GTP using multifunctional initiators.

Chapter 6 summarizes of the precise synthese of acrylate polymers by the organocatalyzed GTP as the overall conclusions of this thesis.

1.5 References and Notes

(1) Müller, A. H. E.; Matyjaszewski, K. *Controlled and Living Polymerizations, From Mechanism to Applications* (ed. Muller, A. H. E. and Matyjaszewski, K.), **2009**, WILEY-VCH Germany.

(2) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules*, **1993**, *26*, 2987-.

(3) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661-.

(4) Goto, A.; Fukuda, T. *Prog. Polym. Sci.* **2004**, *29*, 329-.

(5) Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J. -P.; Tordo, P.; Gnanou, Y. *J Am. Chem. Soc.* **2000**, *122*, 5929-.

(6) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J Am. Chem. Soc.* **1999**, *121*, 3904-.

(7) Wang, J. -S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614-5615.

(8) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921-2990.

(9) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721-1723.

(10) Patten, T. E.; Matyjaszewski, K. *Acc. Chem. Res.* **1999**, *32*, 895-903.

(11) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689-3746.

(12) Tsarevski, N. V.; Matyjaszewski, K. *Chem. Rev.* **2007**, *107*, 2270-2299.

(13) Matyjaszewski, K. *J. Macromol. Sci. Pure Appl. Chem.* **1997**, *34*, 1785-1801.

(14) Qiu, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 5643-5648.

(15) Matyjaszewski, K.; Wang, J. -L.; Grimaud, T.; Shipp, D. A. *Macromolecules* **1998**, *31*, 1527-1534.

(16) Davis, K. A.; Paik, H. -J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 1767-1776.

(17) Mori, H.; Müller, A. H. E. *Prog. Polym. Sci.* **2003**, *28*, 1403-1439.

(18) Teodorescu, M.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4826-4831.

(19) Neugebauer, D.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 2598-2603.

(20) Tsarevski, N. V.; Braunecker, W. A.; Brooks, S. J.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 6817-6824.

(21) Matyjaszewski, K.; Jo, S. M.; Paik, H. -J.; Gaynor, S. G. *Macromolecules* **1997**, *30*, 6398-6400.

(22) Tang, H.; Radosz, M.; Shen, Y. *AICHE J.* **2009**, *55*, 737-746.

(23) Percec, V.; Popov, A. V.; Ramirez-Castilo, E.; Hinojosa-Falcon, L. A. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 2276-2280.

(24) Sheiko, S. S.; Sumelin, B. S.; Matyjaszewski, K. *Prog. Polym. Sci.* **2008**, *33*, 759-785.

(25) Oh, J. K.; Drumright, R.; Siegwart, D. J.; Matyjaszewski, K. *Prog. Polym. Sci.* **2008**, *33*, 448-477.

(26) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337-377.

(27) Moad, G. Rizzardo, E.; Thang, S. H. *Polymer* **2008**, *49*, 1079-1131.

(28) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379-410.

(29) Perrier, S.; Takolpuckdee, P. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 5347-5393.

(30) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2006**, *59*, 669-692.

(31) Lowe, A. B.; McCormick, C. L. *Prog. Polym. Sci.* **2007**, *32*, 283-351.

(32) Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1996**, *29*, 7717-7726.

(33) Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656-2657.

(34) Szwarc, M. *Nature* **1956**, *178*, 1168-1169.

(35) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*,

Marcel Dekker, Inc., **1996** New York, Basel, Hong Kong.

(36) Szwarc, M.; Rembaum, A. *J. Polym. Sci.* **1956**, *22*, 189-191.

(37) Glusker, D. L.; Stiles, E.; Yonkoskie, B. *J. Polym. Sci.* **1961**, *49*, 297-313.

(38) Krause, S.; Defonso, L.; Glusker, D. L. *J. Polym. Sci. Part A: General Papers* **1965**, *3*, 1617-1630.

(39) Schreiber, H. *Makromol. Chem.* **1960**, *36*, 86-88.

(40) Goode, W. E.; Owens, F. H.; Myers, W. L. *J. Polym. Sci.* **1960**, *47*, 75-89.

(41) Davis, T.; Haddleton, D.; Richards, S. *J. Macromol. Sci. Macromol.Sci., Rev. Macromol. Chem. Phys.* **1994**, *34*, 243-324.

(42) Fayt, R.; Forte, R.; Jacobs, R.; Jerome, R.; Ouhadi, T.; Teyssie, P.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442-1444.

(43) Jerome, R.; Forte, R.; Varshney, S. K.; Fayt, R.; Teyssie, P. *The anionic polymerization of acrylates: A challenge, in Recent Advances in Mechanistic and Synthetic Aspects of Polymerization*, **1987**, (eds M., Fontanille and A., Guyoy), D. Reidel, Dordrecht, Netherlands, *215*, p.101-117.

(44) Janata, M.; Lochmann, L.; Vlček, P.; Dybal, J.; Müller, A. H. E. *Makromol. Chem.* **1992**, *193*, 101-112.

(45) Janata, M.; Lochmann, L.; Müller, A. H. E. *Makromol. Chem.* **1993**, *194*, 625-636.

(46) Ishizone, T.; Yoshimura, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1998**, *31*, 8706-8712.

(47) Ishizone, T.; Yoshimura, K.; Yanase, E.; Nakahama, S. *Macromolecules* **1999**, *32*, 955-957.

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

(49) Brittain, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 7440-7444.

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

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

(52) Brittain, W. J. Dicker, I. B. *Macromolecules* **1989**, *22*, 1054-1057.

(53) Hertler, W. R. *Macromolecules* **1987**, *20*, 2976-2982.

(54) Hertler, W. R.; Reddy, G. S.; Sogah, D. Y. *J. Org. Chem.* **1988**, *53*, 3532-3539.

(55) Mai, P. M.; Müller, A. H. E. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 247-253.

(56) Doherty, M. A.; Gores, F.; Mai, P. M.; Müller, A. H. E. *Polym. Prep.* **29**, 73.

(57) Müller, A. H. E. *Macromolecules* **1994**, *27*, 1685-1690.

(58) Farham, W. B.; Sogah, D. Y. *Polym. Prepr.* **1986**, *27*, 167.

(59) Bywater, S. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 339-350.

(60) Quirk, R. P.; Bidinger, G. P. *Polym. Bull.* **1989**, *22*, 63-70.

(61) Matyjaszewski, K. *New Polym. Mater.* **1990**, *2*, 115.

(62) Quirk, R. P; Ren, J. *Macromolecules* **1992**, *25*, 6612-6620.

(63) Webster, O. W. *Maklomol. Chem., Macromol. Symp.* **1993**, *67*, 365-371.

(64) Quirk, R. P.; Kim, J. S. *J. Phys. Org. Chem.* **1995**, *8*, 242-248.

(65) Quirk, R. P.; Ren, J.; Bidinger, G. *Maklomol. Chem., Macromol. Symp.* **1993**, *67*, 351-363.

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

(67) Hertler, W. R.; Sogah, D. Y.; Webster, O. W.; Trost, B. M. *Macromolecules* **1984**, *17*, 1415-1419.

(68) Zhuang, R.; Muller, A. H. E. *Macromolecules* **1995**, *28*, 8035-8042.

(69) Zhuang, R.; Muller, A. H. E. *Macromolecules* **1995**, *28*, 8043-8050.

(70) Brittain, W. J.; Dicker, I. B. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 373-386.

(71) Webster, O. W. *J. Polym. Sci. Part A: Polym. Chem.* **2000,** *38*, 2855-2860.

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

(73) (a) Raynaud, J.; Ciolino, A.; Beceiredo, A.; Destarac, M.; Bonnette, F.; Kato, T.; Gnanou, Y.; Taton, D. *Angew. Chem. Int. Ed.* **2008**, *47*, 5390-5393. (b) Raynaud, J.; Liu, N.; Févre, M.; Gnanou, Y.; Taton, D. *Polym. Chem.* **2011**, *2*, 1706-1712.

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

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

(76) Webster, O. W. *Adv. Polym. Sci.* **2004,** *167*, 1-34.

(77) Ute, K.; Tarao, T.; Kitayama, T. *Polym. J.* **2005**, *37*, 578-583.

(78) Zhuang, R.; Müller, A. H. E. *Macromolecules* **1995**, *28*, 8043-8050.

(79) Ute, K.; Ohnuma, H.; Shimizu, I.; Kitayama, T. *Polym. J.* **2006**, *38*, 999-1003.

(80) Ute, K.; Ohnuma, H.;Kitayama, T. *Polym. J.* **2000**, *32*, 1060-1062.

(81) Schubert, W.;Bandermann, F. *Macromol. Chem. Rapid Commun.* **1985**, *6*, 335-339.

(82) Bandermann, F.; Speikamp, H. D. *Makromol. Chem.* **1989**, *190*, 2721-2726.

(83) Gnaneshwar, R.; Sivaram, S. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 2514-2531.

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

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

(86) Kakuchi, T.; Chen, Y.; Kitakado, J.; Mori, K.; Fuchise, K.; Satoh, T.; Kakuchi, T. *Macromolecules*, **2011**, *44*, 4641-4647.

(87) Kakuchi, R.; Chiba, K.; Fuchise K.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42*, 8747-8750.

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

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

(90) Schubert, W.; Bandermann, F. *Makromol. Chem.* **1989**, *190*, 2161-2171.

(91) Hertler, W. R.; Sogah, D. Y.; Webster, O. W.; Trost, B. M. *Macromolecules* **1984**, *7*, 5-13.

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

(93) Zhang, Y.-T.; Lay, F.; Carcía, P.; List, B; Chen, Y-X.*Chem. Eur. J.* **2010**, *16*, 10462-10473.

(94) Epple, U.; Scheider, H. A. *Polymer* **1990**, *31*, 961-966.

(95) Krupers, M. J.; Moller, M. *Journal of Fluorine Chemistry* **1997**, *82*, 119-124.

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

(97) Tasdelen, M. A.; Kahveci, M. U.; Yagci, Y. *Prog. Polym. Sci.* **2011**, *36*, 455-567.

(98) (a) Hirao, A.; Hayashi, M.; Loykulnant, S.; Sugiyama, K.; Ryu, S. W.; Haraguchi, N.; Matsuo, A; Higashihara, T. *Prog. Polym. Sci.* **2005**, *30*, 111-182. (b) Hirao, A.; Hayashi, M. *Acta. Polym.* **1999**, *50*, 219-231.

(99) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921-2990.

(100) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337-377.

(101) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661-3688.

(102) Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Letp, T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559-5562.

(103) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules*, **1999**, *32*, 6977-6980.

(104) Sogah, D. Y.; Webster, O. W. *J. Polym. Sci. Polym. Lett. Ed.***1983**, *21*, 927-931.

(105) Quirk, R. P.; Ren, J. *Polym. Int.* **1993**, *32*, 205-212.

(106) Hadjichristidis, N. ; Pitsikalis, M.;Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747-3792.

(107) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Mays, J. *Prog. Polym. Sci.* **2006**, *31*, 1068-1132.

(108) Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317-350.

(109) Sakamoto, K.; Aimiya, T.; Kira, M. *Chem. Lett.* **1997**, 1245-1246.

(110) Zhu, Z.; Rider, J.; Yang, C.-Y.; Gilmartin, M. E.; Wnek, G. E. *Macromolecules* **1992**, *25*, 7330-7333.

(111) Simmons, M.; Yamasaki, E. N.; Patrickios, C. S. *Polymer* **2000**, *41*, 8523-8529.

(112) Themistou, E.; Patrickios, C. S. *Macromolecules* **2004**, *37*, 6734-6743.

(113) Kali, G.; Georgiou, T. K.; Iván, B.; Patrickios, C. S.; Loizou, E.; Thomann, Y.; Tiller, J. C. *Macromolecules*, **2007**, *40*, 2192-2200.

(114) Georgiou, T. K.; Patrickios, C. S.; Werner, P.; Iván, B. *Macromolecules* **2007**, *40*, 2335-2343.

(115) Kassi, E.; Patrickios, C. S. *Macromolecules* **2010**, *43*, 1411-1415.

(116) Chen, Y; Fuchise, K.; Narumi, A.; Kawaguchi, S.; Satoh, T.; Kakuchi, T. *Macromolecules* **2011**, *44*, 9091-9098.

(117) Chen, Y.; Takada, K.; Fuchise, K.; Satoh, T.; Kakuchi, T. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 3277-3285.

(118) Kikuchi, S.; Chen, Y.; Fuchise, K.; Takada, K.; Kitakado, J.; Sato, S.; Satoh, T.; Kakuchi, T. *Polym. Chem.* **2014**, *5*, 4701-4709.

Chapter 2

Synthesis of High-Molecular-Weight Acrylate Polymers by Brønsted Acid-Promoted Group Transfer Polymerization

2.1 Introduction

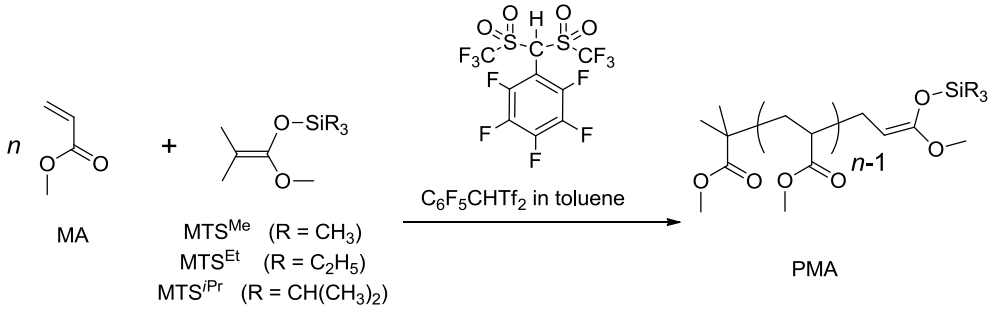
Webster and Sogah developed the concept of group transfer polymerization (GTP) in 1983, one of the important living polymerization methods, and the GTP of (meth)acrylates generally guarantees an excellent molecular control even at room temperature.[1,2] Since they established the GTP, there are many efforts to precisely control the polymerizations of (meth)acrylates,[3,4] acrylamides,[5] and (meth)acrylonitrile,[6] leading to well-defined polymers, and both Lewis bases and Lewis acids has been employed as catalysts.[7]

Organocatalysts have developed and were found to be new and useful catalysts for the GTP. Taton and coworkers first reported the *N*-heterocyclic carbene-catalyzed GTPs of methyl methacrylate (MMA) and *tert*-butyl acrylate (*t*BA), which produced well-defined homopolymers and block copolymers.[4,5] Kakuchi and coworkers reported that the phosphazene base, 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranyliden-amino]-2Λ^5,4Λ^5-catenadi(phosphazene) (*t*-Bu-P_4), a very strong organic base, was extremely efficient for the syntheses of the poly(methyl methacrylate)s (PMMAs) and 3-, 4-, and 6-armed star-shaped PMMAs.[8,9] In addition, Kakuchi and coworkers found that trifluoromethanesulfonimide (Tf_2NH), a highly strong Brønsted acid, could promote the GTP of MMA using MTS^{Me} to afford the syndiotactic PMMA without any obvious side reactions.[10] Furthermore, the Tf_2NH-promoted GTP of *N*,*N*-dimethylacrylamide using the specially designed initiator, (*Z*)-1-(dimethylamino)-1-trimethylsiloxy-1-propene, produced the well-defined poly(*N*,*N*-dimethylacrylamide) with a low polydispersity (M_w/M_n).[11] Thus, of great interest in GTP is to further elucidate the scope and limit of organocatalysts, monomers, and initiators applicable to polymer synthesis. In addition, living polymerization of acrylate monomers is still challenging task because the anionic polymerization and GTP of *n*-alkyl acrylates are generally hard to control and are usually disturbed by inherent side reactions of

the ester carbonyl group and the labile α-hydrogen of the monomer units in the polymer with the anionic initiators and the active chain ends.[12] Specifically, the anionic polymerization and GTP of methyl acrylate (MA) has been so far difficult, though Matyjaszewski and coworkers reported that the poly(methyl acrylate) (PMA) with the high molecular weight and the low M_w/M_n was obtained from the activators regenerated by the electron transfer atom transfer radical polymerization of MA.[13] Therefore, the living polymerization of *n*-alkyl acrylates still remains a challenging task in the anionic polymerization and the GTP chemistry.

In this chapter, the author describes the GTP of MA proceeding in a living fashion using the very strong Brønsted acid of pentafluorophenylbis(triflyl)methane ($C_6F_5CHTf_2$)[14] as the promoter, as shown in Scheme 2-1. This chapter describes 1) the living polymerization using the GTP by optimizing the initiator structure of the trialkylsilyl ketene acetals, such as MTS^{Me}, 1-methoxy-1-triethylsiloxy-2-methyl-1-propene (MTS^{Et}), and 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene (MTS^{iPr}), 2) the living nature of the polymerization confirmed by the MALDI-TOF MS measurement, the post-polymerization experiment, and the block copolymerization of MA and *n*BA, and 3) the synthesis of a high-molecular-weight PMA and P*n*BA with degree of polymerization more than 1000.

Scheme 2-1. $C_6F_5CHTf_2$-Promoted group transfer polymerization (GTP) of methyl acrylate (MA) using MTS^{Me}, MTS^{Et}, and MTS^{iPr}



2.2 Experimental Section

Materials

n-Butyllithium (1.6 mol L^{-1} in *n*-hexane), dry dichrolomethane (CH_2Cl_2, > 99.5%; water content, < 0.001%), methanol (methanol), dry tetrahydrofuran (THF), toluene, *tert*-butyl alcohol, and pyridine were purchased from Kanto Chemicals Co., Inc. CH_2Cl_2 was dried over CaH_2 and distilled under an argon atmosphere. Toluene was distilled from sodium benzophenone ketyl. Methyl acrylate (MA), *n*-butyl acrylate (*n*BA) 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS^{Me}), diisopropylamine, methyl isobutyrate, chlorotriethylsilane, triisopropylsilyl trifluoromethanesulfonate, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU), pentafluorophenylbis(triflyl)methane ($C_6F_5CHTf_2$), and *trans*-3-indoleacrylic acid were purchased from Tokyo Kasei Kogyo Co., Ltd. MA, *n*BA, diisopropylamine, methyl isobutyrate, and chlorotriethylsilane were dried over CaH_2 and distilled under an argon atmosphere. MTS^{Me} and DMPU were purified by fractional distillation under an argon atmosphere. Sodium trifluoroacetate was purchased from Sigma-Aldrich Chemicals Co. and used as received. 1-Methoxy-1-triethylsiloxy-2-methyl-1-propene (MTS^{Et}) and 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene (MTS^{iPr}) were prepared according to the method reported by Yamamoto et al. [15] and Fu et al., [16] respectively. All other chemicals were purchased and used without purification.

Instruments

The ^1H (400 MHz) spectrum was recorded using a JEOL JNM-A400II. 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_2O, 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 set of Water 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 ($M_{n,SEC}$) and polydispersity (M_w/M_n) of polymers were calculated on the basis of a poly(methyl methacrylate) calibration. The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed using an Applied Biosystems Voyager-DE STR-H mass spectrometer with a 25 kV acceleration voltage. The positive ions were detected in the reflector mode (25 kV). A nitrogen laser (337 nm, 3 ns pulse width, 106-107 W cm^{-2}) operating at 3 Hz was used to produce the laser desorption, and 500 shots were summed. The spectra were externally calibrated using insulin (bovine) with a linear calibration. Samples for the MALDI-TOF MS were prepared by mixing a polymer (1.5 mg mL^{-1}, 10 μL), the matrix (*trans*-3-indoleacrylic acid, 10 mg mL^{-1}, 90 μL), and the cationizing agent (sodium trifluoroacetate, 10 mg mL^{-1}, 10 μL) in THF.

Polymerization of Methyl Acrylate (MA) and *n*-Butyl Acrylate (*n*BA)

A typical procedure for the polymerization is as follows: to a solution of MTS^{iPr} (14.4 μL, 50.0 μmol) and a stock solution of $C_6F_5CHTf_2$ in CH_2Cl_2 (17.7 μL, 1.00 μmol, 56.5 mmol L^{-1}) in toluene (5.00 mL) was gradually added MA (0.430 g, 5.00 mmol) at room temperature. The polymerization was quenched after 0.1 h by adding a small amount of *tert*-butyl alcohol and pyridine. Aliquots were removed from the reaction mixture to determine the conversion

of MA based on its ^{1}H NMR spectrum. The reaction mixture was dialyzed using a Spectra/Por 6 Membrane (MWCO: 1000) against methanol. The methanol was then removed by evaporation to provide PMA as a sticky solid. Yield: 0.409 g (95.1%); $M_{n,SEC}$ = 11300, M_w/M_n = 1.03.

The polymerization of *n*-butyl acrylate (*n*BA) was carried out with using *n*BA (0.641 g, 5.00 mmol) in the same manner as for the polymerization of MA. Yield: 0.604 g (94.3%); $M_{n,SEC}$ = 14800, M_w/M_n = 1.03.

Postpolymerization Experiments and Block Copolymerization

The polymerization of MA in toluene at room temperature was carried out under the condition of $[MA]_0/[MTS^{iPr}]_0/[C_6F_5CHTf_2]_0$ = 50/1/0.02 and $[MA]_0$ = 1.0 mol L^{-1} using the previously described typical procedure for 0.1 h. The post-polymerization was subsequently started by adding 50 equivalents of MA to the reaction mixture after an aliquot was removed from the reaction mixture to determine the conversion of MA and the $M_{n,SEC}$ value of the product. After 0.1 h, the post-polymerization was quenched by adding a small amount of *t*-butyl alcohol and pyridine. The following purification procedures were the same as the typical polymerization of MA. Yield: 0.370 g (86.0%); $M_{n,SEC}$ = 11500, M_w/M_n = 1.02. The block copolymerization was carried out using the same procedures except that *n*BA was used as the second monomer instead of MA. Yield: 0.471 g (88.0%); $M_{n,SEC}$ = 14200, M_w/M_n = 1.02.

2.3 Results and Discussion

2.3.1 $C_6F_5CHTf_2$-Promoted Group Transfer Polymerization of MA using MTS^{Me}, MTS^{Et}, and MTS^{iPr}

The polymerization of MA promoted by $C_6F_5CHTf_2$ was carried out using 1-trimethylsiloxy-, 1-triethylsiloxy-, and 1-triisopropylsiloxy-1-methoxy-2-methyl-1-propene (MTS^{Me}, MTS^{Et}, and MTS^{iPr}, respectively) as initiators in order to clarify the effect of the initiator structure on the polymerization. Table 2-1 summarizes the results of the polymerization under the condition of $[MA]_0/[Initiator]_0/[C_6F_5CHTf_2]_0$ = 100/1/0.02 in toluene at room temperature. Dichloromethane (CH_2Cl_2) was employed as another polymerization solvent, though the polymerization was sluggish and uncontrolled. Thus, toluene was utilized as the most suitable solvent for the polymerization. The conversion of MA during the polymerization using MTS^{Me} was ca. 59% after 0.1 h (run 1), and scarcely increased even after 24 h (run 2), suggesting that the polymerization was terminated by side reactions within 0.1 h. The dispersity (M_w/M_n) of the obtained PMA was as broad as ca. 1.4, though the number average molecular weight ($M_{n,SEC}$) of 5400 was close to the calculated theoretical molecular weight ($M_{n,calcd}$) of 5600. The polymerization control was partly improved when using MTS^{Et} (runs 3 and 4) and the monomer conversion increased to ca. 88%, the $M_{n,SEC}$s increased to 13000, and the M_w/M_n decreased to ca. 1.2. However, the polymerization was still terminated before the MA was quantitatively consumed. The polymerization using MTS^{iPr} (run 5) was well controlled to produce PMA with 1.03 of M_w/M_n and 11300 of $M_{n,SEC}$, which corresponded to 9000 of $M_{n,calcd}$. The author proposed a mechanism for the $C_6F_5CHTf_2$-promoted GTP of MA, as shown in Scheme 2-2. First, the silicon Lewis acid of $C_6F_5C(SiR_3)Tf_2$ was generated from the reaction between MTS and

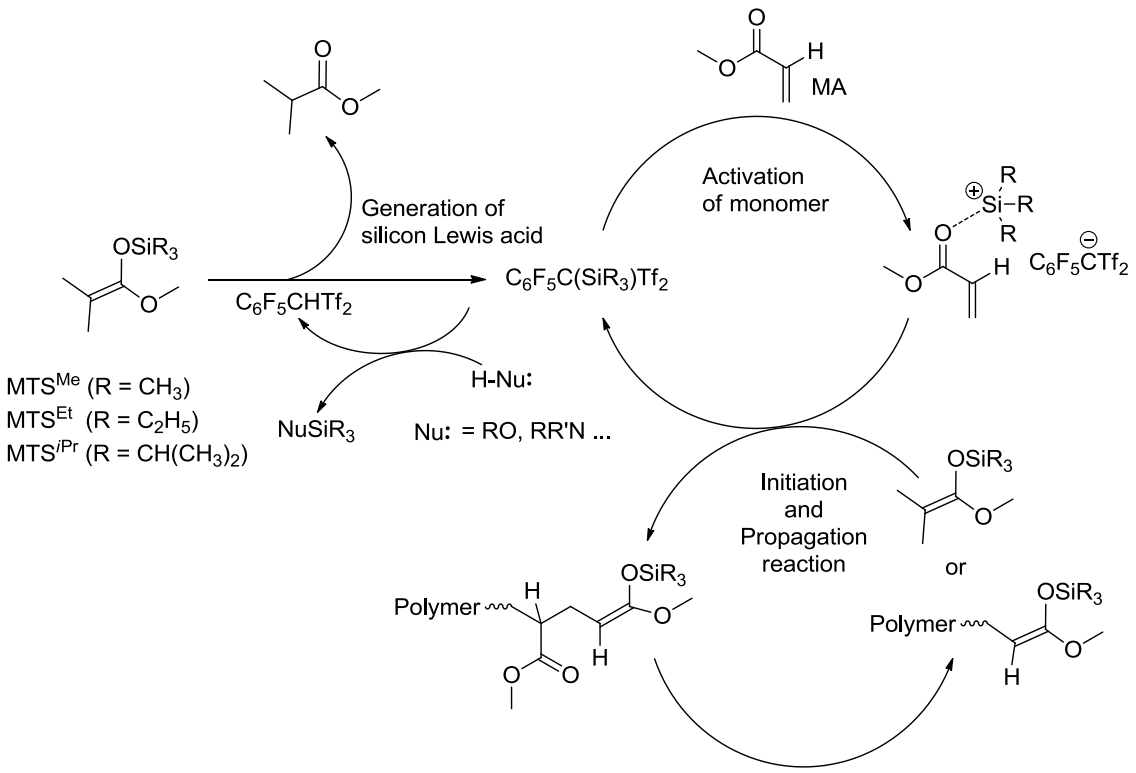
$C_6F_5CHTf_2$ and coordinated to MA to increase the electrophilicity of MA. Then, the silyl enolate group in the PMA chain end attacked the activated MA to propagate the PMA chain, in which the SiR_3 group in the propagating end transferred to the new chain end. Meanwhile, the SiR_3 group of the activated MA released to regenerate $C_6F_5C(SiR_3)Tf_2$. Thus, the polymerization proceeded through the activated monomer mechanism regardless of the silyl group in the silyl enolate, which diffed from the associative and dissociative mechanisms. The trimethylsilyl and triethylsilyl groups of the silyl enolates at PMA chain ends were unstable compared with the triisopropylsilyl group, which caused side reactions, such as backbiting and abstraction of α-hydrogen. In order to obtain the well-defined PMA using MTS^{iPr}, we quickly quenched the polymerization system after all MA was just consumed. However, when the quench was delayed, the cyclization reaction at the chain end of PMA was observed by the MALDI-TOF MS measurement. Thus, the bulky triisopropylsilyl group at a propagating chain end suppressed the side reaction of backbiting, i.e., MTS^{iPr} was as the most suitable initiator for the $C_6F_5CHTf_2$-promtoed GTP of MA.

Table 2-1. $C_6F_5CHTf_2$-Promoted Group Transfer Polymerization (GTP) of Methyl Acrylate (MA) using MTS^{Me}, MTS^{Et}, and MTS^{iPr} in Toluene [a]

run	initiator	time / h	conv / % [b]	$M_{n,calcd}$ / g mol^{-1} [c]	$M_{n,SEC}$ / g mol^{-1} [d]	M_w/M_n [d]
1	MTS^{Me}	0.1	59.0	5 600	5 400	1.40
2	MTS^{Me}	24	59.5	5 600	5 400	1.39
3	MTS^{Et}	0.1	87.8	8 200	13 100	1.22
4	MTS^{Et}	24	88.1	8 200	13 900	1.23
5	MTS^{iPr}	0.1	> 99	9 000	11 300	1.03

[a] Ar atmosphere; $[MA]_0$, 1.0 mol L^{-1}; $[MA]_0/[initiator]_0/[C_6F_5CHTf_2]_0$, 100/1/0.02; temperature, room temperature (i.e. 23 ± 5ºC). [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([MA]_0/([initiator]_0-[C_6F_5CHTf_2]_0) \times$ (conv) × (MW of MA, 86.09) + (MW of the initiator residue, 102.13). [d] Determined by SEC in THF using poly(methyl methacrylate) standards.

Scheme 2-2. A Proposed Mechanism for the $C_6F_5CHTf_2$-Promoted GTP of MA



2.3.2 Living Nature for $C_6F_5CHTf_2$-Promoted Group Transfer Polymerization of MA

In order to provide a detailed insight into the polymerization reaction, we carried out the ^{1}H NMR and MALDI-TOF MS measurement for the obtained PMA ($M_{n,SEC}$ = 5800, M_w/M_n = 1.05). The ^{1}H NMR spectrum of PMA, the methoxy proton (*a*) and methyl proton (*e*) of the α-end was observed at 3.79 ppm and 1.15 ppm, the peaks of the repeating unit of MA were observed at 3.65, 2.31, and 2.00 to 1.39 ppm due to the methoxy proton (*b*), methylene proton (*c*), and methyne proton (*d*), respectively (Figure 2-1). From the MALDI-TOF MS analysis, exactly one series of peaks was observed, as shown in Figure 2-2a. The difference in the *m/z* values among each molecular ion peak was only 86.0, which corresponded to the molecular weight of MA unit. In addition, the *m/z* value of 4426.4 of a molecular ion peak in Figure 2-2b well agreed with the predicted molecular weight of PMA consisting of 50 monomeric units, one initiator residue and the desilylated chain end cationized with one sodium ion ($C_{205}H_{310}O_{102}Na$ = 4426.90). These results indicated that the $C_6F_5CHTf_2$-promoted GTP of MA was initiated from MTS^{iPr} and proceeded without any side reaction, such as the backbiting reaction.

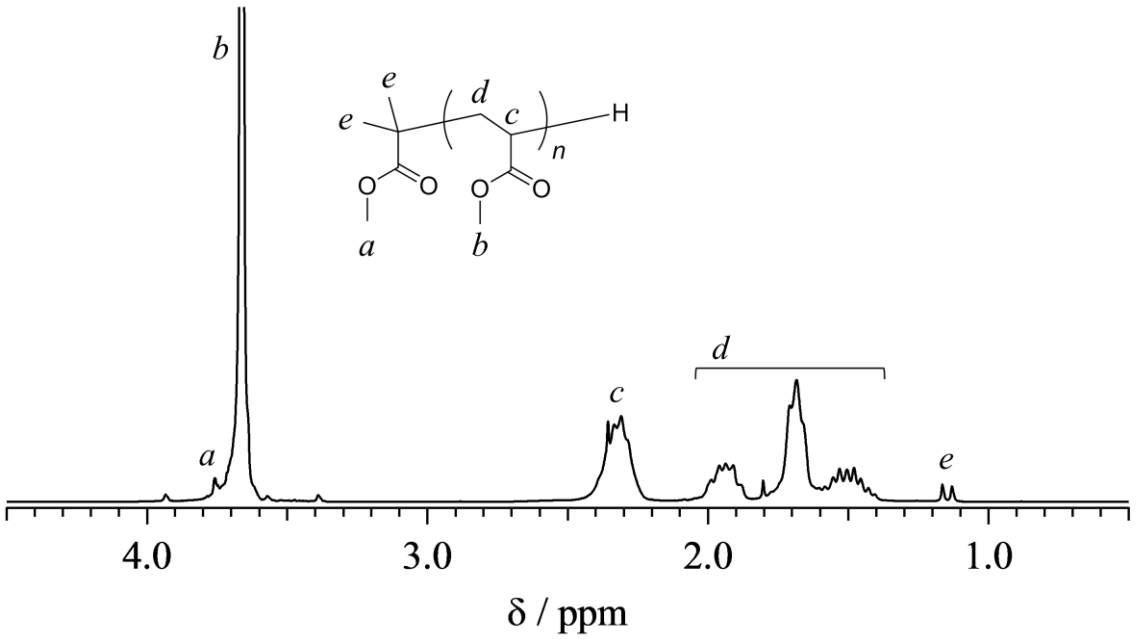


Figure 2-1. ^{1}H NMR spectrum of the obtained PMA measured in $CDCl_3$.

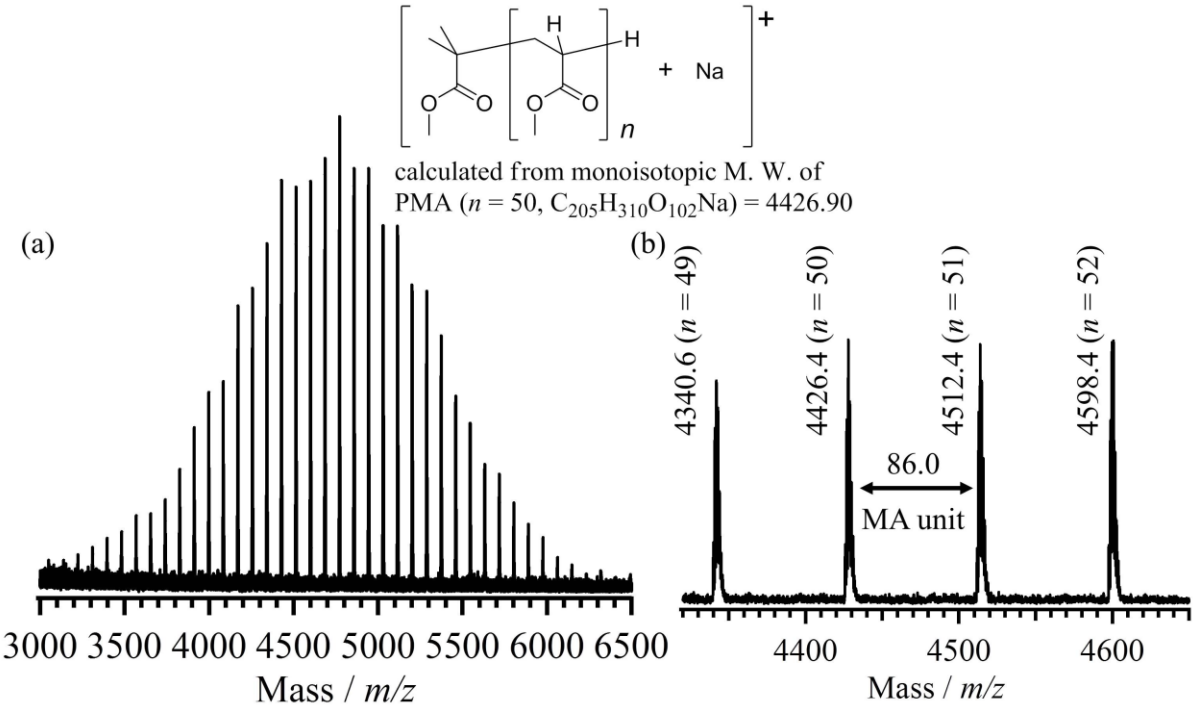


Figure 2-2. MALDI-TOF MS spectrum (reflector mode) of the obtained PMA ($[MA]_0/[MTS^{iPr}]_0/[C_6F_5CHTf_2]_0$, 50/1/0.02, conversion > 99%, $M_{n,SEC}$, 5800; M_w/M_n, 1.05).

In addition, the living nature of the $C_6F_5CHTf_2$-promoted GTP of MA using MTS^{iPr} was confirmed by a kinetic study. The GTP of MA was carried out in toluene at 27°C under the condition of $[MA]_0$ = 1.0 mol L^{-1} and $[MA]_0/[MTS^{iPr}]_0/[C_6F_5CHTf_2]_0$ = 400/1/0.02. As shown in Figure 2-3, the molecular weight of the obtained PMA linearly increased from 10500 to 37000 with the increasing conversion, and the M_w/M_n values of the obtained PMAs were in the range of 1.02-1.03. The first-order kinetic plots of the polymerization showed a straight line, which proved the constant number of active chain ends and constant rate of propagation in the whole stage of the polymerization.

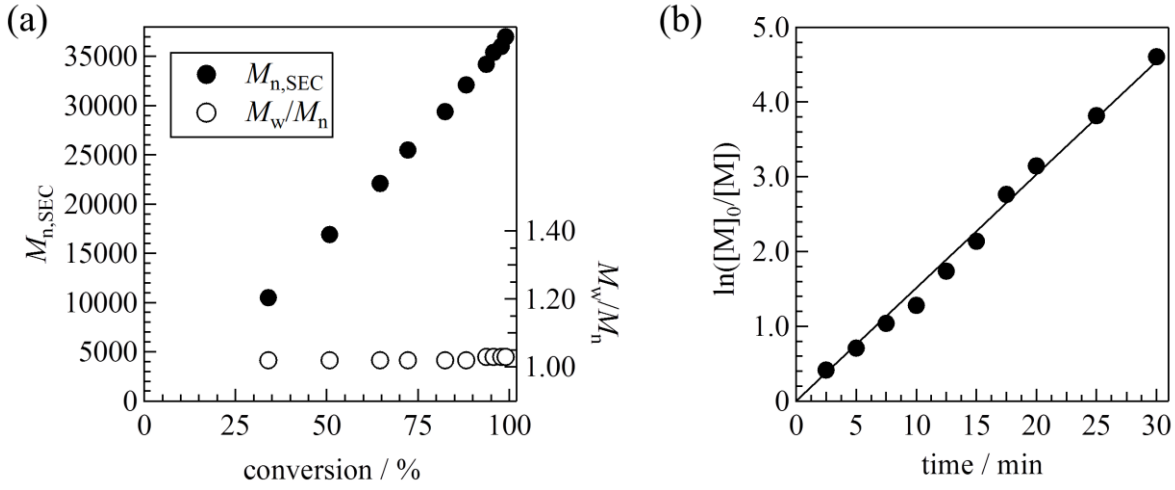


Figure 2-3. (a) Dependence of molecular weight ($M_{n,SEC}$) and polydispersity (M_w/M_n) on the monomer conversion and (b) first-order kinetic plots for the GTP of MA in toluene at 27°C ($[MA]_0$, 1.0 mol L^{-1}; $[MA]_0/[MTS^{iPr}]_0/[C_6F_5CHTf_2]_0$, 400/1/0.02).

The characteristics of the $C_6F_5CHTf_2$-promoted GTP of MA using MTS^{iPr} indicated that the chain end of the propagating PMA retained the triisopropylsilyl ketene acetal structure to allow further polymerization. Thus, we attempted to demonstrate the post-polymerization experiment for MA (Table 2-2, run 6). First, the polymerization of MA was carried out under the condition of $[MA]_0/[MTS^{iPr}]_0/[C_6F_5CHTf_2]_0$ = 50/1/0.02. MA was quantitatively consumed after a 0.1 h polymerization to produce the PMA with $M_{n,SEC}$ of 6000 and M_w/M_n of 1.03. The polymerization was further continued by adding 50 equivalents of MA to afford the PMA with $M_{n,SEC}$ of 11500 and M_w/M_n of 1.02. Both products of the first and second polymerizations showed monomodal molecular weight distributions (MWDs), as show in Figure 2-4. These results indicated that the chain end of the propagating PMA possessed a truly living nature. Thus, we have realized the living polymerization of MA through the GTP process using $C_6F_5CHTf_2$ as a good promoter and MTS^{iPr} as an efficient initiator much like Tf_2NH.

Table 2-2. Postpolymerization Experiment of Methyl Acrylate (MA) using MTS^{iPr} in Toluene [a]

run	monomer		$[M]_0/[MTS^{iPr}]_0$	$M_{n,calcd}$ / g mol^{-1} [b]	$M_{n,SEC}$ / g mol^{-1} [c]	M_w/M_n [c]
6	first	MA	50	4 700	6 000	1.03
	second	MA	50	10 400	11 500	1.02

[a] Ar atmosphere; $[M]_0$, 1.0 mol L^{-1}; $[C_6F_5CHTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temperature (i.e. 23 ± 5ºC); time, 0.1 h; monomer conv, > 99% (determined by ^{1}H NMR in $CDCl_3$). [b] Calculated from $([MA]_0/([MTS^{iPr}]_0-[C_6F_5CHTf_2]_0) \times (conv) \times (MW\ of\ MA, 86.09) + (MW\ of\ the\ MTS^{iPr}\ residue, 102.13)$. [c] Determined by SEC in THF using poly(methyl methacrylate) standards.

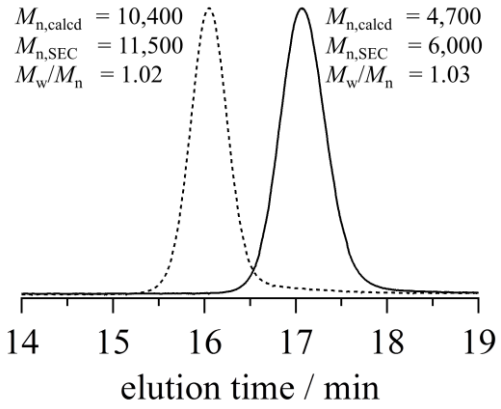


Figure 2-4. SEC traces of the products obtained from the first polymerization (solid line) and the second polymerization (dotted line) in the postpolymerization (eluent, THF; flow rate, 1.0 mL min^{-1}).

2.3.3 Block Copolymerization of MA and *n*BA.

The block copolymerizations of MA and *n*-butyl acrylate (*n*BA) were carried out with different monomer additions, i.e., the polymerization of MA followed by *n*BA (Table 2-3, run 7) and *vice versa* (run 8). Figures 2-5a and 2-5b show the SEC traces for both of the block copolymerizations. After the polymerization of MA under the condition of $[MA]_0/[MTS^{iPr}]_0/[C_6F_5CHTf_2]_0$ = 50/1/0.02, 50 equivalents of *n*BA was added to the reaction mixture. The product of the first polymerization showed a monomodal MWD in the SEC trace, which shifted to a higher molecular weight region in the SEC trace of the product of the second polymerization, while maintaining a narrow MWD, as shown in Figure 2-5a. The $M_{n,SEC}$ increased from 6000 to 14200 and the M_w/M_ns decreased from 1.03 to 1.02 after the block copolymerization. The formation of poly(methyl acrylate)-*block*-poly(*n*-butyl acrylate) (PMA-*b*-P*n*BA) was certainly confirmed by a ^{1}H NMR measurement, as shown in Figure 2-6.

Alternatively, *n*BA was first polymerized to form the P*n*BA with the $M_{n,SEC}$ of 7800, and then MA was subsequently polymerized to produce the poly(*n*-butyl acrylate)-*block*-poly(methyl acrylate) (P*n*BA-*b*-PMA) with $M_{n,SEC}$ of 13400 in run 8. As shown in Figure 2-5b, both products had low M_w/M_ns averaging 1.04 to 1.05. In addition, the block copolymerization of MA and *n*BA under condition of $[MA+nBA]_0/[MTS^{iPr}]_0$ = 100+100 and 400+400 proceeded to produce PMA-*b*-P*n*BA with controlled $M_{n,SEC}$ and low M_w/M_n (runs 9 and 10).

Thus, the well-defined and high-molecular-weight PMA-*b*-P*n*BA was easily synthesized by the sequential addition of MA and *n*BA and *vice versa* by applying the living nature of the $C_6F_5CHTf_2$-promoted GTP of the alkyl acrylates.

Table 2-3. Block Copolymerization of Methyl Acrylate (MA) and *n*-Butyl Acrylate (*n*BA) using MTS^{iPr} in Toluene [a]

run	monomer [M]		$[M]_0/[MTS^{iPr}]_0$	$M_{n,calcd}$ / g mol^{-1} [b]	$M_{n,SEC}$ / g mol^{-1} [c]	M_w/M_n [c]
7	first	MA	50	4 700	6 000	1.03
	second	*n*BA	50	12 500	14 200	1.02
8	first	*n*BA	50	6 800	7 800	1.04
	second	MA	50	11 400	13 400	1.05
9	first	MA	100	13 300	17 400	1.02
	second	*n*BA	100	26 200	28 200	1.05
10	first	MA	400	52 600	53 000	1.03
	second	*n*BA	400	88 100	88 300	1.04

[a] Ar atmosphere; $[M]_0$, 1.0 mol L^{-1}; $[C_6F_5CHTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temperature (i.e. 23 ± 5ºC); time, 0.1 h; monomer conv, > 99% (determined by ^{1}H NMR in $CDCl_3$). [b] Calculated from $([M]_0/([MTS^{iPr}]_0-[C_6F_5CHTf_2]_0) \times$ (conv) × (MW of monomer; MA, 86.09; *n*BA, 128.17) + (MW of the MTS^{iPr} residue, 102.13). [c] Determined by SEC in THF using poly(methyl methacrylate) standards.

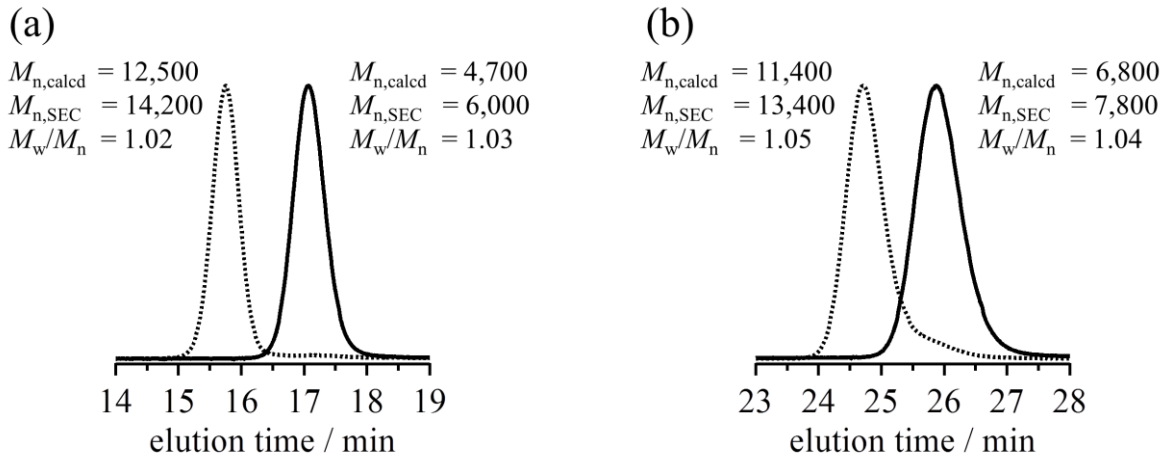


Figure 2-5. SEC traces of the products obtained from the first polymerization (solid line) and the second polymerization (dotted line) in (a) the block copolymerization of MA and *n*BA, and (b) that of *n*BA and MA (eluent, THF; flow rate, 1.0 mL min^{-1}).

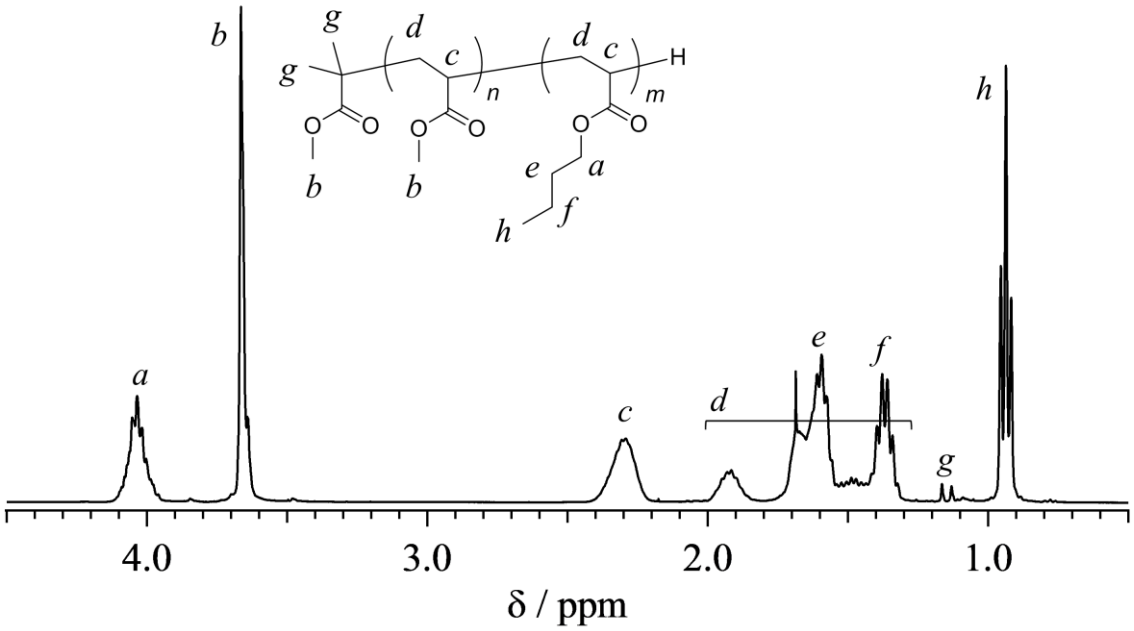


Figure 2-6. ^{1}H NMR spectrum of the obtained poly(methyl acrylate)-*block*-poly(*n*-butyl acrylate) measured in $CDCl_3$.

2.3.4 Synthesis of High-Molecular-Weight PMA and P*n*BA

In order to utilize the living nature for the GTP of MA, the author synthesized PMAs with various molecular weights by the polymerizations under the conditions of $[MA]_0/[MTS^{iPr}]_0$ = 25, 50, 100, 200, 400, and 1000 (Table 2-4). Figure 2-7 shows the SEC traces of the obtained PMAs. Their $M_{n,SEC}$ values increased from 2900 to 108000, which agreed with the $M_{n,calcd}$s calculated from the $[MA]_0/[MTS^{iPr}]_0$ for each PMA. In addition, all the M_w/M_n values were low as 1.03-1.07. The polymerizations of *n*BA were also carried out under the condition of $[n\text{BA}]_0/[MTS^{iPr}]_0$ = 25, 50, 100, 200, 400, and 1000 (Table 2-5). Their $M_{n,SEC}$ value were increased 4300 to 147200 and narrow MWD (Figure 2-8). Thus, the $C_6F_5CHTf_2$-promoted GTP of MA and *n*BA were capable of providing the PMA and P*n*BA with a narrow MWD and wide range of molecular weight. These results led to the conclusion that the $C_6F_5CHTf_2$-promoted GTP of acrylates were found to possess a living nature and produced well-defined poly(acrylate)s at room temperature. In particular, the author realized the synthesis of high molecular weight PMA and PnBA with molecular weight of more than 100000.

Table 2-4. $C_6F_5CHTf_2$-Promoted Group Transfer Polymerization (GTP) of Methyl Acrylate (MA) using MTS^{iPr} in Toluene [a]

run	$[MA]_0/[MTS^{iPr}]_0$	time / h	$M_{n,calcd}$ / g mol^{-1} [b]	$M_{n,SEC}$ / g mol^{-1} [c]	M_w/M_n [c]
9	25	0.1	2 500	2 900	1.07
10	50	0.1	4 700	5 800	1.05
5	100	0.1	9 000	11 300	1.03
11	200	0.1	17 800	20 000	1.03
12	400	1.0	35 400	40 000	1.04
13[d]	1000	1.0	90 900	108 000	1.07

[a] Ar atmosphere; $[MA]_0$, 1.0 mol L^{-1}; $[C_6F_5CHTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temperature (i.e. 23 ± 5ºC); monomer conv > 99% (determined by ^{1}H NMR in $CDCl_3$). [b] Calculated from $([MA]_0/([MTS^{iPr}]_0-[C_6F_5CHTf_2]_0) \times$ (conv) × (MW of MA, 86.09) + (MW of MTS^{iPr} residue, 102.13). [c] Determined by SEC in THF using poly(methyl methacrylate) standards. [d] $[C_6F_5CHTf_2]_0/[MTS^{iPr}]_0$, 0.05.

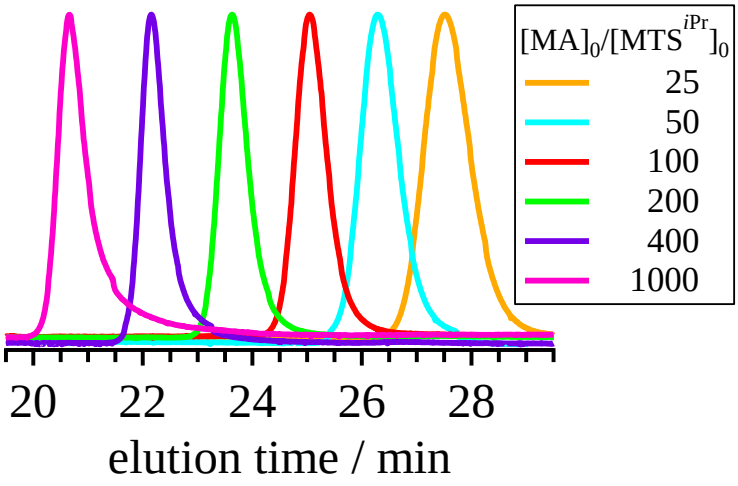


Figure 2-7. SEC traces of the obtained PMAs (eluent, THF; flow rate, 1.0 mL min^{-1}).

Table 2-5. $C_6F_5CHTf_2$-Promoted Group Transfer Polymerization (GTP) of *n*-Butyl Acrylate (*n*BA) using MTS^{iPr} in Toluene [a]

run	$[n\text{BA}]_0/[\text{MTS}^{iPr}]_0$	time / h	$M_{n,calcd}$ / g mol^{-1} [b]	$M_{n,SEC}$ / g mol^{-1} [c]	M_w/M_n [c]
14	25	0.1	3 500	4 300	1.09
15	50	0.1	6 800	7 400	1.04
16	100	0.1	13 300	14 800	1.03
17	200	0.3	26 400	29 600	1.03
18	400	8.0	52 600	54 000	1.03
19	1000	10.0	131 000	147 200	1.07

[a] Ar atmosphere; $[n\text{BA}]_0$, 1.0 mol L^{-1}; $[C_6F_5CHTf_2]_0/[\text{MTS}^{iPr}]_0$, 0.02; temperature, room temperature (i.e. 23 ± 5ºC); monomer conv > 99% (determined by ^{1}H NMR in $CDCl_3$). [b] Calculated from $([n\text{BA}]_0/([\text{MTS}^{iPr}]_0-[C_6F_5CHTf_2]_0) \times (\text{conv}) \times (\text{MW of } n\text{BA, 128.17}) + (\text{MW of MTS}^{iPr} \text{ residue, 102.13})$. [c] Determined by SEC in THF using poly(methyl methacrylate) standards.

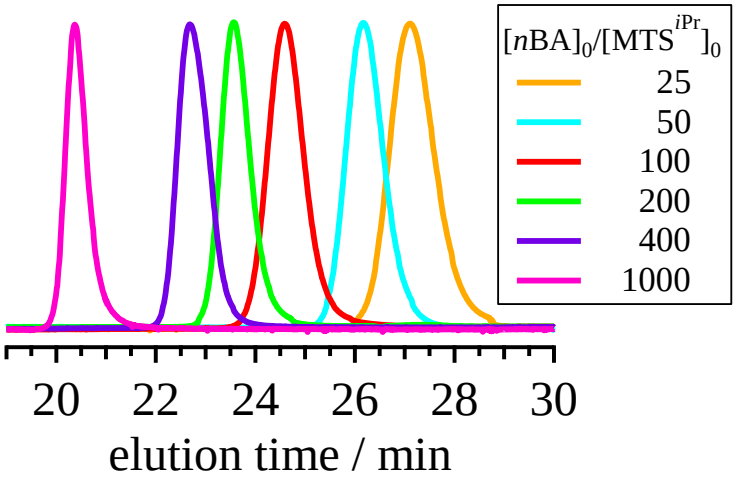


Figure 2-8. SEC traces of the obtained P*n*BAs (eluent, THF; flow rate, 1.0 mL min^{-1}).

2.4 Conclusions

Pentafluorophenylbis(triflyl)methane ($C_6F_5CHTf_2$) and 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene (MTS^{iPr}) were revealed to act as an effective promoter and initiator, respectively, for the group transfer polymerization (GTP) of methyl acrylate (MA). All the homopolymerizations, the post-polymerization, and the block copolymerization proceeded through a living manner to produce well-defined poly(methyl acrylate) (PMA) and its block copolymers. In particular, the living polymerization for the $C_6F_5CHTf_2$-promoted GTP of MA and *n*BA using MTS^{iPr} produced PMA and P*n*BA with a high molecular weight and low molecular weight distribution, i.e., the PMA with the $M_{n,SEC}$ of 108000 and M_w/M_n of 1.07, i.e., the P*n*BA with the $M_{n,SEC}$ of 147200 and M_w/M_n of 1.07. To the best of our knowledge, this is the first reliable demonstration of the living polymerization of MA and *n*BA using the GTP process.

2.5 References and Note

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

(2) Webster, O. W. *J. Polym. Sci. Part A: Polym. Chem.* **2000,** *38*, 2855-2860.

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

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

(5) Raynaud, J.; Liu, N.; Févre, M.; Gnanou, Y.; Taton, D. *Polym. Chem.* **2011**, *2*, 1706-1712.

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

(7) Webster, O. W. *Adv. Polym. Sci.* **2004,** *167*, 1-34.

(8) Kakuchi, T.; Chen, Y.; Kitakado, J.; Mori, K.; Fuchise, K.; Satoh, T.; Kakuchi, T. *Macromolecules*, **2011**, *44*, 4641-4647.

(9) Chen, Y.; Fuchise, K.; Narumi, A; Kawaguchi, S.; Satoh, T.; Kakuchi, T. *Macromolecules* **2011**, *44*, 9091-9098.

(10) Kakuchi, R.; Chiba, K.; Fuchise K.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42*, 8747-8750.

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

(12) Davis, T.; Haddleton, D.; Richards, S. *J. Macromol. Sci. Macromol.Sci., Rev. Macromol. Chem. Phys.* **1994**, *C34*, 243.

(13) Kwak, Y.; Magenau, A. J. D.; Matyjaszewski, K. *Macromolecules*, **2011**, *44*, 811-819.

(14) Ishihara, K.; Hasegawa, A.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2001**, *40*, 4077-4079.

(15) Hasegawa, A.; Naganawa, Y.; Fushimi, M.; Ishihara, K.; Yamamoto, H. *Org. Lett* **2006**, *8*,

3175-3178.

(16) Liu, S. -Y.; Hills, I. D.; Fu, G. *J. Am. Chem. Soc.* **2005**, *127*, 15352-15353.

Chapter 3

Synthesis of Well-Defined Acrylate Block Polymers by Organocatalyzed Group Transfer Polymerization

3.1 Introduction

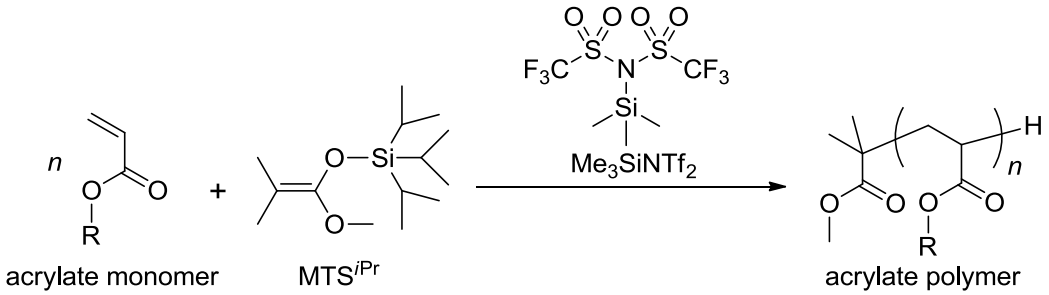
Block polymers exhibit various properties in the bulk and solution phases depending on the type of polymer segments used and their combinations.[1-3] For example, AB diblock copolymers with various combinations of A and B polymer segments have been widely designed and synthesized using many controlled/living polymerization methods to study and apply their physical properties as polymeric materials.[4-7] In addition, the ABA and BAB triblock copolymers and (AB)*n* alternate multiblock copolymers have been synthesized for comparison with AB diblock copolymers in terms of the interest in their morphologies.[8-11] The anionic polymerization by sequentially and pre-orderly adding designed monomers, i. e., the sequential anionic polymerization, is one of the reliable methods for preparing multiblock polymers with predictable molecular weights and narrow molecular weight distributions. For the ABA and BAB triblock copolymers, Hirao et al. and Hadjichristidis et al. reported the synthesis of poly(2-vinylpyridine)-*b*-polystyrene-*b*-poly(2-vinylpyridine) (P2VP-*b*-PS-*b*-P2VP), poly(methyl methacrylate)-*b*-P2VP-*b*-poly(methyl methacrylate) (PMMA-*b*-P2VP-*b*-PMMA), and PS-*b*-poly(dimethylsiloxane)-*b*-PS (PS-*b*-PDMS-*b*-PS).[9-12] For the (AB)*n* alternate multiblock copolymer, the ABABAB hexablock, ABABABAB octablock, and ABABABABABAB dodecablock copolymers were synthesized using the α-chain-end-functionalized AB diblock copolymer of PS-*b*-PMMA.[9,10,11] Recently, more complicated multiblock polymer objects, such as those consisting of more than three different polymer segments, have attracted much attention from the viewpoint of the development of advanced nanomaterials. For instance, Stadler et al. reported the synthesis of the ABC triblock terpolymers of PS-*b*-P2VP-*b*-poly(*tert*-butyl methacrylate) (PS-*b*-P2VP-*b*-P*t*BMA).[13] In addition, the ABCD tetrablock quaterpolymer of PS-*b*-polyisoprene-*b*-PDMS-*b*-P2VP (PS-*b*-PI-*b*-PDMS-*b*-P2VP), and the ABCDE

pentablock quintopolymer of PS-*b*-PI-*b*-PDMS-*b*-P*t*BMA-*b*-P2VP were synthesized by the combination of the sequential polymerization and selective linking methods.[14,15] However, the anionic polymerization of acrylate monomers hardly controlled the molecular weights and their distributions of the obtained polymers due to the side reactions of the ester carbonyl group and the susceptible α-hydrogen with the anionic initiators and the active chain ends. Therefore, multiblock polymers containing acrylate polymer segments are limited using the sequential anionic polymerization method, meaning that the synthesis of multiblock polymers even though they consist of only acrylate polymer segments, i.e., multiblock acrylate polymers, is a remaining and challenging task. The sequential controlled/living radical polymerization is currently an efficient technique for the synthesis of well-defined acrylate polymers. For instance, Whittaker et al. reported that poly(methyl acrylate)-*b*-poly(*n*-butyl acrylate)-*b*-poly(ethyl acrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(ethyl acrylate)-*b*-poly(*n*-butyl acrylate)-*b*-poly(*n*-butyl acrylate)-*b*-poly(methyl acrylate) (PMA-*b*-P*n*BA-*b*-PEA-*b*-PEHA-*b*-PEA-*b*-P*n*BA-*b*-P*n*BA-*b*-PMA) and PMA-*b*-PEA-*b*-P*n*BA-*b*-poly(*tert*-butyl acrylate)-*b*-PMA-*b*-PEA-*b*-P*n*BA-*b*-poly(*tert*-butyl acrylate)-*b*-PMA-*b*-PEA were synthesized as octablock and decablock acrylate polymers, respectively, by the iterative Cu(0)-mediated radical polymerization.[16,17]

Group transfer polymerization (GTP), one of the anionic polymerizations, is well known as the polymerization method for (meth)acrylate monomers using conventional Lewis acids and bases.[18-22] Recently, organocatalysts have been found to sufficiently control the GTP, which leads to producing well-defined (meth)acrylate polymers with predicted molecular weights and narrow molecular weight distribution. For instance, Taton et al. and Waymouth et al. reported that *N*-heterocylic carbenes efficiently catalyzed the GTPs of methyl methacrylate, *N*,*N*-dimethylaminoethyl methacrylate, *N*,*N*-dimethyacrylamide, *tert*-butyl acrylate (*t*BA),

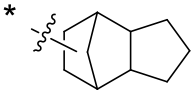
and *n*-butyl acrylate (*n*BA) to produce the respective well-defined homopolymers as well as their di- and triblock polymers.[23-28] In addition, Kakuchi et al. reported that strong Brønsted acids, such as trifluoromethanesulfonylimide and 1-[bis(trifluoromethanesulfonyl)-methyl]-2,3,4,5,6-pentafluorobenzene, and the Lewis acid of *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNTf_2) performed as promoters and organocatalyst, respectively, for the controlled/living GTPs of (meth)acrylate and acrylamide monomers.[29-35] Particularly, the organic-acid-catalyzed GTP using the initiator of 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene (MTS^{iPr}) was the most suitable polymerization method for acrylate monomers, such as methyl acrylate (MA) and *n*BA, leading to high-molecular-weight acrylate polymers with the molecular weight of up to 10^3 kg mol^{-1} and those with α,ω-end-functional groups.[33,35] Thus, it is important to elucidate the scope and limit of this GTP system in terms of applicable acrylate monomers and synthesis of multiblock acrylate polymers. Hence, the objective of this chapter is to establish the Me_3SiNTf_2-catalyzed GTP using MTS^{iPr} as a versatile method for synthesizing well-defined acrylate polymers, as shown in Scheme 3-1. This chapter describes (1) the GTP characteristics of MA, ethyl acrylate (EA), *n*BA, 2-ethylhexyl acrylate (EHA), cyclohexyl acrylate (*c*HA), dicyclopentanyl acrylate (d*c*PA), and *t*BA as alkyl acrylates and 2-methoxyethyl acrylate (MEA), 2-(2-ethoxyethoxy)ethyl acrylate (EEA), allyl acrylate (AlA), propargyl acrylate (PgA), 2-(triisopropylsiloxy)ethyl acrylate (TIPS-HEA), and triisopropylsilyl acrylate (TIPSA) as functional acrylates, (2) the homopolymer chain extension by the sequential post-polymerizations (nine times) of MA, EA, *n*BA, and MEA, and (3) the synthesis of AB and BA diblock copolymers, (PEHA-*b*-P*n*BA-*b*-PEA)$_4$ dodecablock terpolymer, (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$ dodecablock quaterpolymer, and Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA hexablock sestopolymer.

Scheme 3-1. Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of Acrylate Monomers Using MTS^{iPr} as the Initiator



R	acrylate monomer	acrylate polymer
CH_3	MA	PMA
C_2H_5	EA	PEA
$CH_2CH_2CH_2CH_3$	*n*BA	P*n*BA
$CH_2CH(C_2H_5)C_4H_9$	EHA	PEHA
cyclo-C_6H_{11}	*c*HA	P*c*HA
$C_{10}H_{15}$*	d*c*PA	Pd*c*PA
$C(CH_3)_3$	*t*BA	P*t*BA
$CH_2CH_2OCH_3$	MEA	PMEA
$CH_2CH_2OSi(CH(CH_3)_2)_3$	TIPS-HEA	P(TIPS-HEA)
$CH_2CH_2OCH_2CH_2OCH_2CH_3$	EEA	PEEA
$CH_2CH_2N(CH_3)_2$	DMAEA	PDMAEA
$CH_2CH{=}CH_2$	AIA	PAIA
$CH_2C{\equiv}CH$	PgA	PPgA
$Si(CH(CH_3)_2)_3$	TIPSA	PTIPSA

*



3.2 Experimental Section

Materials

Dichloromethane (CH_2Cl_2, >99.5%; water content, <0.001%), toluene (>99.5%; water content, <0.001%), tetrahydrofuran (THF, >99.5%; water content, <0.001%), triethylamine (>99.0%), methanol (>99.5%), and *tert*-butyl alcohol (>98.0%) were purchased from Kanto Chemicals Co., Inc. Methyl acrylate (MA, >99.8%), ethyl acrylate (EA, >99.0%), *n*-butyl acrylate (*n*BA, >99.0%), 2-ethylhexyl acrylate (EHA, 99.0%), cyclohexyl acrylate (*c*HA, >98.0%), dicyclopentanyl acrylate (d*c*PA, >95.0%), *tert*-butyl acrylate (*t*BA, >98.0%), 2-methoxyethyl acrylate (MEA, >98.0%), 2-(2-ethoxyethoxy)ethyl acrylate (EEA, 98.0%), 2-(dimethylamino)ethyl acrylate (DMAEA, >97.0%), allyl acrylate (AlA, >98.0%), 2-hydroxyethyl acrylate (>95.0%), acrylic acid (>99.0%), acryloyl chloride (>95.0%), *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNTf_2, >95.0%), triisopropylsilyl chloride (*i*Pr_3SiCl), *trans*-3-indoleacrylic acid (>98.0%), and sodium hydride (55wt%, dispersion in liquid paraffin) were purchased from Tokyo Kasei Kogyo Co., Ltd. Sodium trifluoroacetate (98%) was purchased from the Sigma-Aldrich Chemicals Co. MA, EA, *n*BA, EHA, *c*HA, d*c*PA, *t*BA, MEA, EEA, DMAEA, AlA and CH_2Cl_2 were distilled from CaH_2 and degassed by three freeze-pump-thaw cycles prior to their use. Toluene was distilled from sodium benzophenone ketyl. 1-Methoxy-1-triisopropylsiloxy-2-methyl-1-propene (MTS^{iPr}) and propargyl acrylate (PgA) were synthesized by previously reported procedures.[36,37] A spectra/Por 6 membrane (molecular weight cutoff: 1000) was used for the dialysis. All other chemicals were purchased from available suppliers and used without purification.

Measurements

The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a JEOL JNM-A400II. The polymerization solution was prepared in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere (H_2O, 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. Size exclusion chromatography (SEC) measurements of the obtained polymers were performed at 40 °C using a Jasco GPC-900 system equipped with two Shodex KF-804 L columns (linear, 8 mm × 300 mm) using THF at the flow rate of 1.0 mL min^{-1}. SEC measurements for the poly(*n*-butyl acrylate)s were performed at 40 °C using a Shodex® GPC-101 gel permeation chromatography (GPC) system (Shodex® DU-2130 dual pump, Shodex® RI-71 RI detector, and Shodex® ERC-3125SN degasser) equipped with two Shodex KF-804 L columns (linear, 8 mm × 300 mm) using THF at the flow rate of 1.0 mL min^{-1}. The number-average molecular weight ($M_{n,SEC}$) and dispersity (M_w/M_n) of the polymers were determined by the RI based on PMMA standards with the M_w (M_w/M_n)s of 1.25 × 10^6 g mol^{-1} (1.07), 6.59 × 10^5 g mol^{-1} (1.02), 3.003 × 10^5 g mol^{-1} (1.02), 1.385 × 10^5 g mol^{-1} (1.05), 6.015 × 10^4 g mol^{-1} (1.03), 3.053 × 10^4 g mol^{-1} (1.02), and 1.155 × 10^4 g mol^{-1} (1.04), 4.90 × 10^3 g mol^{-1} (1.10), 2.87 × 10^3 g mol^{-1} (1.06), and 1.43 × 10^3 g mol^{-1} (1.15). The $M_{n,NMR}$s of the polymers were determined by their ^{1}H NMR spectra in $CDCl_3$ based on the initiator residue and monomer units. The preparative SEC was performed using $CHCl_3$ (3.5 mL min^{-1}) at room temperature (20 ± 5 ºC) using a JAI LC-9201 equipped with a JAI JAIGEL-2H column (20 mm × 600mm^2; exclusion limit, 5 × 10^3) and a JAI RI-50s refractive index detector.

Synthesis of 2-(Triisopropylsiloxy)ethyl Acrylate (TIPS-HEA)

iPr_3SiCl (16.6 g, 86.1 mmol) was dropwise added to a solution of 2-hydroxyethyl acrylate (10.0 g, 86.1 mmol) and triethylamine (8.71 g, 86.1 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature and sequentially washed with 1 mol L^{-1} HCl (100 mL × 2), conc. aq. $NaHCO_3$ (100 mL), and distilled water (100 mL). The organic phase was dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by distillation under reduced pressure to give TIPS-HEA as a transparent liquid. Yield, 12.51 g (53.3%). b.p., 67 °C/0.02 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.40 (dd, *J* = 17.4, 1.4 Hz, 1H, -CH=C^{E}H^Z*H*), 6.12 (dd, *J* = 17.4, 10.6 Hz, 1H, -C*H*=C^{E}H^{Z}H), 5.81 (dd, *J* = 10.4, 2.0 Hz, -CH=C^E*H*^{Z}H), 4.26 (t, *J* = 5.2 Hz, 2H, -COC*H*$_2$CH$_2$OSi-), 3.93 (t, *J* = 5.2 Hz, 2H, -COCH$_2$C*H*$_2$OSi-), 1.01−1.13 (m, 21H, -OSi[C*H*(C*H*$_3$)$_2$]$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.2, 130.8, 128.4, 65.9, 61.5, 17.9, 11.9. Anal. Calcd for $C_{14}H_{28}O_3Si$ (272.46): C, 61.72; H, 10.36. Found: C, 61.40; H, 10.30.

Synthesis of Triisopropylsilyl Acrylate (TIPSA)

iPr_3SiCl (30.1 g, 156 mmol) was dropwise added to a solution of acrylic acid (11.3 g, 156 mmol) and triethylamine (15.8 g, 156 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The following procedure was similar to that for synthesizing TIPS-HEA, which gave TIPSA as a transparent liquid. Yield, 19.5 g (54.6%). b.p., 87 °C/6.0 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.37 (dd, *J* = 17.4, 1.4 Hz, 1H, -CH=C^{E}H^Z*H*), 6.12 (dd, *J* = 17.2, 10.4 Hz, 1H, -C*H*=C^{E}H^{Z}H), 5.84 (dd, *J* = 10.2, 1.4 Hz, -CH=C^E*H*^{Z}H), 1.01−1.13 (m, 21H, -OSi[C*H*(C*H*$_3$)$_2$]$_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 165.8, 130.8, 130.3, 17.8, 12.0. Anal. Calcd for $C_{12}H_{24}O_2Si$ (288.40): C, 63.10; H, 10.59. Found: C, 63.02; H, 10.57.

Me_3SiNTf_2-Catalyzed GTP of Acrylates Initiated by MTS^{iPr}

A typical procedure is as follows. A stock solution of Me_3SiNTf_2 (10 μL, 1.0 μmol, 0.10 mol L^{-1} in toluene) was added to a solution of MA (430 mg, 0.449mL, 5.0 mmol) and MTS^{iPr} (14.4 μL, 12.9 mg, 50.0 μmol) in toluene (4.48 mL) under an argon atmosphere at room temperature (23 ± 5 °C). After stirring for 1 h, the polymerization was quenched by adding a small amount of methanol. The crude product was purified by reprecipitation in *n*-hexane, dialysis, and preparative size exclusion chromatography (SEC) in $CHCl_3$ to give the poly(methyl acrylate) (PMA) as a white solid. Yield, 425 mg (99 %). $M_{n,NMR}$, 8,600 g mol^{-1}; $M_{n,SEC}$, 9,700 g mol^{-1}; M_w/M_n, 1.03. The GTP of the acrylates (5.0 mmol) produced PEA (yield, 491 mg, 98%), P*n*BA (yield, 612 mg, 96%), PEHA (yield, 892 mg, 97%), P*c*HA (yield, 748 mg, 97%), Pd*c*PA (yield, 490 mg, 95%; monomer, 2.5 mmol), P*t*BA (yield, n. d., no polymerization), PMEA (yield, 638 mg, 98%), PEEA (yield, 885 mg, 94%), PDMAEA (yield, n.d, no polymerization), PAlA (yield, 522 mg, 93%), PPgA (yield, 518 mg, 94%), P(TIPS-HEA) (yield, 1.31 g, 96%), and PTIPSA (yield, 1.09 g, 95%) in a controlled manner.

Chain Extension by Postpolymerization

A typical procedure is as follows. The polymerization of MA (86 mg, 1.0 mmol) with MTS^{iPr} (14.4 μL, 50 μmol) and Me_3SiNTf_2 (10 μL, 1.0 μmol, 0.10 mol L^{-1} in toluene) in toluene (0.89 mL) at room temperature was carried out under the condition of $[MA]_0/[MTS^{iPr}]_0/[Me_3SiNTf_2]_0$ = 20/1/0.02 and $[MA]_0$ = 1.0 mol L^{-1} for 5 min as the first polymerization ($(PMA)_1$). The second polymerization was subsequently started by adding 20 equivalents of MA (86.1 mg, 1.0 mmol) in toluene (0.89 mL) to the polymerization mixture after an aliquot was removed from the reaction mixture to determine the monomer conversion and the molecular weight and dispersity of the resulting polymer ($(PMA)_2$). The continuous

postpolymerizations for the synthesis of $(PMA)_{3\sim10}$ were carried out by the same procedure after the complete consumption of MA was confirmed. After all the post-polymerizations, a small amount of methanol was added to the reaction mixture to terminate the polymerization. The obtained polymers were purified by dialysis and preparative SEC to give the $(PMA)_{10}$ as a clear solid (yield, 851 mg; 99 %). The syntheses of $(PEA)_{10}$, (P*n*BA)$_{10}$, and $(PMEA)_{10}$ were carried out using the same procedure with 1.0 mmol, for each polymerization, of acrylates to give the respective acrylate polymers in quantitative yields ($(PEA)_{10}$; yield, 970 mg; 97 %; (P*n*BA)$_{10}$; yield, 1.22 g; 95 %; $(PMEA)_{10}$; yield, 1.24 g; 95 %).

Synthesis of Di- and Multiblock Acrylate Polymers

The diblock copolymerizations were carried out using *n*BA (160 mg, 1.25 mmol) with MEA (162 mg, 1.25 mmol), AlA (140 mg, 1.25 mmol), and PgA (137 mg, 1.25 mmol). The multiblock polymerizations of MA (86 mg, 1.0 mmol), EA (100 mg, 1.0 mmol), *n*BA (128 mg, 1.0 mmol), EHA (184 mg, 1.0 mmol), *c*HA (154 mg, 1.0 mmol), d*c*PA (206 mg, 1.0 mmol), and MEA (130 mg, 1.0 mmol) were carried out using MTS^{iPr} (28.8 μL, 100 μmol) and Me_3SiNTf_2 (20 μL, 2.0 μmol, 0.1 mol L^{-1} in toluene) to produce (PHEA-*b*-P*n*BA-*b*-PEA)$_4$ (1.57 g, 95%), (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$ (1.28 g, 96%), and Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA (842 mg, 98%).

3.3 Results and Discussion

3.3.1 Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of Alkyl Acrylates

Previously, Kakuchi et al. and the author reported trifluoromethanesulfonyimide ($HNTf_2$) or 1-[bis(trifluoromethanesulfonyl)methyl]-2,3,4,5,6-pentafluorobenzene ($C_6F_5CHTf_2$), a strong Brønsted acid, to be an efficient promoter for the group transfer polymerization (GTP) of methyl (meth)acrylate with silyl ketene acetals as the initiator to synthesize well-defined (meth)acrylate polymer with predictable molecular weight and their distribution. However, initiator was consumed by the reaction with Brønsted acid, $HNTf_2$ or $C_6F_5CHTf_2$, generating *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNTf_2) or 1-[triisopropylsilylbis(trifluoromethanesulfonyl)methyl]-2,3,4,5,6-pentafluorobenzene ($C_6F_5C(i\text{Pr})_3Tf_2$) as the true silicon Lewis acid catalyst.[29-34] Therefore, Me_3SiNTf_2 was considered to be a suitable catalyst for the GTP of acrylate monomers. Thus, the GTP of the acrylate monomers was carried out using Me_3SiNTf_2 and 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene ($MTS^{i\text{Pr}}$) as the organocatalyst and initiator, respectively. We initially determined the GTP characteristics of the alkyl acrylates, such as methyl acrylate (MA), ethyl acrylate (EA), *n*-butyl acrylate (*n*BA), 2-ethylhexyl acrylate (EHA), cyclohexyl acrylate (*c*HA), dicyclopentanyl acrylate (dcPA), and *tert*-butyl acrylate (*t*BA). In order to compare their polymerization rates, the polymerizations of MA, EA, *n*BA, EHA, *c*HA, and dcPA were carried out under the conditions of the fixed monomer (M)-to-initiator molar ratio ($[M]_0/[MTS^{i\text{Pr}}]_0$) of 200 in toluene at room temperature. The kinetic experiments exhibited a distinct first-order relationship between the reaction time and monomer conversion, as shown in Figure 3-1. There was no significant difference in the polymerization rates among MA, EA, and *n*BA, whose rates were higher than that of EHA.

Although the loading amount of the catalyst was greater than that used for the polymerizations of MA, EA, *n*BA, and EHA, no polymerization proceeded for *c*HA and d*c*PA within the polymerization time of 30 min. There was an obvious difference in the polymerization ability between the primary and secondary alkyl acrylates for the Me_3SiNTf_2-catalyzed GTP using MTS^{iPr}.

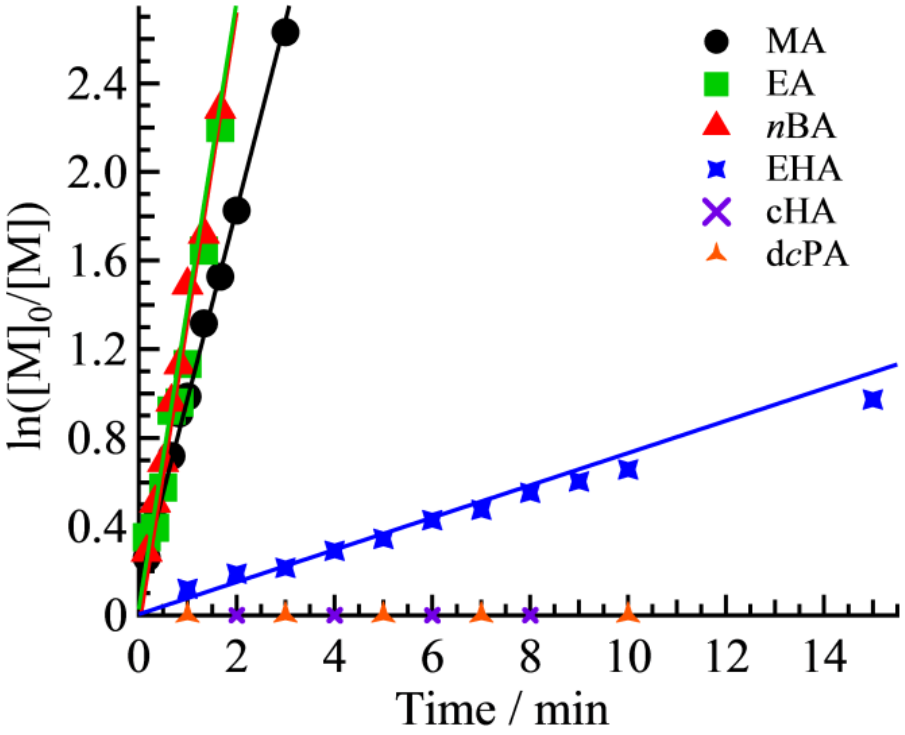


Figure 3-1. Kinetic plots for the Me_3SiNTf_2–catalyzed GTP of MA, EA, *n*BA, EHA, *c*HA, and d*c*PA using MTS^{iPr} in toluene ($[M]_0/[MTS^{iPr}]_0/[Me_3SiNTf_2]_0$, 200/1/0.02; $[M]_0$, 1.0 mol L^{-1}; temperature, 27 °C).

In order to ensure the synthesis of the targeted molecular weight polymers, which is one of the important characteristics for the living polymerization system, the polymerizations of MA, EA, *n*BA, EHA, and *c*HA were carried out under the conditions with the $[M]_0/[MTS^{iPr}]_0$s of

100, 400, and 1000 in toluene at room temperature. All the polymerization results are listed in Figure 3-2 and Table 3-1. The loading amount of the catalyst, i.e., the $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$, was 0.02 for the $[M]_0/[MTS^{iPr}]_0$s of 100 and 400, whereas a higher amount of catalyst was required for the $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$ of 0.05 and the $[M]_0/[MTS^{iPr}]_0$ of 1000. The polymerization time increased with the increasing $[M]_0/[MTS^{iPr}]_0$, and all of the monomers were consumed except for *c*HA. The number average molecular weights of the obtained polymers estimated using SEC measurements ($M_{n,SEC}$s) linearly increased with the increasing $[M]_0/[MTS^{iPr}]_0$, and the molecular weight distributions (M_w/M_ns) of the obtained polymers were as low as 1.02 – 1.06 with monomodal distributions, as shown in Figure 3-3. For the $[M]_0/[MTS^{iPr}]_0$ of 1000, the $M_{n,SEC}$s (M_w/M_ns) were 97 500 g mol^{-1} (1.04) for PMA, 108 400 g mol^{-1} (1.04) for PEA, 141 900 g mol^{-1} (1.05) for P*n*BA, and 220 000 g mol^{-1} (1.06) for PEHA, which agreed with the predicted values ($M_{n,calcd.}$s) of 86 100, 100 200, 128 300, and 184 400 g mol^{-1}, respectively. For the polymerization of *c*HA, the monomer conversion was 90.5 % even after 24 h. Although the $M_{n,SEC}$ of 166 700 g mol^{-1} approximately agreed with the $M_{n,calcd.}$ of 139 700 g mol^{-1}, the molecular weight distribution slightly increased for the M_w/M_n of 1.15. Though the polymerization of d*c*PA needs long polymerization time as 24 h, it proceeded to produce well-defined P*dc*PA with $M_{n,NMR}$ (M_w/M_n) of 10 670 (1.08). On the other hand, the polymerization of *t*BA did not proceed at all even though given a polymerization time of 20 h, which was caused by the ester cleavage of the monomer in the presence of the strong Lewis acid of Me_3SiNTf_2. These results indicated that the polymerization ability of the primary alkyl acrylate was much higher than that of the secondary alkyl acrylate, and the tertiary alkyl acrylate possessed no polymerization ability for the Me_3SiNTf_2-catalyzed GTP using MTS^{iPr} as an initiator.

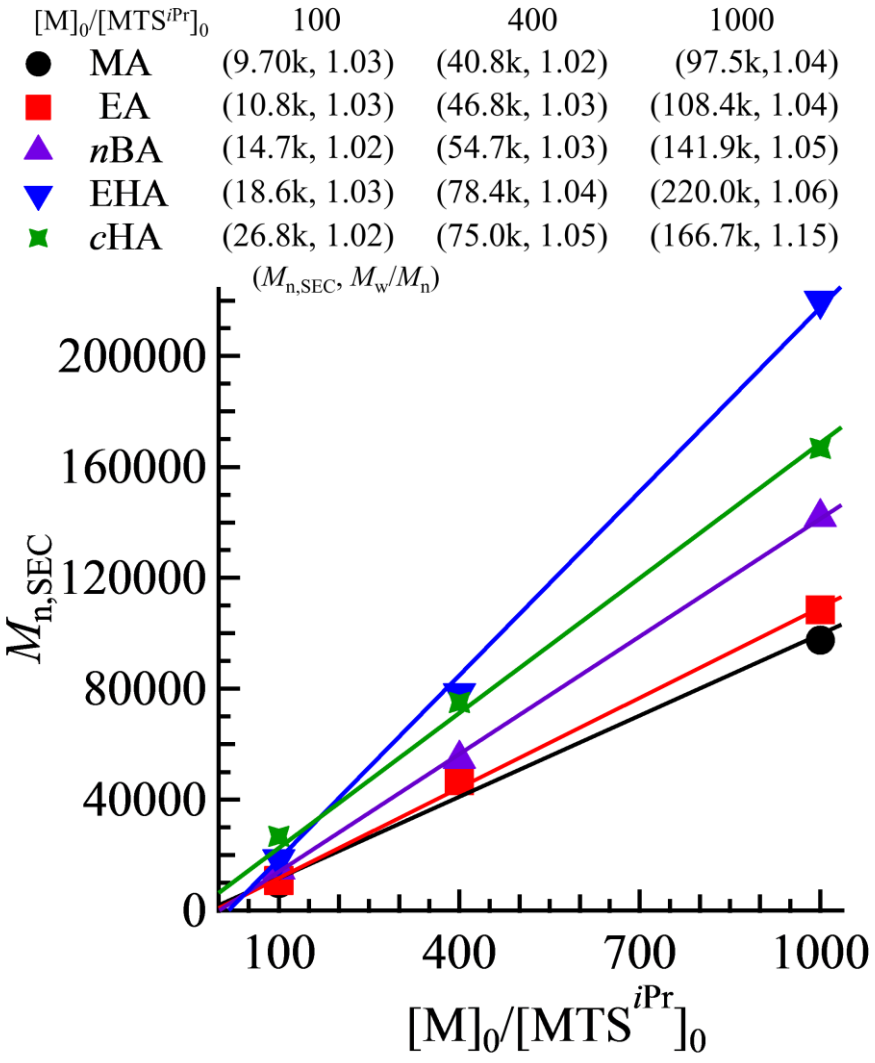


Figure 3-2. Plots for the molecular weights ($M_{n,SEC}$) of the obtained polymers vs. the initial molar ratios of the monomer and initiators ($[M]_0/[MTS^{iPr}]_0$) MA; EA; *n*BA; EHA; and *c*HA along with the values of molecular weight and molecular weight distribution.

Table 3-1. Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of MA, EA, *n*BA, EHA, *c*HA, d*c*PA, and *t*BA [a]

run	monomer (M)	$[M]_0$ /$[MTS^{iPr}]_0$	time / h	conv / % [b]	$M_{n,calcd.}$ / g mol^{-1} [c]	$M_{n,SEC}$ ($M_{n,NMR}$) / g mol^{-1} [d]	M_w/M_n [d]
1	MA	100	1	> 99	8 700	9 700 (8 600)	1.03
2	MA	400	3	> 99	34 500	40 800	1.02
3	MA	1000 [e]	6	> 99	86 100	97 500	1.04
4	EA	100	1	> 99	10 100	10 800 (10 100)	1.03
5	EA	400	3	> 99	40 200	46 800	1.03
6	EA	1000 [e]	6	> 99	100 200	108 400	1.04
7	*n*BA	100	1	> 99	12 900	14 800 (13 200)	1.02
8	*n*BA	400	3	> 99	51 400	54 700	1.03
9	*n*BA	1000 [e]	6	> 99	128 300	141 900	1.05
10	EHA	100	1	> 99	18 500	18 600 (18 600)	1.03
11	EHA	400	3	> 99	73 800	78 400	1.04
12	EHA	1000 [e]	6	> 99	184 400	220 000	1.06
13	*c*HA	100	1	> 99	15 500	26 800 (16 600)	1.02
14	*c*HA	400	3	> 99	61 800	75 000	1.05
15	*c*HA	1000 [e]	24	90.5	139 700	166 700	1.15
16	d*c*PA	50	24	> 99	10 420	17 800 (10 670)	1.08
17	*t*BA	100	24	< 1	-	-	-

[a] Argon atmosphere; solvent, toluene; initiator, MTS^{iPr}, $[M]_0$, 1.0 mol L^{-1}; $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temp. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([M]_0/([MTS^{iPr}]_0) \times$ (conv) × (MW of monomer; MA, 86.09; EA, 100.12; *n*BA, 128.17; EHA, 184.28; *c*HA, 154.21; d*c*PA, 206.29; *t*BA, 128.17) + (MW of initiator residue, 102.13). [d] Determined by SEC in THF using poly(methyl methacrylate) standards. [e] $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$, 0.05.

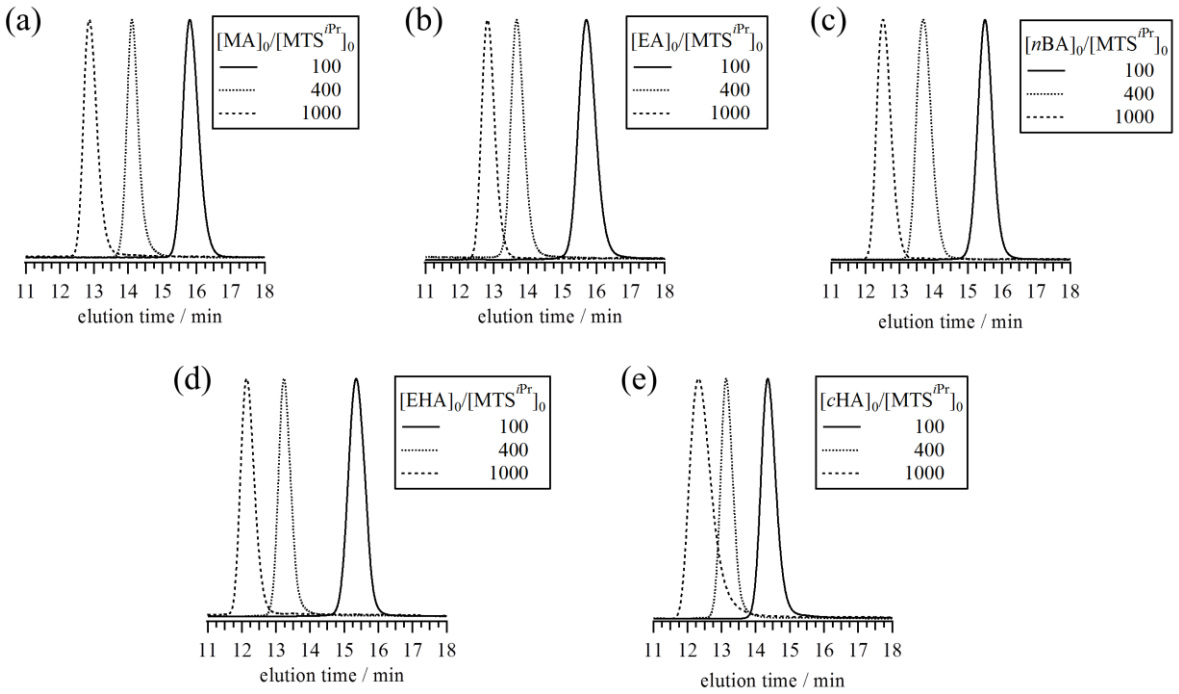


Figure 3-3. SEC traces of the obtained polyacrylates (a) PMA, (b) PEA, (c) *n*BA, (d), EHA, and (e) *c*HA (eluent, THF; flow rate, 1.0 mL min^{-1}).

3.3.2 Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of Functional Acrylates.

In order to elucidate the scope and limit of the applicable monomers, the author examined the polymerization of functional acrylates, such as 2-methoxyethyl acrylate (MEA), 2-(2-ethoxyethoxy)ethyl acrylate (EEA), 2-(triisopropylsiloxy)ethyl acrylate (TIPS-HEA), 2-(dimethylamino)ethyl acrylate (DMAEA), allyl acrylate (AlA), propargyl acrylate (PgA), and triisopropylsilyl acrylate (TIPSA) using the MTS^{iPr} initiator. Table 3-2 summarizes the polymerization results. The polymerizations of MEA with the $[MEA]_0/[MTS^{iPr}]_0$s of 100, 400, and 1000 produced the targeted molecular weight PMEAs, such as the $M_{n,SEC}$s of 14 400, 58800, and 140 300 g mol^{-1}, respectively, which well agreed with the $M_{n,calcd.}$s of 13 100,

52200, and 130 200 g mol^{-1}, respectively (runs 18-20). In addition, the molecular weight distributions of the PMEAs were as narrow as M_w/M_n of 1.03 – 1.05. In order to more hydrophilic acrylate polymers relative to PMEA, the GTPs of EEA and TIPS-HEA were examined. For the polymerization condition of $[M]_0/[MTS^{iPr}]_0/[Me_3SiNTf_2]_0$ = 100/1/0.02, the $M_{n,SEC}$ of poly(2-(2-ethoxyethoxy)ethyl acrylate) (PEEA) was 18 900 g mol^{-1} and the $M_{n,NMR}$ of poly(2-(triisopropylsiloxy)ethyl acrylate) (P(TIPS-HEA)) was 26 700 g mol^{-1}, which agreed with the $M_{n,calcd.}$s of 18 900 and 27 300 g mol^{-1}, respectively (runs 21 and 22). The M_w/M_n of PEEA was 1.06 even though a small peak was observed in the high molecular weight region, and that of P(TIPS-HEA) was 1.02. On the other hand, the polymerization of DMAEA did not proceed after 20 h, which should have been caused by the incentive that the dimethyamino group in the monomer deactivating the catalytic performance of Me_3SiNTf_2 (run 23). The deprotection of the triisopropylsilyl group in the P(TIPS-HEA) using tetra-*n*-butylammonium fluoride smoothly proceeded to produce the well-defined poly(2-hydoxyethyl acrylate). The Me_3SiNTf_2-catalyzed GTPs of AlA and PgA under the condition of $[M]_0/[MTS^{iPr}]_0$ = 100/1 produced gel-free polymers with the $M_{n,NMR}$s of 11 800 and 11 000 g mol^{-1}, respectively, which agreed with the predicted values by the initial monomer-to-initiator ratio (runs 24 and 25). The characteristic proton signals of the allyl and ethynyl groups were observed at 5.91, 5.30-5.15 ppm, and 2.55 ppm respectively, together with those of the acrylate polymer main-chain at 2.60-2.40 ppm, in the ^{1}H NMR spectra, indicating that the polymerization of AlA and PgA proceeded through a controlled/living GTP mechanism in even in the presence of the reactive allyl and ethynyl groups (Figures 3-15 and 3-17). In addition, the GTP of TIPSA proceeded without cleavage of the silyl ester linkage to produce the poly(triisopropylsilyl acrylate) (PTIPSA) with the $M_{n,NMR}$ of 23 520 g mol^{-1} though the polydispersity slightly increased for the M_w/M_n of 1.15 (run 26). PTIPSA was also

deprotected using tetra-*n*-butylammonium fluoride to produce poly(acrylic acid), which could be used as the hydrophilic polymer segment in amphiphilic materials.[8]

For the GTP of the functional acrylates, the GTP characteristics of MEA were similar to those of the primary alkyl acrylate. The GTPs of EEA, TIPS-HEA, AlA, PgA, and TIPSA could be controlled at any initial monomer-to-initiator ratio not more than 100. The amino group containing the acrylate of DMAEA possessed no GTP reactivity. Importantly, AlA, PgA, and TIPSA are new functional monomers applicable for the anionic polymerization method, and their polymers should be expected to serve as precursors for producing various macromolecular architectures.

Table 3-2. Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of MEA, EEA, TIPS-HEA, DMAEA, AlA, PgA, and TIPSA Using MTS^{iPr} as an Initiator [a]

run	monomer (M)	$[M]_0/[MTS^{iPr}]_0$ $/[Me_3SiNTf_2]_0$	time / h	conv / % [b]	$M_{n,calcd.}$ / g mol^{-1} [c]	$M_{n,SEC}$ ($M_{n,NMR}$ [b]) / g mol^{-1} [d]	M_w/M_n [d]
18	MEA	100/1/0.02	1	> 99	13 100	14 400 (13 700)	1.03
19	MEA	400/1/0.02	3	> 99	52 200	58 800	1.03
20	MEA	1000/1/0.05	18	> 99	130 200	140 300	1.05
21	EEA	100/1/0.02	1	> 99	18 900	18 900	1.06
22	TIPS-HEA	100/1/0.02	3	> 99	27 300	21 200 (26 700)	1.02
23	DMAEA	100/1/0.02	20	< 1	-	-	-
24	AlA	100/1/0.02	1	> 99	11 300	11 000 (11 800)	1.04
24	PgA	100/1/0.05	3	> 99	11 100	18 600 (11 000)	1.10
26	TIPSA	100/1/0.02	21	91.5	21 000	10 700 (23 520)	1.15

[a] Argon atmosphere; solvent, toluene; $[M]_0$, 1.0 mol L^{-1}; temperature, room temp. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([M]_0/([MTS^{iPr}]_0)$ × (conv) × (MW of monomer; MEA, 130.14; EEA, 188.22; TIPS-HEA, 272.46; DMAEA, 143.19; AlA, 112.13; PgA, 110.11; TIPSA, 228.40) + (MW of initiator residue, 102.13). [d] Determined by SEC in THF using poly(methyl methacrylate) standard.

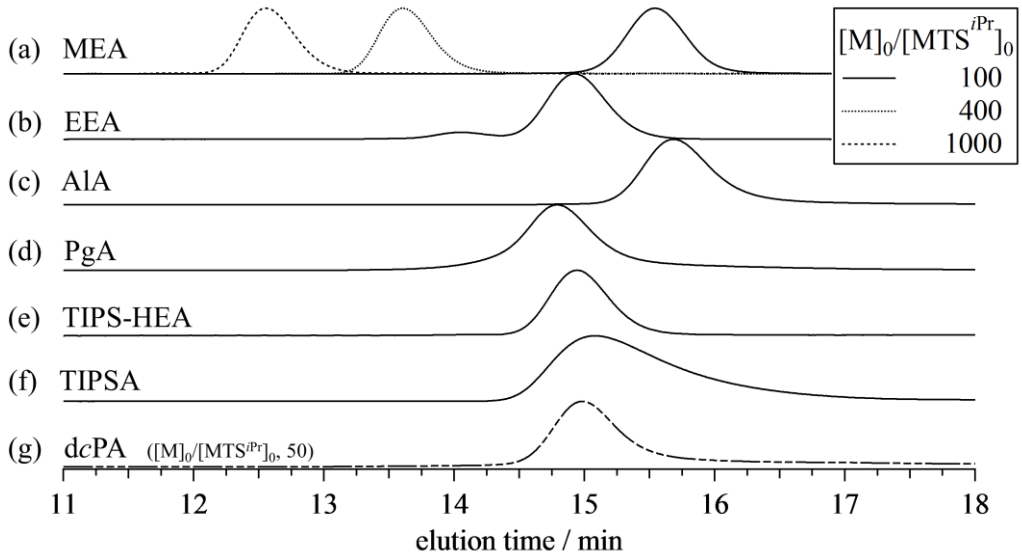


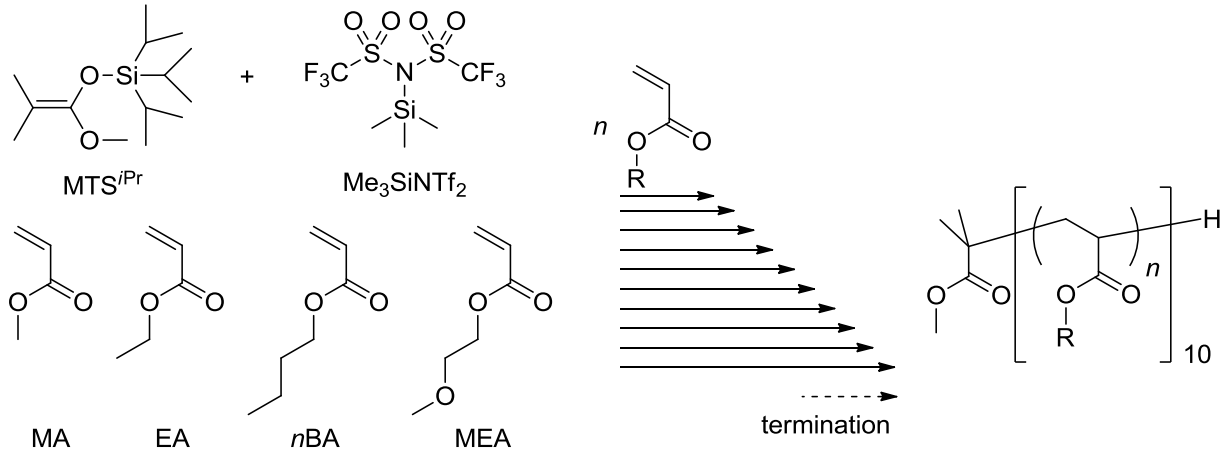
Figure 3-4. SEC traces of the functional acrylate polymers obtained from GTP of (a) MEA, (b) EEA, (c) AlA, (d) PgA, (e) TIPS-HEA, (f) TIPSA, and (G) d*c*PA (eluent, THF; flow rate, 1.0 mL min^{-1}).

3.3.3 Synthesis of Di- and Multiblock Acrylate Polymers.

The Me_3SiNTf_2-catalyzed GTP using the initiator of MTS^{iPr} was an efficient controlled/living system for producing well-defined acrylate homopolymers, which should be applicable to the synthesis of acrylate block polymers. Thus, we first investigated the stability of the propagating chain end of the acrylate polymer by a chain extension experiment. For the postpolymerizations of MA, EA, *n*BA, and MEA, the first GTP was carried out under the conditions for the $[M]_{first}/[MTS^{iPr}]_0$ of 20 and the $[M]_0$ of 1.0 mol L^{-1} in toluene at room temperature, after all the first monomer was consumed, the second GTP was sequentially started by adding the second monomer with $[M]_{second}/[MTS^{iPr}]_0$, and the same procedure was repeated for another eight times (Scheme 3-2). The postpolymerization results for MA, EA, *n*BA, and MEA are listed in Tables 3-3, 3-4, 3-5, and 3-6, respectively. The molecular weight

($M_{n,NMR}$) of the obtained polymers linearly increased with the increasing number of GTPs, as shown in Figure 3-5; from the $M_{n,NMR}$ of 1920 g mol^{-1} for $(PMA)_1$ to the $M_{n,NMR}$ of 17 380 g mol^{-1} for $(PMA)_{10}$, from 2100 g mol^{-1} for $(PEA)_1$ to 20 230 g mol^{-1} for $(PEA)_{10}$, from 2800 g mol^{-1} for (P*n*BA)$_1$ to 26 100 g mol^{-1} for (P*n*BA)$_{10}$, and from 2770 g mol^{-1} for $(PMEA)_1$ to 26760 g mol^{-1} for $(PMEA)_{10}$. All the $M_{n,NMR}$s of the obtained acrylate polymers well agreed with the $M_{n,calcd}$s. In addition, Figure 3-6 shows the monomodal SEC traces of $(PMA)_n$, $(PEA)_n$, (P*n*BA)$_n$, and $(PMEA)_n$, and the molecular weight distributions were as narrow as the M_w/M_ns of 1.02 – 1.10 for $(PMA)_n$, 1.02 – 1.09 for $(PEA)_n$, 1.03 – 1.11 for (P*n*BA)$_n$, and 1.02 – 1.11 for $(PMEA)_n$. In addition, all of the polymerization results were risted in the Tables 3-3, 3-4, 3-5, and 3-6 and Figures 3-7, 3-8, 3-9, and 3-10 of ^{1}H NMR spectra. These results strongly indicated that the propagating chain end should retain the structure of MTS^{iPr} even though the postpolymerizations were carried out nine times, which promises the synthesis of various block acrylate polymers.

Scheme 3-2. Chain Extension Experiments of MA, EA, *n*BA, and MEA by Me_3SiNTf_2-Catalyzed GTP



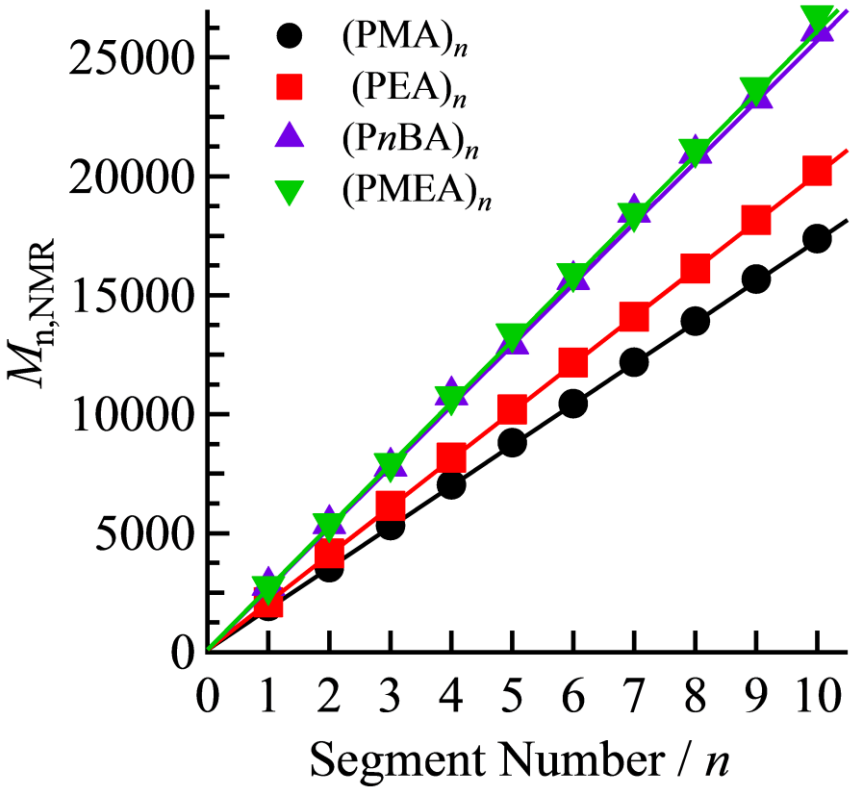


Figure 3-5. Chain extensions of MA, EA, *n*BA, and MEA produced by the sequential GTPs (PMA (●), PEA (■), P*n*BA (▲), and PMEA (▼)).

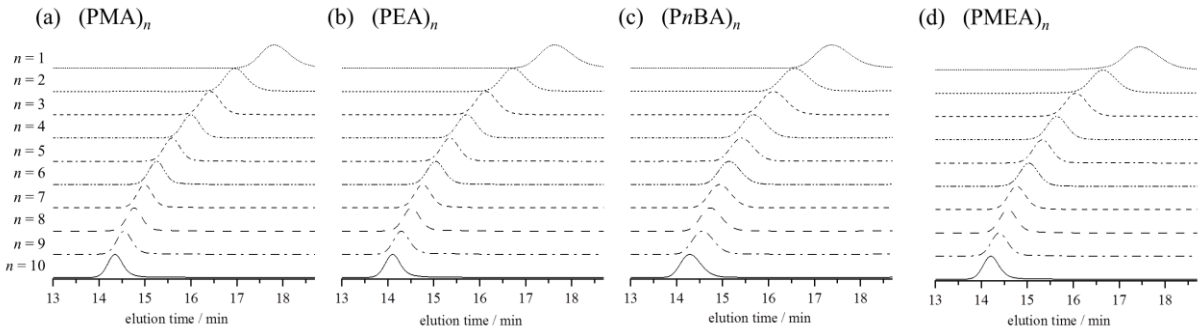


Figure 3-6. SEC traces of (a) $(PMA)_n$, (b) $(PEA)_n$, (c) $(PnBA)_n$, and (d) $(PMEA)_n$ obtained from the sequential GTPs of MA, EA, *n*BA, and MEA (eluent, THF; flow rate, 1.0 mL min^{-1}).

Table 3-3. Sequential Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of MA using MTS^{iPr} [a]

run	PMA	$M_{n,calcd.}$ / g mol^{-1} [b]	$M_{n,NMR}$ / g mol^{-1} [c]	$M_{n,SEC}$ / g mol^{-1} [d]	M_w/M_n [d]
27-1	$(PMA)_1$	1 820	1 920	2 340	1.10
27-2	$(PMA)_2$	3 540	3 550	5 080	1.04
27-3	$(PMA)_3$	5 260	5 320	7 760	1.02
27-4	$(PMA)_4$	6 980	7 030	10 450	1.02
27-5	$(PMA)_5$	8 700	8 800	13 900	1.02
27-6	$(PMA)_6$	10 420	10 440	17 194	1.03
27-7	$(PMA)_7$	12 140	12 180	20 710	1.02
27-8	$(PMA)_8$	13 860	13 920	24 320	1.03
27-9	$(PMA)_9$	15 580	15 680	28 860	1.02
27-10	$(PMA)_{10}$	17 300	17 380	33 370	1.02

[a] Argon atmosphere; solvent, toluene; $[MA]_0$, 1.0 mol L^{-1}; $[MA]_0/[MTS^{iPr}]_0$, 20; $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temp.; polymerization time, 5 min; monomer conversion, > 99%. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([MA]_0/([MTS^{iPr}]_0) \times (conv) \times (MW\ of\ MA, 86.09) + (MW\ of\ initiator\ residue, 102.13)$. [d] Determined by SEC in THF using poly(methyl methacrylate) standards.

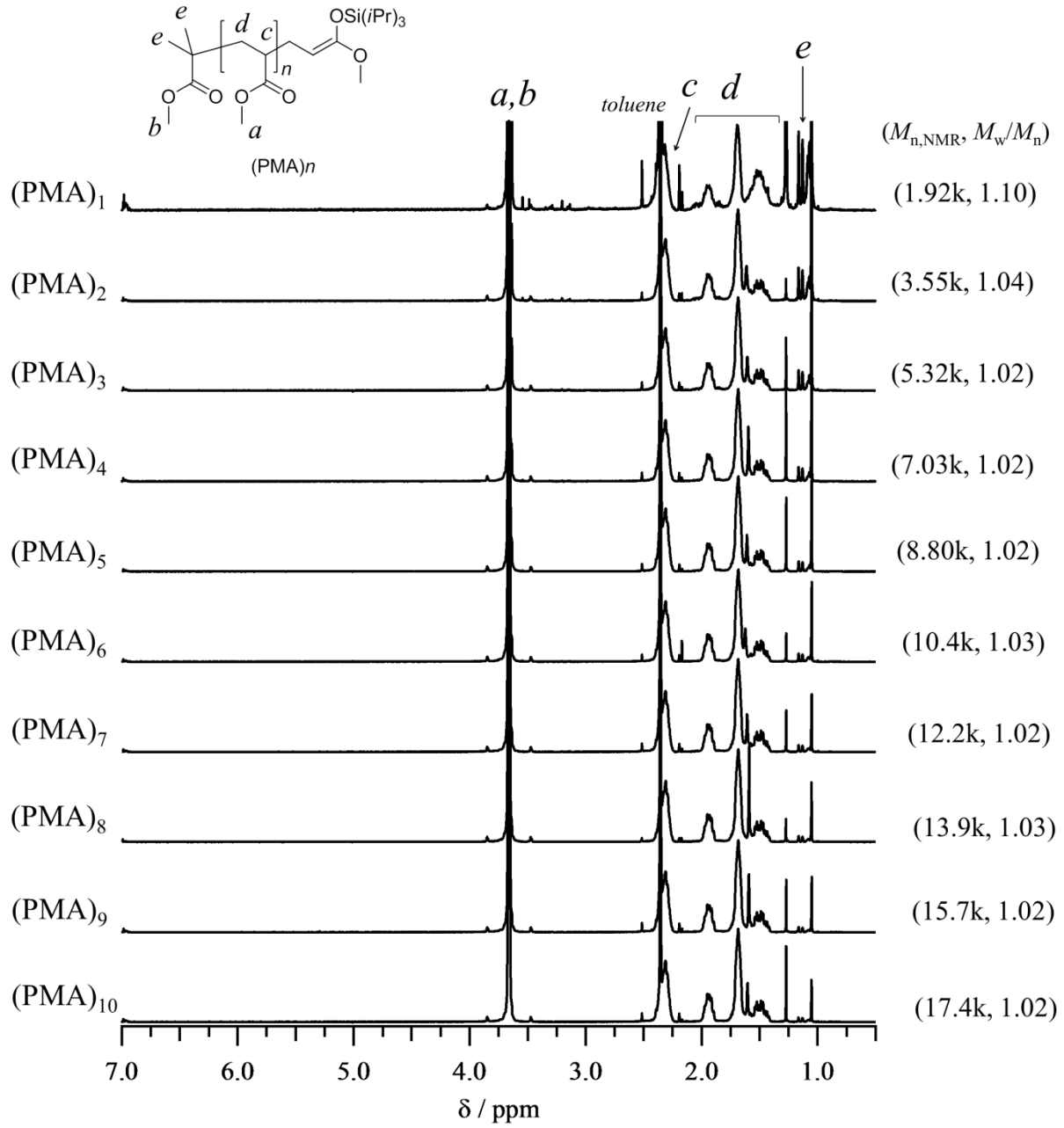


Figure 3-7. ^{1}H NMR spectra of the $(PMA)_n$ obtained from chain extension experiment (solvent, $CDCl_3$).

Table 3-4. Sequential Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of EA using MTS^{iPr} [a]

run	PEA	$M_{n,calcd.}$ / g mol^{-1} [b]	$M_{n,NMR}$ / g mol^{-1} [c]	$M_{n,SEC}$ / g mol^{-1} [d]	M_w/M_n [d]
28-1	$(PEA)_1$	2 100	2 100	2 870	1.09
28-2	$(PEA)_2$	4 100	4 150	6 070	1.04
28-3	$(PEA)_3$	6 100	6 150	9 420	1.03
28-4	$(PEA)_4$	8 100	8 170	12 700	1.02
28-5	$(PEA)_5$	10 100	10 210	16 360	1.02
28-6	$(PEA)_6$	12 100	12 170	20 260	1.02
28-7	$(PEA)_7$	14 100	14 100	24 600	1.02
28-8	$(PEA)_8$	16 100	16 120	29 300	1.03
28-9	$(PEA)_9$	18 100	18 160	34 990	1.02
28-10	$(PEA)_{10}$	20 100	20 230	40 430	1.02

[a] Argon atmosphere; solvent, toluene; $[EA]_0$, 1.0 mol L^{-1}; $[EA]_0/[MTS^{iPr}]_0$, 20; $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temp.; polymerization time, 5 min; monomer conversion, > 99%. [b] Determined by ^1H NMR in $CDCl_3$. [c] Calculated from $([EA]_0/([MTS^{iPr}]_0) \times (conv) \times (MW\ of\ EA, 100.12) + (MW\ of\ initiator\ residue, 102.13)$. [d] Determined by SEC in THF using poly(methyl methacrylate) standards.

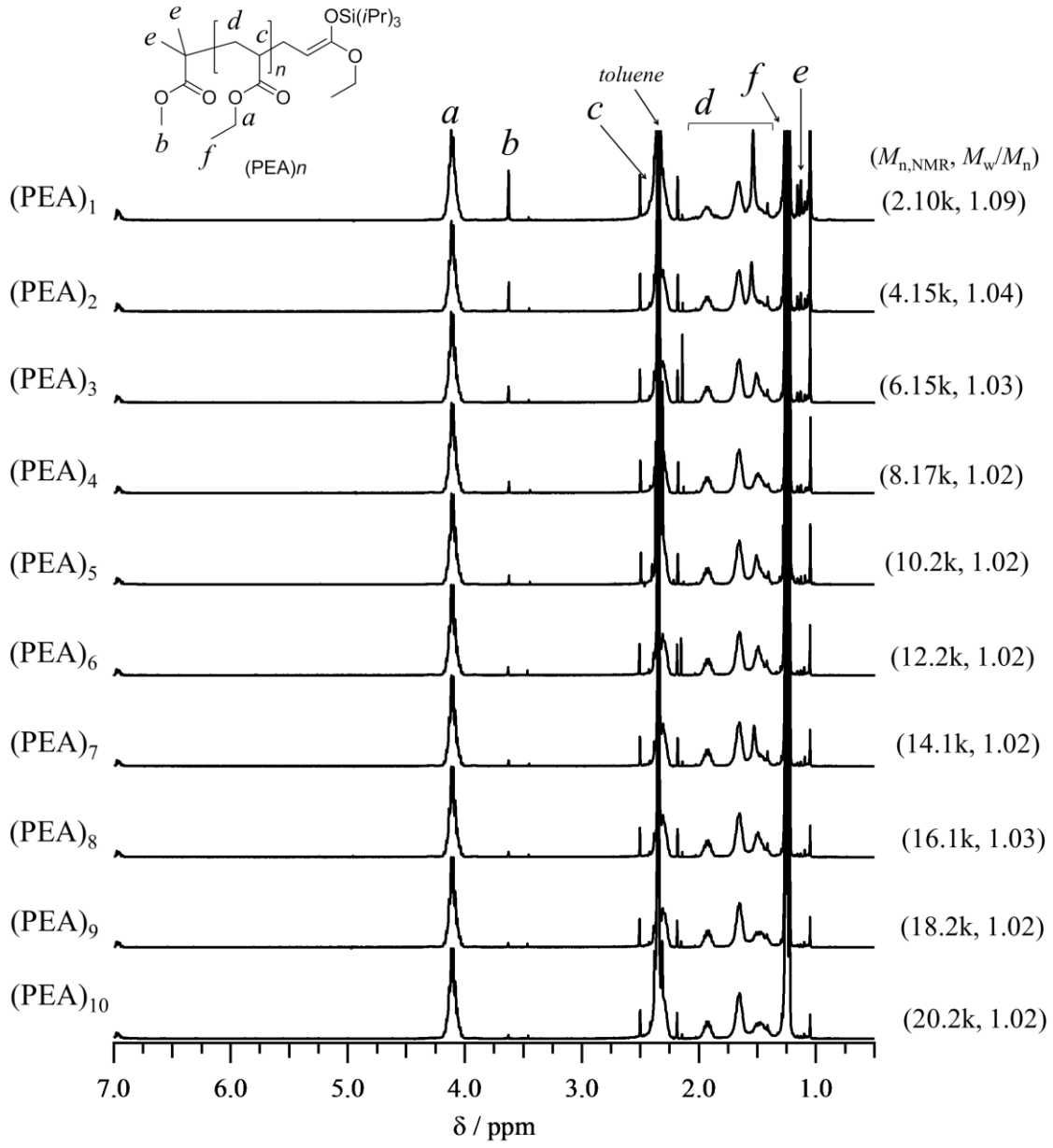


Figure 3-8. ^{1}H NMR spectra of the $(PEA)_n$ obtained from chain extension experiment (solvent, $CDCl_3$).

Table 3-5. Sequential Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of *n*BA using MTS^{iPr} [a]

run	P*n*BA	$M_{n,calcd.}$ / g mol^{-1} [b]	$M_{n,NMR}$ / g mol^{-1} [c]	$M_{n,SEC}$ / g mol^{-1} [d]	M_w/M_n [d]
29-1	$(PnBA)_1$	2 660	2 800	2 760	1.11
29-2	$(PnBA)_2$	5 220	5 400	5 550	1.05
29-3	$(PnBA)_3$	7 780	7 810	7 910	1.04
29-4	$(PnBA)_4$	10 340	10 800	10 720	1.03
29-5	$(PnBA)_5$	12 900	12 940	12 870	1.03
29-6	$(PnBA)_6$	15 460	15 660	15 540	1.03
29-7	$(PnBA)_7$	18 020	18 480	17 970	1.03
29-8	$(PnBA)_8$	20 580	20 970	20 660	1.03
29-9	$(PnBA)_9$	23 140	23 270	23 320	1.03
29-10	$(PnBA)_{10}$	25 700	26 100	28 270	1.04

[a] Argon atmosphere; solvent, toluene; $[n\text{BA}]_0$, 1.0 mol L^{-1}; $[n\text{BA}]_0/[MTS^{iPr}]_0$, 20; $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temp.; polymerization time, 5 min; monomer conversion, > 99%. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([n\text{BA}]_0/([MTS^{iPr}]_0) \times (\text{conv}) \times (\text{MW of } n\text{BA, } 128.17) + (\text{MW of initiator residue, } 102.13)$. [d] Determined by SEC in THF using poly(methyl methacrylate) standards.

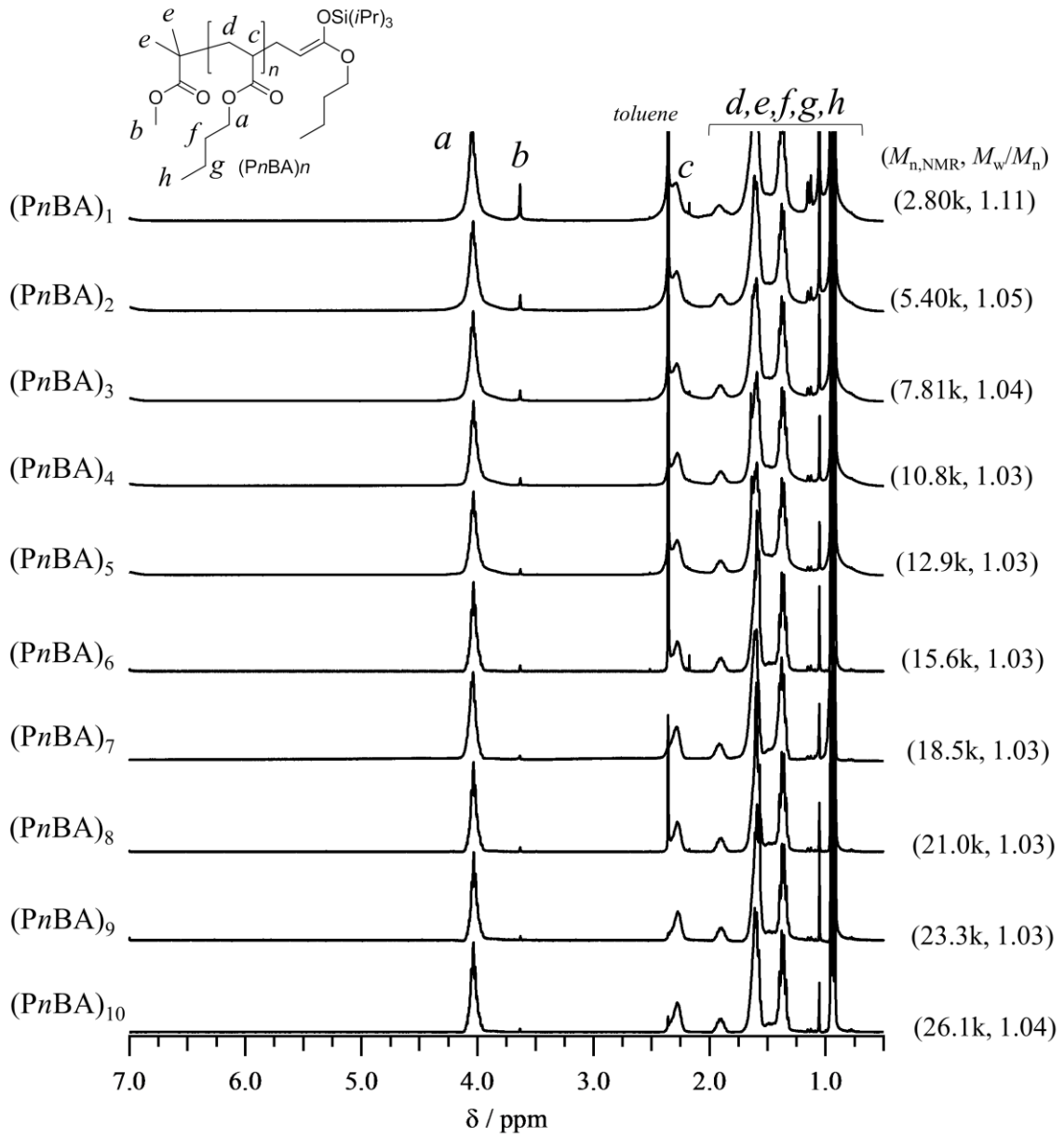


Figure 3-9. ^{1}H NMR spectra of the (P*n*BA)$_n$ obtained from chain extension experiment (solvent, $CDCl_3$).

Table 3-6. Sequential Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of MEA using MTS^{iPr} [a]

run	PMEA	$M_{n,calcd.}$ / g mol^{-1} [b]	$M_{n,NMR}$ / g mol^{-1} [c]	$M_{n,SEC}$ / g mol^{-1} [d]	M_w/M_n [d]
30-1	$(PMEA)_1$	2 700	2 770	3 310	1.11
30-2	$(PMEA)_2$	5 300	5 410	6 190	1.05
30-3	$(PMEA)_3$	7 900	7 930	9 940	1.03
30-4	$(PMEA)_4$	10 500	10 740	13 400	1.02
30-5	$(PMEA)_5$	13 100	13 390	16 580	1.02
30-6	$(PMEA)_6$	15 700	15 920	20 200	1.03
30-7	$(PMEA)_7$	18 300	18 450	24 340	1.02
30-8	$(PMEA)_8$	20 900	21 150	28 090	1.02
30-9	$(PMEA)_9$	23 500	23 730	32 440	1.02
30-10	$(PMEA)_{10}$	26 100	26 760	36 830	1.03

[a] Argon atmosphere; solvent, toluene; $[MEA]_0$, 1.0 mol L^{-1}; $[MEA]_0/[MTS^{iPr}]_0$, 20; $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temp.; polymerization time, 5 min; monomer conversion, > 99%. [b] Determined by ^1H NMR in $CDCl_3$. [c] Calculated from $([MEA]_0/([MTS^{iPr}]_0) \times (conv) \times (MW\ of\ MEA, 130.14) + (MW\ of\ initiator\ residue, 102.13)$. [d] Determined by SEC in THF using poly(methyl methacrylate) standards.

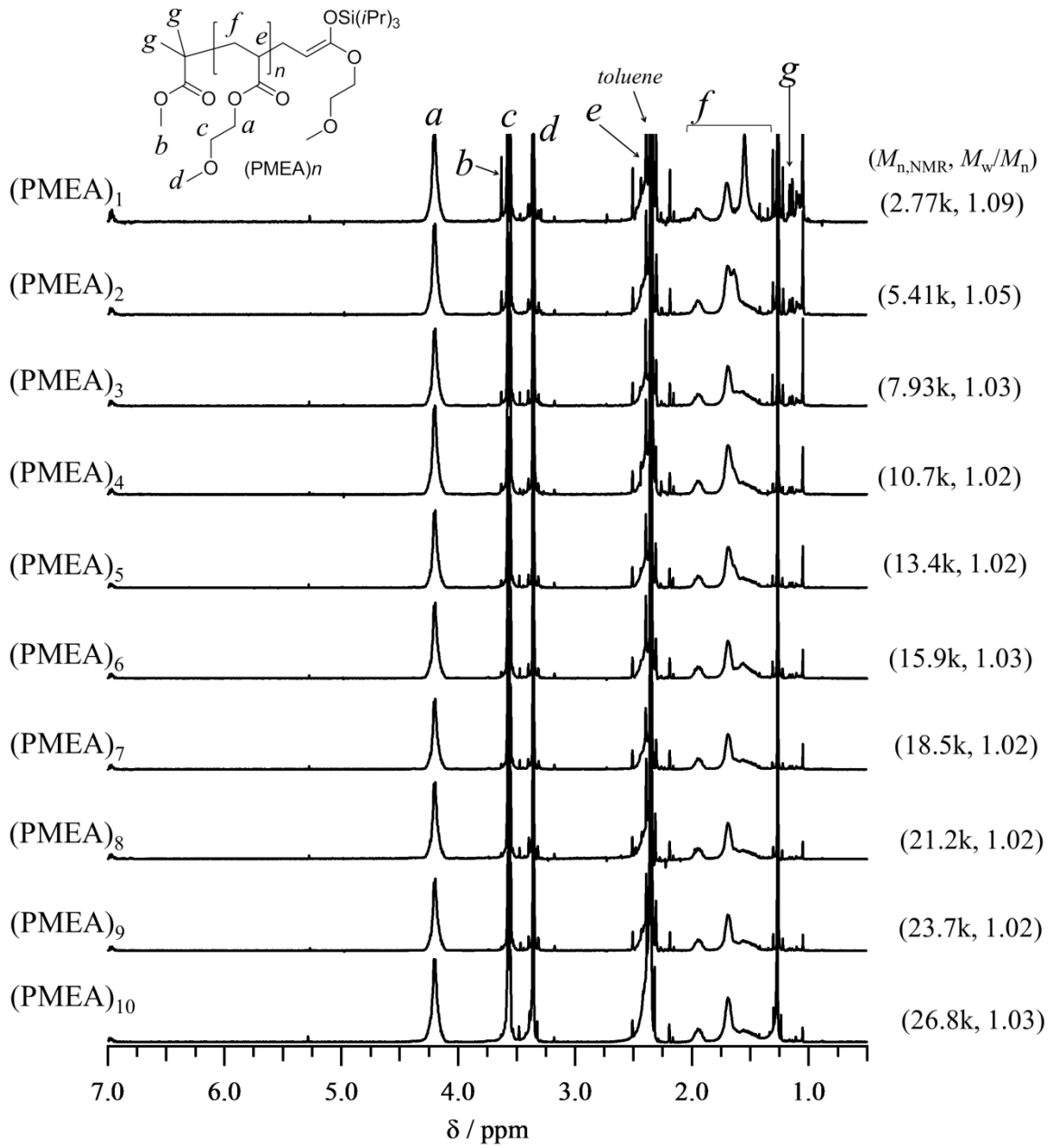


Figure 3-10. ^{1}H NMR spectra of the $(PMEA)_n$ obtained from chain extension experiment (solvent, $CDCl_3$).

For the synthesis of block acrylate polymers, the author synthesized the AB and BA diblock copolymers using the alkyl acrylate of *n*BA and the functional acrylates of MEA, AlA, and PgA. Table 3-7 summarizes the results of the block copolymerization under the condition of the ($[M_{first}+M_{second}]_0/[MTS^{iPr}]_0/[Me_3SiNTf_2]_0$, of 25+25/1/0.02 and the $[M]_0$ of 1.0 mol L^{-1} in toluene at room temperature. In the case of *n*BA with MEA, MEA was added as the second monomer to the reaction mixture after the first GTP of *n*BA was completed. The product of the first GTP showed a monomodal molecular weight distribution in the SEC trace, which shifted to a higher molecular weight region in the SEC trace of the product of the second GTP, while keeping a narrow polydispersity, as shown in Figure 3-11(a). The $M_{n,NMR}$ increased from 3360 to 6640 g mol^{-1} and the M_w/M_ns decreased from 1.09 to 1.04 after the block copolymerization. The structure of P*n*BA-*b*-PMEA was confirmed by a ^{1}H NMR measurement (Figure 3-12). Alternatively, MEA was first polymerized to form the PMEA with the $M_{n,NMR}$ of 3480 g mol^{-1}, and *n*BA was then subsequently polymerized to produce the PMEA-*b*-P*n*BA with the $M_{n,NMR}$ of 6860 g mol^{-1} and the M_w/M_n of 1.05 (Figure 3-13). For the block copolymerization of *n*BA with AlA, the P*n*BA-*b*-PAlA and PAlA-*b*-P*n*BA diblock copolymers had the well-controlled $M_{n,NMR}$s of 6240 and 6580 g mol^{-1}, respectively (Figures 3-14, 3-15,3-16, and 3-17). The M_w/M_n of P*n*BA-*b*-PAlA was as low as 1.07, while that of PAlA-*b*-P*n*BA was relatively high at 1.13 due to a small peak observed in the low molecular weight region of the SEC trace (Figure 3-11b). This small peak was attributed to the unreacted PAlA, meaning that the second GTP of *n*BA initiated by the propagating PAlA chain end was slightly insufficient. The block copolymerization of *n*BA and PgA produced the structurally-defect-free P*n*BA-*b*-PPgA with the $M_{n,NMR}$ and M_w/M_n of 6320 g mol^{-1} and 1.07, and the PPgA-*b*-P*n*BA with value of 6120 and 1.05, respectively. These results indicated that amphiphilic and reactive di- and multiblock acrylate copolymers can be

synthesized using the Me_3SiNTf_2-catalyzed GTP by the appropriate combinations of acrylate monomers.

Table 3-7. Synthesis of P*n*BA-*b*-PMEA, P*n*BA-*b*-PAlA, P*n*BA-*b*-PPgA, and *vice versa* by Sequential Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of *n*BA, MEA, AlA, and PgA Using MTS^{iPr} [a]

run	block copolymer	monomer		$M_{n,calcd.}$ / g mol^{-1} [c]	$M_{n,NMR}$ / g mol^{-1} [c]	M_w/M_n [d]
31	P*n*BA-*b*-PMEA	first	*n*BA	3 310	3 360	1.09
		second	MEA	6 560	6 640	1.04
32	PMEA-*b*-P*n*BA	first	MEA	3 360	3 480	1.13
		second	*n*BA	6 560	6 860	1.05
33	P*n*BA-*b*-PAlA	first	*n*BA	3 310	3 380	1.08
		second	AlA	6 110	6 240	1.07
34	PAlA-*b*-P*n*BA	first	AlA	2 910	3 360	1.09
		second	*n*BA	6 110	6 580	1.13
35	P*n*BA-*b*-PPgA	first	*n*BA	3 310	3 370	1.10
		second	PgA	6 060	6 320	1.07
36	PPgA-*b*-P*n*BA	first	PgA	2 850	2 910	1.07
		second	*n*BA	6 060	6 120	1.05

[a] Argon atmosphere; solvent, toluene; $[M]_0$, 1.0 mol L^{-1}; $[M]_0/[MTS^{iPr}]_0$, 25, $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temp.; polymerization time, 5 min.; monomer conversion, > 99%. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([M]_0/([MTS^{iPr}]_0) \times$ (conv) × (MW of monomer; *n*BA, 128.17; MEA, 130.14; AlA, 112.13; PgA, 110.11) + (MW of initiator residue, 102.13). [d] Determined by SEC in THF using poly(methyl methacrylate) standards.

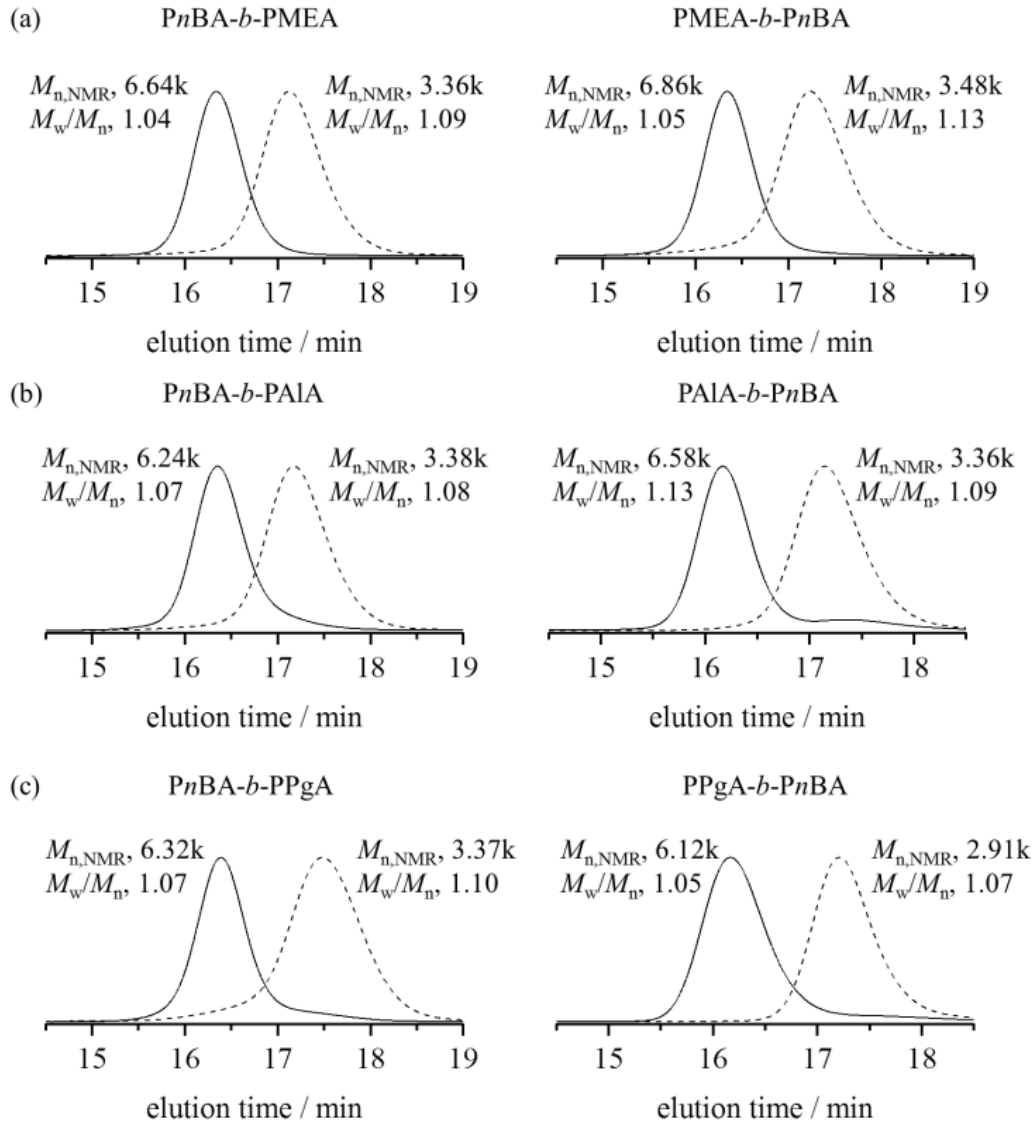


Figure 3-11. SEC traces of the diblock copolymers of (a) *n*BA and MEA, (b) *n*BA and AlA, and (c) *n*BA and PgA ($[M_{first} + M_{second}]_0/[MTS^{iPr}]_0/[Me_3SiNTf_2]_0$, 25+25/1/0.02; $[M]_0$, 1.0 mol L^{-1}) (dashed line, first polymer; solid line, block copolymer; eluent, THF; flow rate, 1.0 mL min^{-1}).

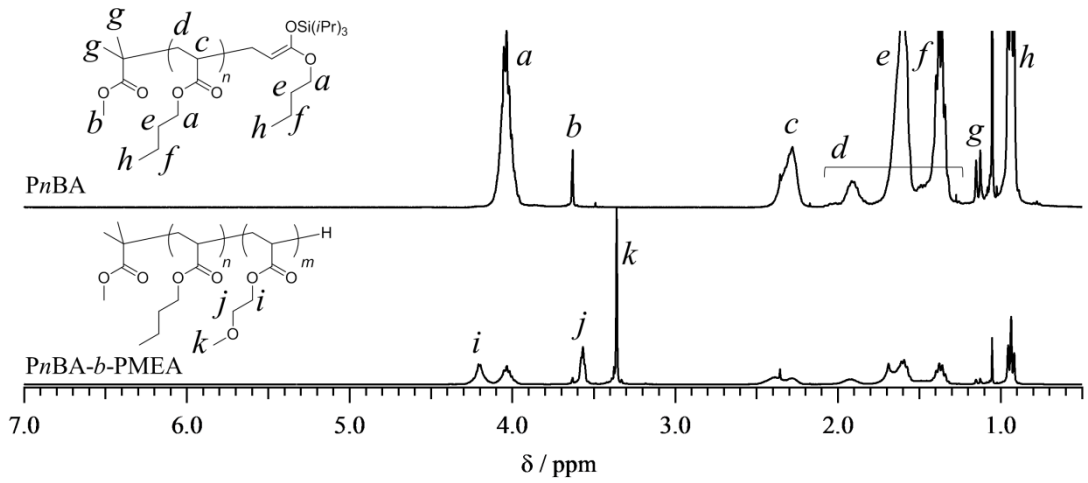


Figure 3-12. ^{1}H NMR spectrum of the block copolymers obtained from sequential GTP of *n*BA and MEA in $CDCl_3$.

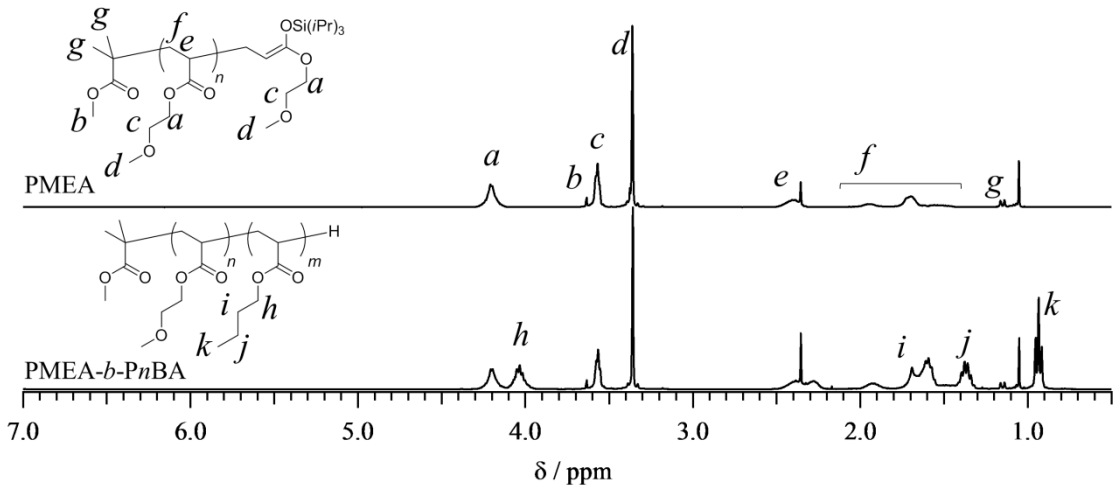


Figure 3-13. ^{1}H NMR spectrum of the block copolymers obtained from sequential GTP of MEA and *n*BA in $CDCl_3$.

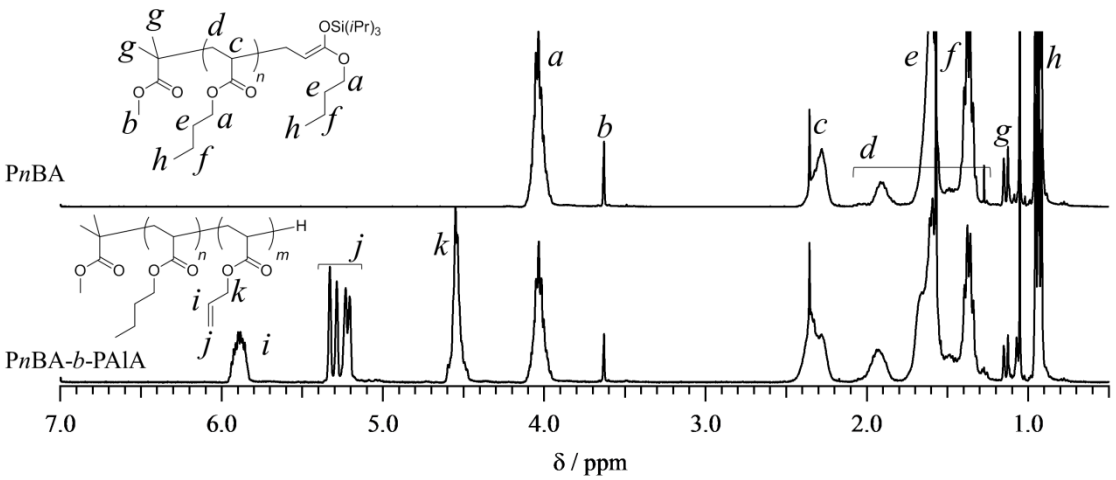


Figure 3-14. ^{1}H NMR spectrum of the block copolymers obtained from sequential GTP of *n*BA and AlA in $CDCl_3$.

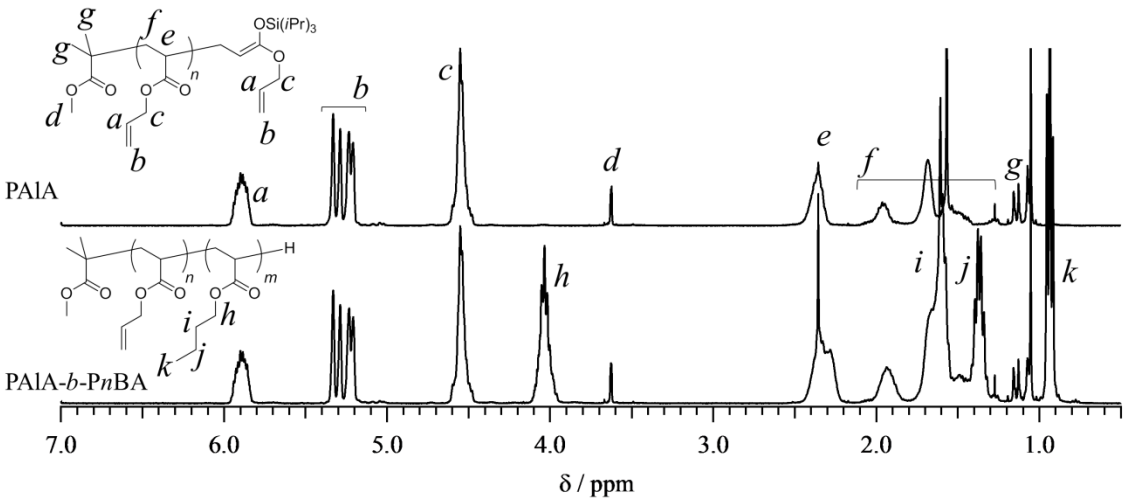


Figure 3-15. ^{1}H NMR spectrum of the block copolymers obtained from sequential GTP of AlA and *n*BA in $CDCl_3$.

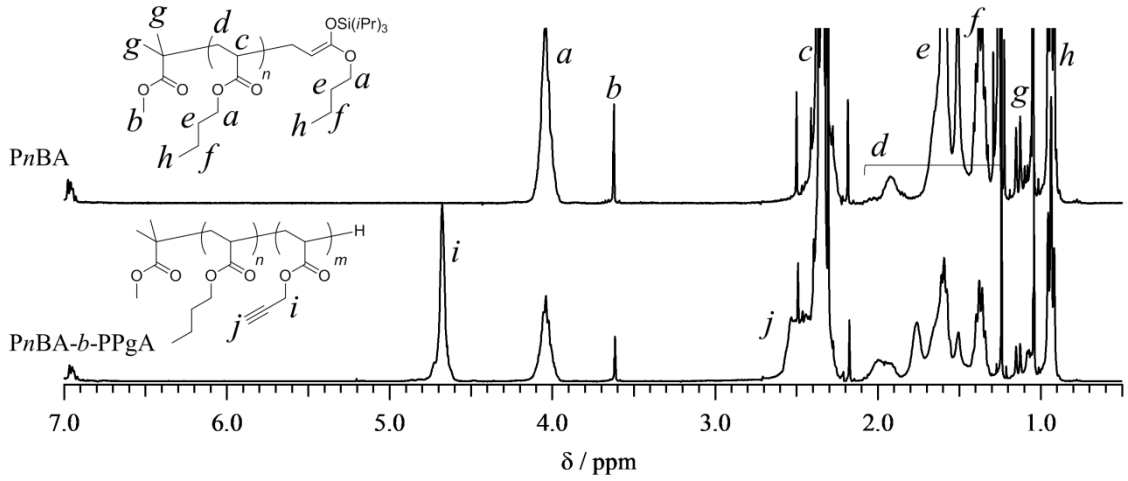


Figure 3-16. ^{1}H NMR spectrum of the block copolymers obtained from sequential GTP of *n*BA and PgA in $CDCl_3$.

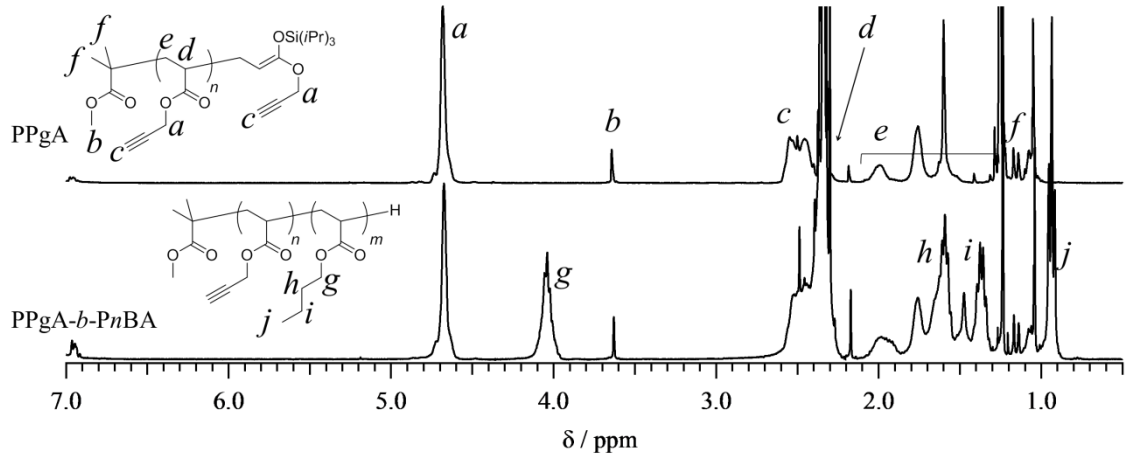


Figure 3-17. ^{1}H NMR spectrum of the block copolymers obtained from sequential GTP of PgA and *n*BA in $CDCl_3$.

Finally, multiblock acrylate polymers were synthesized by the sequential Me_3SiNTf_2-catalyzed GTP using various acrylate monomers, as shown in Scheme 3-3. The synthetic result of the (PEHA-*b*-P*n*BA-*b*-PEA)$_4$ dodecablock terpolymer is listed in Table 3-8. Each GTP was carried out under the condition of the $[M]_0/[MTS^{iPr}]_0$ of 10 and the $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$ of 0.02. The first series of the sequential GTPs of EHA, *n*BA, and EA produced the PEHA with the $M_{n,NMR}$ of 1980 g mol^{-1}, the PEHA-*b*-P*n*BA diblock copolymer with 3350 g mol^{-1}, and the PEHA-*b*-P*n*BA-*b*-PEA triblock terpolymer with 4390 g mol^{-1}, which agreed with the $M_{n,calcd.}$s of 1940, 3220, and 4220 g mol^{-1}, respectively. The SEC traces of the homo, diblock, and triblock polymers were monomodal and the molecular weight distribution (M_w/M_n) decreased from 1.11 to 1.07, as shown in Figure 3-18(a). This procedure was repeated three more times. The SEC traces of the multiblock polymers shifted to a higher molecular weight region with the increasing number of sequential GTPs. Similarly, the (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$ dodecablock quaterpolymer was synthesized by the sequential Me_3SiNTf_2-catalyzed GTP of *n*BA, EA, MEA, and MA. Table 3-9 summarizes the results of the sequential GTPs. With the increasing number of sequential GTPs, the $M_{n,NMR}$ of the multiblock polymers theoretically increased and their SEC traces shifted to the higher molecular weight region while maintaining a monomodal and narrow distribution (Figure 3-18(b)). For the synthesis of the Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA hexablock sestopolymer, the sequential Me_3SiNTf_2-catalyzed GTP of d*c*PA, *n*BA, EHA, EA, MA, and *c*HA produced the homo-, co-, ter-, quarter-, quinto-, and sestopolymers with predictable $M_{n,NMR}$s and narrow M_w/M_ns (Table 3-10). Figure 3-21 shows the ^{1}H NMR spectra of the homo-, co-, ter-, quarter-, quinto-, and sestopolymers in the polymerization mixtures after all the monomers were consumed. The characteristic signal *a* observed at 4.55 ppm was attributed to the methyne proton of the d*c*PA unit and that at 3.63 ppm to the

methoxy proton *b* of the initiator residue (Figure 7(a)), that at 4.04 ppm to the methylene proton *c* of the *n*BA unit (Figure 3-21(b)), that at 3.96 ppm to the methylene proton *d* of the EHA unit (Figure 3-21(c)), that at 4.09 ppm to the methylene proton *e* of the EA unit (Figure 3-21(d)), that at 3.64 ppm to the methoxy proton *f* of the MA unit (Figure 3-21(e)), and that at 4.73 ppm to the methyne proton *g* of the *c*HA unit (Figure 3-21(f)). Similarly, the syntheses of (PEHA-*b*-P*n*BA-*b*-PEA)$_4$ and (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$ were also confirmed by the same method (Figures 3-19 and 3-20), and the structures of the multiblock polymers were assigned as the final products by the ^{1}H NMR spectra (Figures 3-22, 3-23, and 3-24). Finally, the authir obtained the (PEHA-*b*-P*n*BA-*b*-PEA)$_4$ dodecablock terpolymer with the $M_{n,NMR}$ of 16 890 g mol^{-1} and the M_w/M_n of 1.03, the (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$ dodecablock quaterpolymer with the $M_{n,NMR}$ of 13 520 g mol^{-1} and the M_w/M_n of 1.02, and the Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA hexablock sestopolymer with the $M_{n,NMR}$ of 9240 g mol^{-1} and the M_w/M_n of 1.05 (Table 3-11). These results clearly indicated that the sequential GTP was an efficient method for the syntheses of the well-defined multiblock acrylate polymers.

Scheme 3-3. Synthesis of (PEHA-*b*-P*n*BA-*b*-PEA)$_4$ Dodecablock Terpolymer, (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$ Dodecablock Quaterpolymer, and Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA Hexablock Sestopolymer, as (ABC)$_4$, (ABCD)$_3$, and ABCDEF Block Polymers by Sequential Group Transfer Polymerization

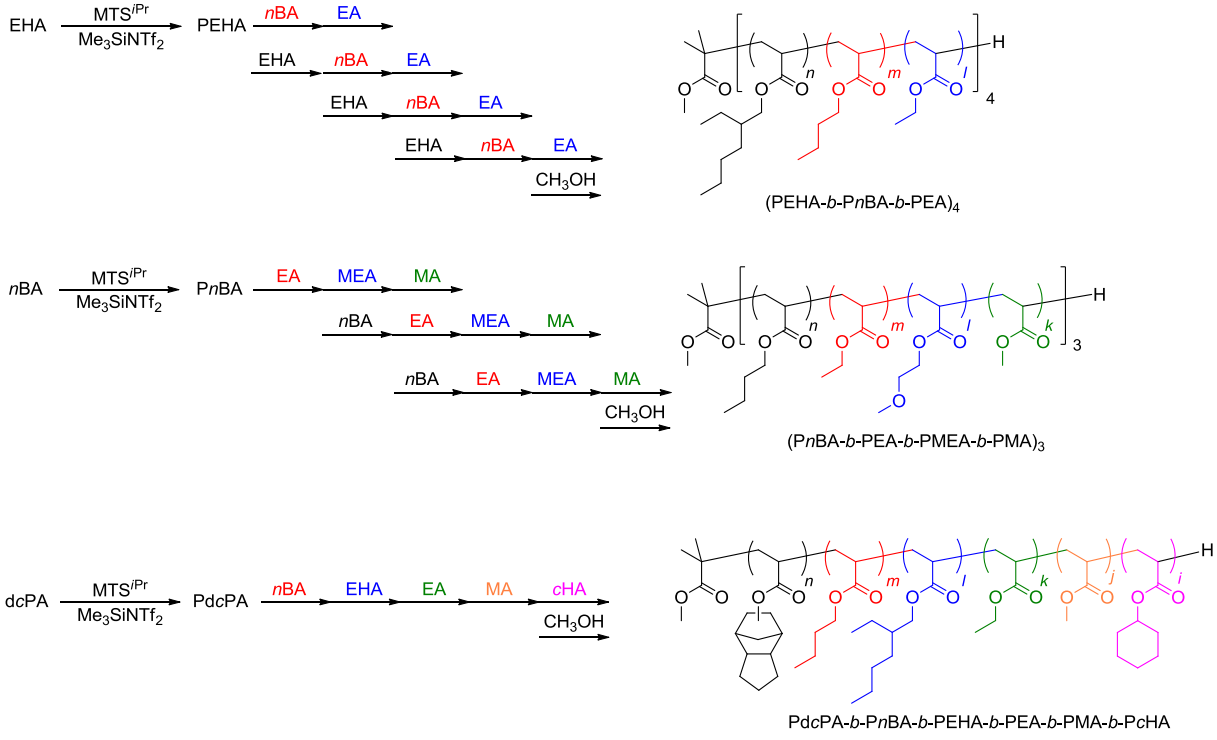


Table 3-8. Synthesis of (PEHA-*b*-P*n*BA-*b*-PEA)$_4$ Dodecablock Terpolymer by Sequential Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of EHA, *n*BA, and EA using MTS^{iPr} [a]

run	block polymer	monomer (M)	$M_{n,calcd.}$ / g mol^{-1} [c]	$M_{n,NMR}$ /g mol^{-1} [c]	M_w/M_n [d]
37-1	PEHA	EHA	1 940	1 980	1.11
37-2	PEHA-*b*-P*n*BA	*n*BA	3 220	3 350	1.09
37-3	PEHA-*b*-P*n*BA-*b*-PEA	EA	4 220	4 390	1.07
37-4	PEHA-*b*-P*n*BA-*b*-PEA-*b*-PEHA	EHA	6 060	6 270	1.04
37-5	PEHA-*b*-P*n*BA-*b*-PEA-*b*-PEHA-*b*-P*n*BA	*n*BA	7 340	7 570	1.04
37-6	(PEHA-*b*-P*n*BA-*b*-PEA)$_2$	EA	8 340	8 590	1.03
37-7	(PEHA-*b*-P*n*BA-*b*-PEA)$_2$-*b*-PEHA	EHA	10 180	10 480	1.03
37-8	(PEHA-*b*-P*n*BA-*b*-PEA)$_2$-*b*-PEHA-*b*-P*n*BA	*n*BA	11 460	11 770	1.03
37-9	(PEHA-*b*-P*n*BA-*b*-PEA)$_3$	EA	12 460	12 720	1.03
37-10	(PEHA-*b*-P*n*BA-*b*-PEA)$_3$-*b*-PEHA	EHA	14 300	14 580	1.03
37-11	(PEHA-*b*-P*n*BA-*b*-PEA)$_3$-*b*-PEHA-*b*-P*n*BA	*n*BA	15 580	15 870	1.02
37-12	(PEHA-*b*-P*n*BA-*b*-PEA)$_4$	EA	16 580	16 890	1.03

[a] Argon atmosphere; solvent, toluene; $[M]_0$, 1.0 mol L^{-1}; $[M]_0/[MTS^{iPr}]_0$, 10, $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temp.; polymerization time, 5 min.; monomer conversion, > 99%. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([M]_0/([MTS^{iPr}]_0) \times (conv) \times (MW\ of\ monomer;\ EHA,\ 184.28;\ nBA,\ 128.17;\ EA,\ 100.12) + (MW\ of\ initiator\ residue,\ 102.13)$. [d] Determined by SEC in THF using poly(methyl methacrylate) standards.

Table 3-9. Synthesis of (P*n*BA-*b*-PEA-*b*-PMEA-PMA)$_3$ Dodecablock Terpolymer by Sequential Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of *n*BA, EA, MEA, and MA Using MTS^{iPr} [a]

run	block polymer	monomer (M)	$M_{n,calcd.}$ /g mol^{-1} [c]	$M_{n,NMR}$ /g mol^{-1} [c]	M_w/M_n [d]
38-1	P*n*BA	*n*BA	1 380	1 390	1.21
38-2	P*n*BA-*b*-PEA	EA	2 380	2 390	1.11
38-3	P*n*BA-*b*-PEA-*b*-PMEA	MEA	3 680	3 720	1.06
38-4	P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA	MA	4 540	4 550	1.04
38-5	P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA-*b*-P*n*BA	*n*BA	5 820	5 930	1.03
38-6	P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA-*b*-P*n*BA-*b*-PEA	EA	6 820	6 830	1.03
38-7	P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA-*b*-P*n*BA-*b*-PEA-*b*-PMEA	MEA	8 120	8 130	1.02
38-8	(P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_2$	MA	8 980	9 000	1.02
38-9	(P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_2$-*b*-P*n*BA	*n*BA	10 260	10 280	1.02
38-10	(P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_2$-*b*-P*n*BA-*b*-PEA	EA	11 260	11 300	1.02
38-11	(P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_2$-*b*-P*n*BA-*b*-PEA-*b*-PMEA	MEA	12 560	12 580	1.02
38-12	(P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$	MA	13 420	13 520	1.02

[a] Argon atmosphere; solvent, toluene; $[M]_0$, 1.0 mol L^{-1}; $[M]_0/[MTS^{iPr}]_0$, 10, $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temp.; polymerization time, 5 min.; monomer conversion, > 99%. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([M]_0/([MTS^{iPr}]_0) \times (conv) \times$ (MW of monomer; *n*BA, 128.17; EA, 100.12; MEA, 130.14; MA, 86.09) + (MW of initiator residue, 102.13). [d] Determined by SEC in THF using poly(methyl methacrylate) standards.

Table 3-10. Synthesis of Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA Hexablock Sestopolymer by Sequential Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of d*c*PA, *n*BA, EHA, EA, MA, and *c*HA using MTS^{iPr} [a]

run	block polymer	monomer (M)	$M_{n,calcd.}$ / g mol^{-1} [c]	$M_{n,NMR}$ / g mol^{-1} [b]	M_w/M_n [d]
39-1	Pd*c*PA	d*c*PA	2 160	2 200	1.25
39-2	Pd*c*PA-*b*-P*n*BA	*n*BA	3 440	3 560	1.12
39-3	Pd*c*PA-*b*-P*n*BA-*b*-PEHA	EHA	5 280	5 630	1.06
39-4	Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA	EA	6 140	6 650	1.05
39-5	Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA	MA	7 140	7 550	1.04
39-6	Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA	*c*HA	8 680	9 240	1.05

[a] Argon atmosphere; solvent, toluene; $[M]_0$, 1.0 mol L^{-1}; $[M]_0/[MTS^{iPr}]_0$, 10; $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temp.; polymerization time, 5 min; monomer conversion, > 99%. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([M]_0/([MTS^{iPr}]_0) \times (conv) \times$ (MW of monomer; d*c*PA, 206.29; *n*BA, 128.17;EHA, 184.28; EA, 100.12; MA, 86.09; *c*HA, 154.21) + (MW of initiator residue, 102.13). [d] Determined by SEC in THF using poly(methyl methacrylate) standards

Table 3-11. Synthesis of (PEHA-*b*-P*n*BA-*b*-PEA)$_4$ Dodecablock Terpolymer, (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$ Dodecablock Quaterpolymer, and Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA Hexablock Sestopolymer by Sequential Me_3SiNTf_2-Catalyzed Group Transfer Polymerization of EHA, *n*BA, EA, MEA, MA, d*c*PA, and *c*HA [a]

run	block polymer	$M_{n,calcd.}$ / g mol^{-1} [c]	$M_{n,NMR}$ / g mol^{-1} [b]	M_w/M_n [d]
37-12	(PEHA-*b*-P*n*BA-*b*-PEA)$_4$	16 580	16 890	1.03
38-12	(P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$	13 420	13 520	1.02
39-6	Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA	8 680	9 240	1.05

[a] Argon atmosphere; solvent, toluene; initiator, MTS^{iPr}; $[M]_0$, 1.0 mol L^{-1}; $[M]_0/[MTS^{iPr}]_0$, 10; $[Me_3SiNTf_2]_0/[MTS^{iPr}]_0$, 0.02; temperature, room temp.; polymerization time, 5 min; monomer conversion, > 99%. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([M]_0/([MTS^{iPr}]_0)$ × (conv) × (MW of monomer; d*c*PA, 206.29; *n*BA, 128.17;EHA, 184.28; EA, 100.12; MA, 86.09; *c*HA, 154.21; MEA, 130.14) + (MW of initiator residue, 102.13). [d] Determined by SEC in THF using poly(methyl methacrylate) standards.

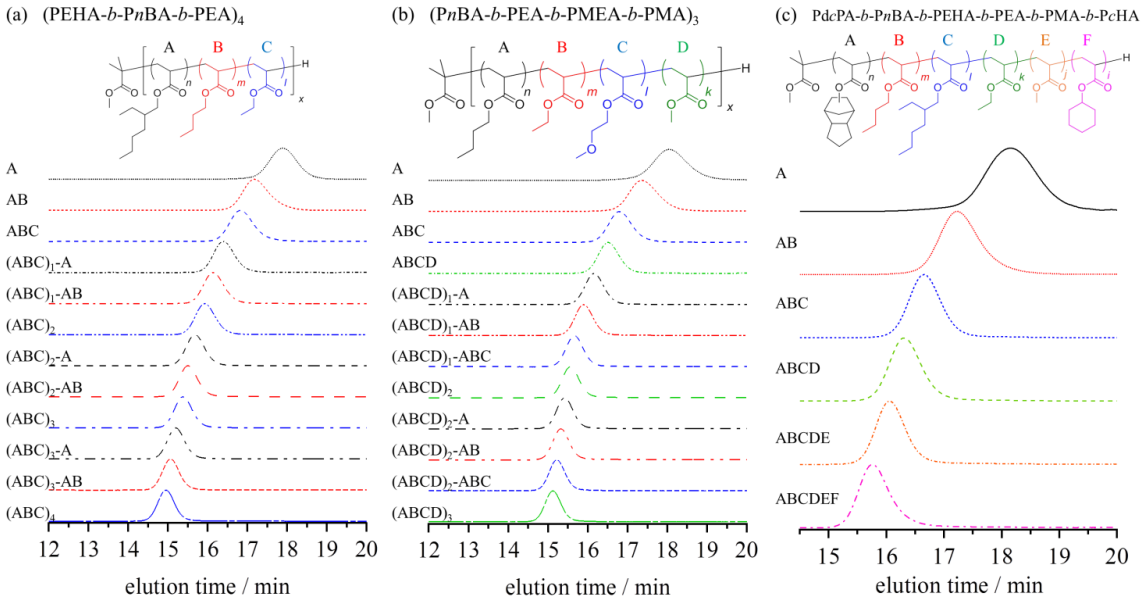


Figure 3-18. SEC traces for the synthesis of (a) (PEHA-*b*-P*n*BA-*b*-PEA)$_4$ dodecablock terpolymer, (b) (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$ dodecablock quaterpolymer, and (c) Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA hexablock sestopolymer (eluent, THF; flow rate, 1.0 mL min^{-1}).

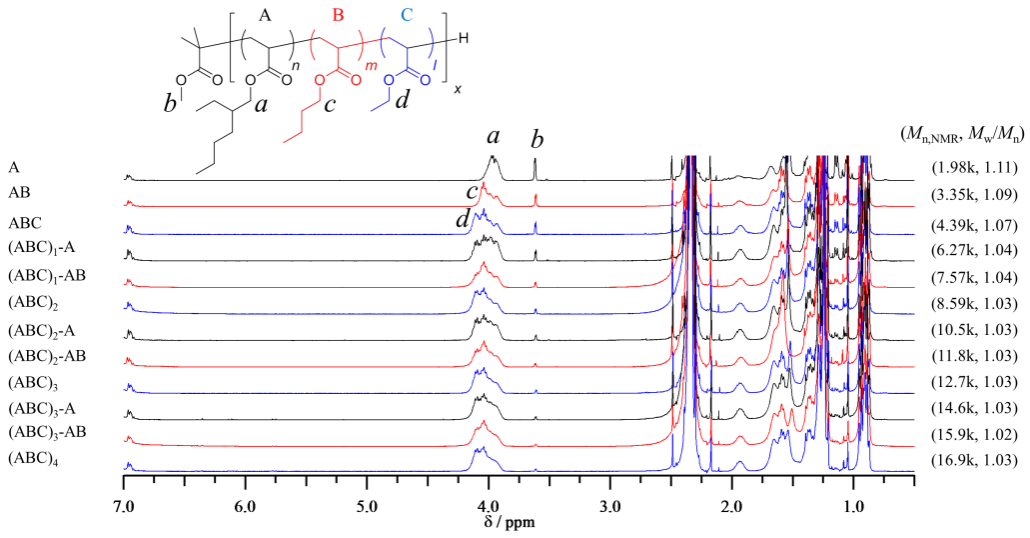


Figure 3-19. ^{1}H NMR spectra of the (PEHA-*b*-P*n*BA-*b*-PEA)$_4$-block terpolymers obtained from chain extension experiment of EHA (A), *n*BA (B), and EA (C) (solvent, $CDCl_3$).

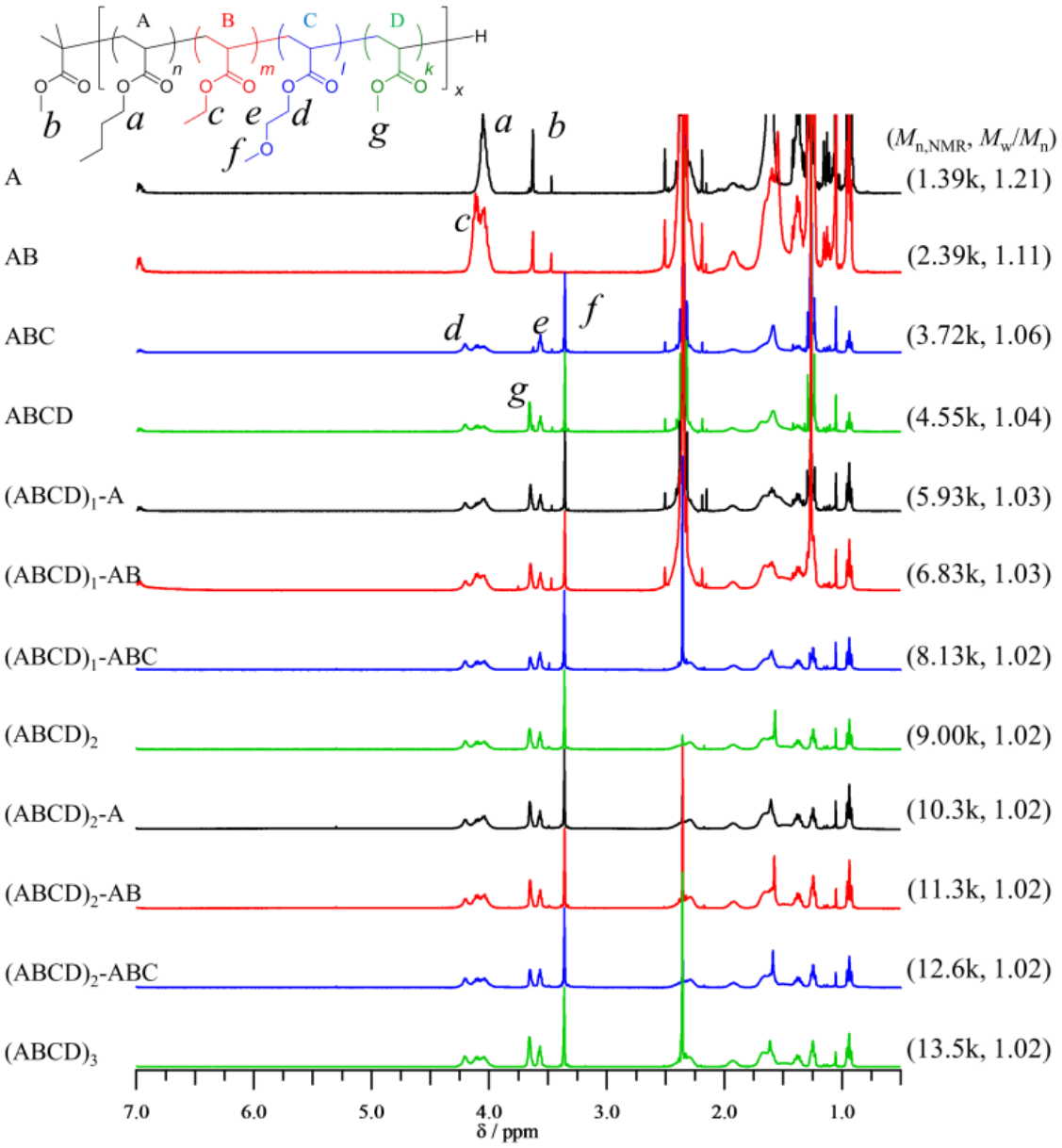


Figure 3-20. ^{1}H NMR spectra of the (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$-block quaterpolymers obtained from chain extension experiment of *n*BA (A), EA (B), MEA (C), and MA (D) (solvent, $CDCl_3$).

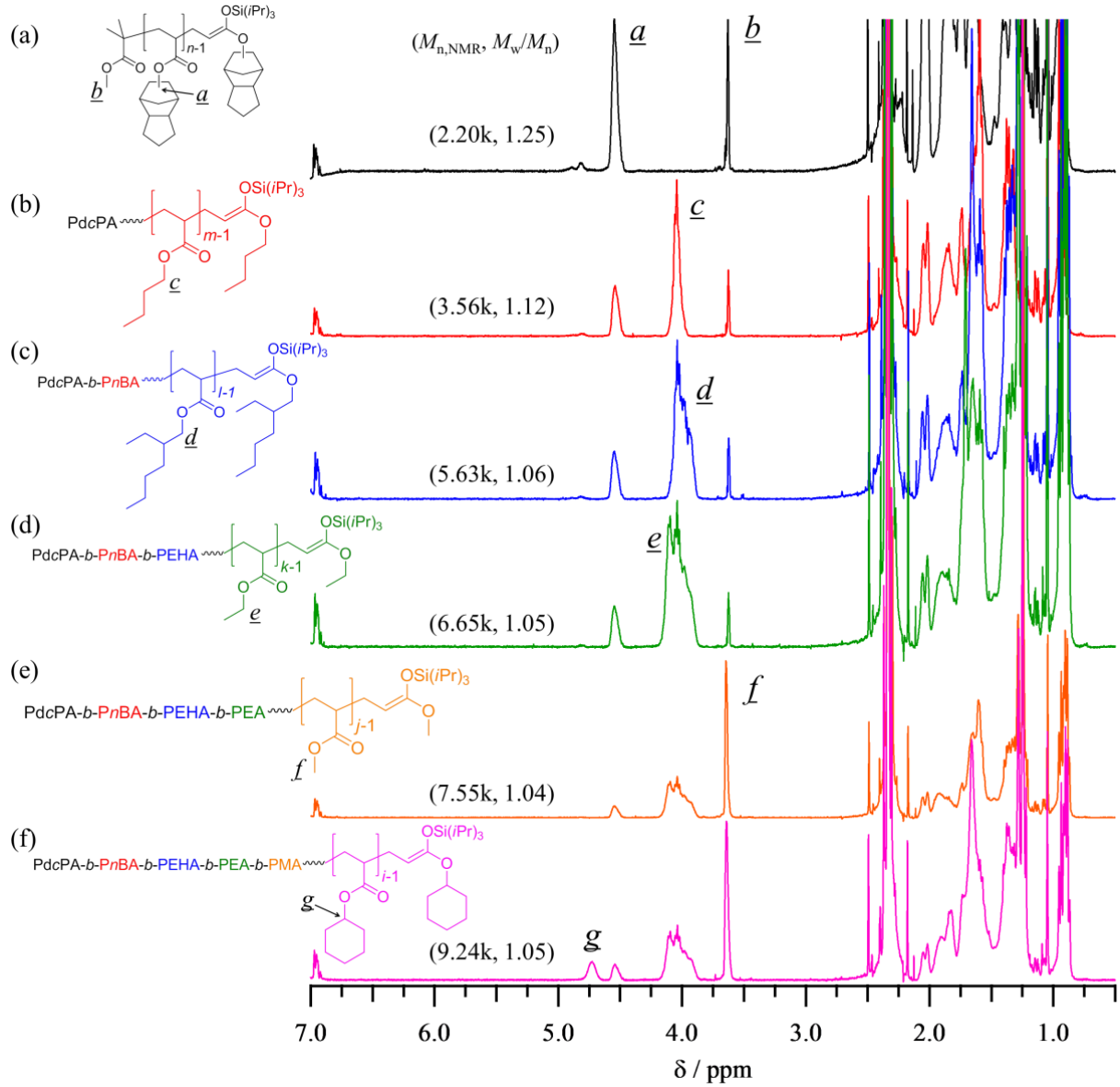


Figure 3-21. ^{1}H NMR spectra of the hexablock sestopolymer obtained by sequential Me_3SiNTf_2-catalyzed GTP; (a) Pd*c*PA, (b) Pd*c*PA-*b*-P*n*BA, (c) Pd*c*PA-*b*-P*n*BA-*b*-PEHA, (d) Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA, (e) Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA, and (f) Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA (solvent, $CDCl_3$).

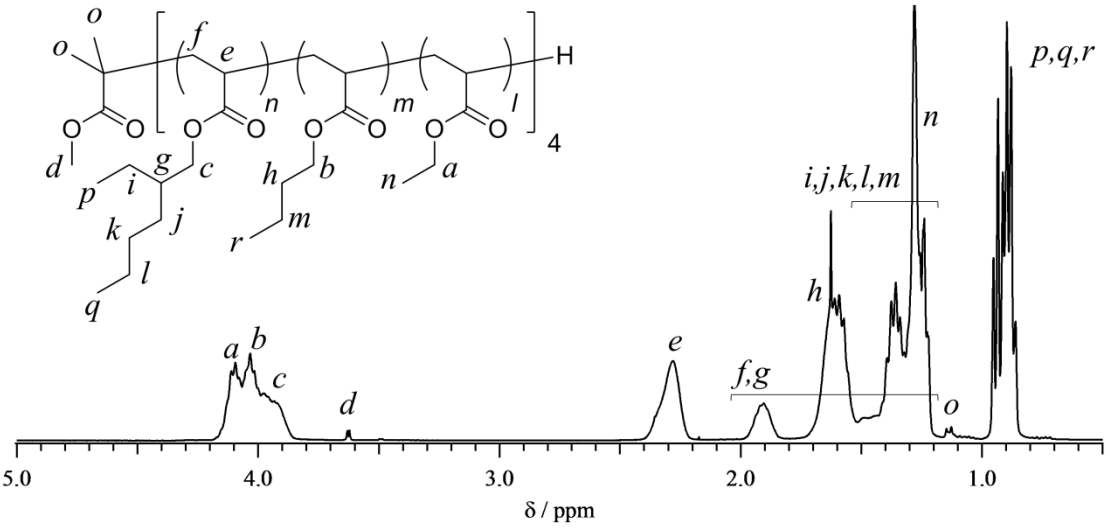


Figure 3-22. ^{1}H NMR spectram of the (PEHA-*b*-P*n*BA-*b*-PEA)$_4$ dodecablock terpolymers obtained from chain extension experiment of EHA, *n*BA, and EA (solvent, $CDCl_3$).

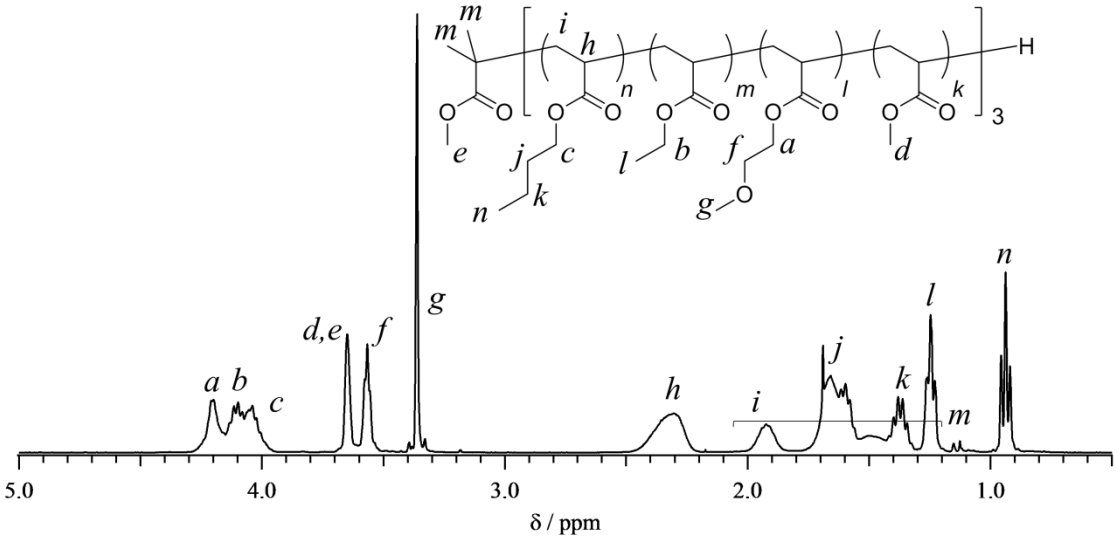


Figure 3-23. ^{1}H NMR spectram of the (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$ dodecablock quintopolymers obtained from chain extension experiment of *n*BA, EA, MEA, and MA (solvent, $CDCl_3$).

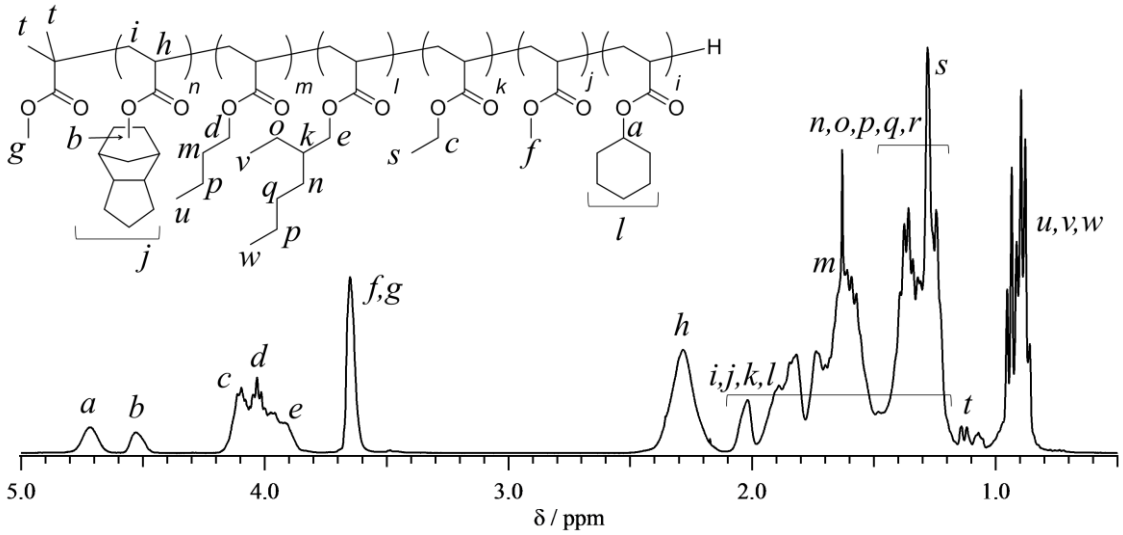


Figure 3-24. ^{1}H NMR spectram of the Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA hexablock sestopolymers obtained from chain extension experiment of d*c*PA, *n*BA, EHA, EA, MA, and *c*HA (solvent, $CDCl_3$).

3.4 Conclusions

The organocatalyzed group transfer polymerization (GTP) of acrylate monomers was studied in order to clarify its scope and limits. The primary alkyl acrylate possessed a high GTP ability compared to the secondary alkyl acrylate, and the tertiary alkyl acrylate exhibited no polymerization ability. The GTPs of the allyl acrylate and propargyl acrylate proceeded without gelation and that of the triisopropylsilyl acrylate without cleavage of the silyl ester linkage, correspondingly producing their well-defined acrylate polymers. These GTP characteristics were caused by the living nature that the triisopropylsilyl ketene acetal of the initiator and the propagating chain-end efficiently reacted with the acrylate monomer activated by the strong organic Lewis acid, which was proved by the sequential GTP leading to the polymer chain extension. In addition, the (PEHA-*b*-P*n*BA-*b*-PEA)$_4$ dodecablock terpolymer, (P*n*BA-*b*-PEA-*b*-PMEA-*b*-PMA)$_3$ dodecablock quaterpolymer, and Pd*c*PA-*b*-P*n*BA-*b*-PEHA-*b*-PEA-*b*-PMA-*b*-P*c*HA hexablock sestopolymer were synthesized by the sequential GTP method. To the best of our knowledge, the synthesis of the multiblock acrylates polymers was the first reliable demonstration of the precisely designed acrylate polymers using the living anionic polymerization, i.e., the organocatalyzed GTP.

3.5 References and Notes

(1) Hamley, I. W. *Adv. Polym. Sci.* **1999**, *148*, 113-137.

(2) Nair, L. S.; Laurencin, C. T. *Prog. Polym. Sci.* **2007**, *32*, 762-798.

(3) Hamley, I. W. *Prog. Polym. Sci.* **2009**, *34*, 1161-1210.

(4) Rodríguez-Hernández, J.; Chécot, F.; Gnanou, Y.; Lecommandoux, S. *Prog. Polym. Sci.* **2005**, *30*, 691-724.

(5) Hadjichristidis, N.; Iatrou, H.; Pisikalis, M; Pispas, S.; Avgeropoulos, A. *Prog. Polym. Sci.* **2005**, *30*, 725-782.

(6) Yagci, Y.; Tasdelen, M. A. *Prog. Polym. Sci.* **2006**, *31*, 1133-1170.

(7) Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317-350.

(8) Mori, H.; Müller, A. H. E. *Prog. Polym. Sci.* **2003**, *28*, 1403-1439.

(9) Hirao, A.; Matsuo, Y.; Oie, T.; Goseki, R.; Ishizone, T. *Macromolecules* **2011**, *44*, 6345-6355.

(10) Matsuo, Y.; Oie, T.; Goseki, R.; Ishizone, T.; Sugiyama, K.; Hirao, A. *Macromol. Symp.* **2013**, *323*, 26-36.

(11) Sugiyama, K.; Oie, T.; El-Magd, A. A.; Hirao, A. *Macromolecules* **2010**, *43*, 1403-1410.

(12) Bellas, V.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **2000**, *33*, 6993-6997.

(13) Giebeler, E.; Stadler, R. *Macromol. Chem. Phys.* **1997**, *198*, 3815-3525.

(14) Fragouli, P. G.; Iatrou, H.; Hadjichristidis, N. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 514-519.

(15) Fragouli, P.; Iatrou, H.; Lohse, D. J.; Hadjichristidis, N. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 3938-3946.

(16) Soeriyadi, A. H.; Boyer, C.; Nyström, F.; Zetterlund, P. B.; Whitteaker, M. R. *J. Am. Chem. Soc.* **2011**, *133*, 11128-11131.

(17) Boyer, C.; Soeriyadi, A. H.; Zetterlund, P. B.; Whittaker, M. R. *Macromolecules* **2011**, *44*, 8028-8033.

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

(19) Hartler, W. R.; Sogah, D. Y.; Webster, O. W. *Macromolecules* **1984**, *17*, 1415-1417.

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

(21) Webster, O. W. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 2855-2560.

(22) Webster, O. W. *Adv. Polym Sci.* **2004**, *167*, 1-34.

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

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

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

(26) Raynaud, J.; Lie, N.; Gnanou, Y.; Taton, D. *Macromolecules* **2010**, *43*, 8853-8861.

(27) Raynaud, J.; Lie, N.; Févre, M.; Gnanou, Y.; Taton, D. *Polym. Chem.* **2011**, *2*, 1706-1712.

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

(29) Kakuchi, R.; Chiba, K.;Fuchise, K.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42*, 8747-8750.

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

(31) Chen, Y.; Takada, K.; Fuchise, K.; Satoh, T.; Kakuchi, T. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 3277-3285.

(32) Fuchise, K.; Chen, Y.; Takada, K.; Satoh, T.; Kakuchi, T. *Macromol. Chem. Phys.* **2012**, *213*, 1604-1644.

(33) Takada, K.; Fuchise, K.; Chen, Y.; Satoh, T.; Kakuchi, T. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 3560-3566.

(34) Fuchise, K.; Chen, Y.; Satoh, T.; Kakuchi, T. *Polym. Chem.* **2013**, *4*, 4278-4291.

(35) Takada, K.; Fuchise, K.; Kubota, N.; Ito, T.; Chen, Y.; Satoh, T.; Kakuchi, T. *Macromolecules* **2014**, *47*, 5514-5525.

(36) Liu, S.-Y.; Hills, I. D.; Fu, G. J. *J. Am. Chen. Soc.* **2005**, *127*, 15352-15353.

(37) Harvey, D. F.; Lund, K. P.; Neil, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 8424-8434.

Chapter 4

Synthesis of End-Functionalized Poly(n-butyl acrylate) by Organocatalyzed Group Transfer Polymerization

4.1 Introduction

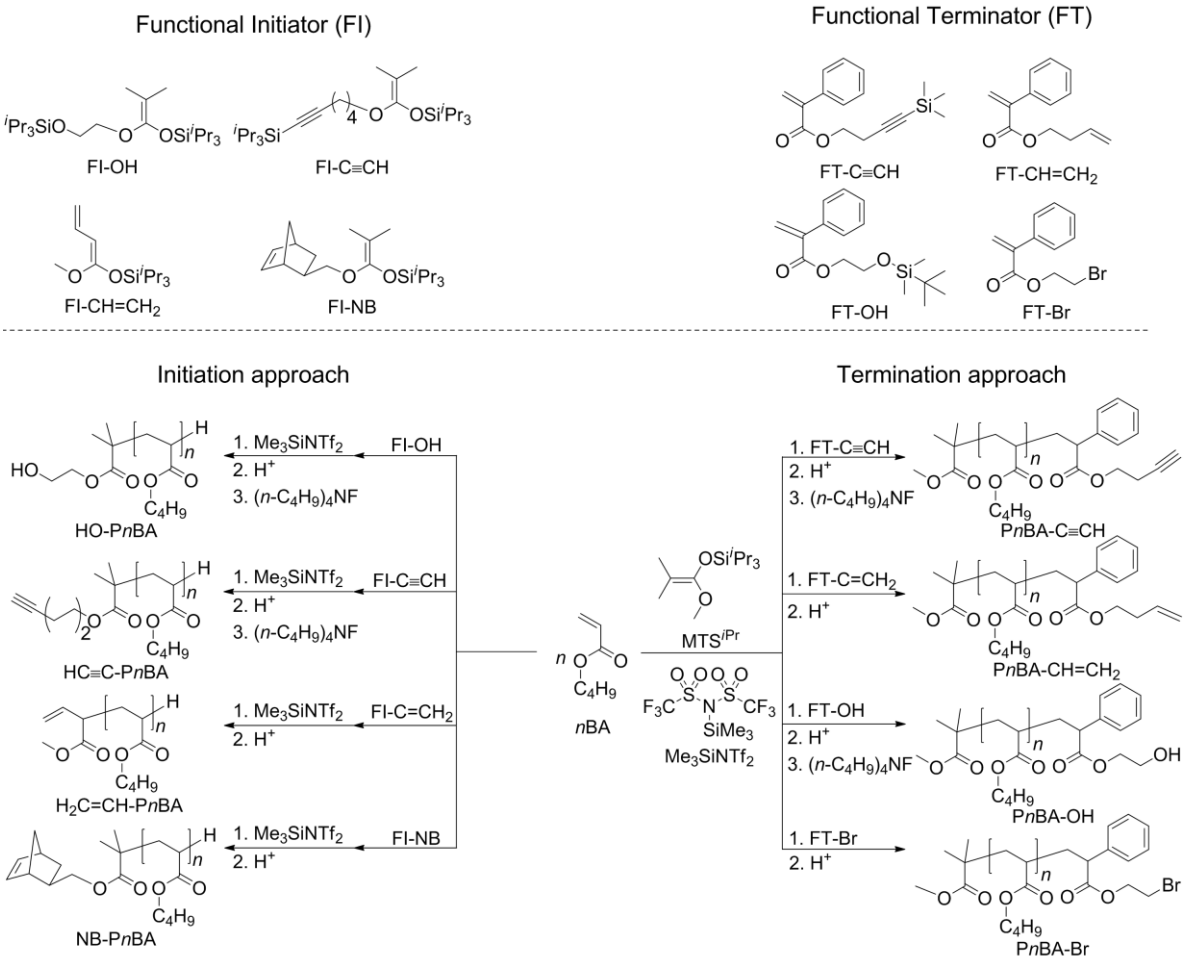
Acrylate polymers are some of the important plastic materials possessing a notable transparency, flexibility, and extensibility and are primarily utilized in paints and other surface coatings, adhesives, and textiles. In general, acrylate polymers involving their copolymers are produced using radical polymerization methods in industry, and the recent progress in the controlled/living radical polymerization has enabled the preparation of well-defined acrylate polymers.[1-4] Additionally, the controlled/living polymerization is generally applicable for the synthesis of end-functionalized polymers, block copolymers, and various macromolecular architectures, such as cyclic, star-shaped, dendritic, and hyper-branched polymers. Particularly, end-functionalized polymers are versatile building blocks for constructing such macromolecular architectures, which are potentially applicable as future materials.[5-9] Thus, it is important to develop controlled/living polymerization systems for precisely preparing end-functionalized acrylate polymers.

For acrylate monomers, anionic polymerization is one of the common methods in relation to methacrylate monomers.[8,10,11] Contrary to radical polymerization processes, the anionic polymerization of acrylate monomers is usually disrupted by inherent side reactions of the ester carbonyl group and the labile α-hydrogen of the monomer units in the polymer with the anionic initiators and the active chain ends. Therefore, there were many efforts to synthesize well-defined polyacrylates by the anionic polymerization of alkyl acrylates;[12-24] for instance, Müller et al. reported that the anionic polymerization of *tert*-butyl acrylate (*t*BA) using lithium *tert*-butoxide in the presence of lithium chloride was sufficiently controlled to produce poly(*tert*-butyl acrylate)s,[16,17] Ishizone et al. reported the controlled polymerization of *t*BA using the diphenylmethyl anion in the presence of dialkylzinc or triethylbrane,[18,19] and Chen et al. reported that triphenylmethyl tetrakis(pentafluorophenyl)borane was promoted the

oxidative GTP of *n*-butyl acrylate (*n*BA) to produce well-defined polymers with high-molecular-weights.[21] Furthermore, Taton et al. reported the synthesis of block copolymers consisting of methacrylates, acrylates, *N*,*N*-dimethylacrlamide, and methacrylonitrile using the GTP catalyzed by *N*-heterocyclic carbene.[20,22-24] Recently, we succeeded in the synthesis of a high-molecular-weight poly(methyl acrylate) with a well-defined structure by the organocatalytic group transfer polymerization (GTP) as the controlled/living anionic polymerization.[25,26] Webster and coworkers reported the preparation of α-end-functionalized polymers based on the conventional GTP, in which ethyl acrylate was only investigated as an acrylate monomer using a silyl ketene acetal with a functional group in the homopolymerization and copolymerization with methyl methacrylate (MMA), leading to an α-hydroxyl-functionalized homopolymer with a low molecular weight and an α-hydroxyl-functionalized copolymer with a high polydispersity, respectively.[19,27] In addition, Quirk et al., and Sivaram et al. reported the termination reaction of the conventional GTP using benzaldehyde and methyl 2-phenylacrylate, in which their derivatives were used as the functional terminators for the GTP leading to ω-end-functionalized polymers with hydroxyl and amino groups though MMA was only investigated and the efficiency of the end-functionalizations was poor.[28,29] Thus, the precise synthesis of end-functionalized acrylate polymers is still challenging from the viewpoint of the living anionic polymerization involving the GTP method. Hence, the autor shows the end-functionalization of acrylate polymers using the initiation and termination approaches based on the organocatalytic GTP through the molecular design and synthesis of functional initiators (FIs) and functional terminators (FTs). This chapter describes the synthesis of the α-, ω-, and α,ω-end-functionalized poly(*n*-butyl acrylate)s (P*n*BAs) by the GTP of *n*BA using triisopropylsilyl ketene acetals as FIs and 2-phenylacrylates as FTs, in which

N-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNTf_2) is used as the organocatalyst, as shown in Scheme 4-1. The obtained P*n*BA structures involving the end-functional groups are confirmed based on the ^1H NMR and MALDI-TOF MS measurements.

Scheme 4-1. Synthesis of α- and ω-End-Functionalized Poly(*n*-butyl acrylate)s (P*n*BAs) by *N*-(Trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNTf_2)-Catalyzed Group Transfer Polymerization of *n*-Butyl Acrylate (*n*BA) using Functional Initiator (FI) and Terminator (FT)



4.2 Experimental Section

Materials

Dichloromethane (CH_2Cl_2, >99.5%; water content, <0.001%), toluene (>99.5%; water content, <0.001%), tetrahydrofuran (THF, >99.5%; water content, <0.001%), *n*-butyllithium (*n*-BuLi, 1.6 mol L^{-1} in *n*-hexane), imidazole (>98.0%), triethylamine (>99.0%), methanol (>99.5%), 2-propanol (>99.5%), *tert*-butyl alcohol (>98.0%), and pyridine (>99.0%) were purchased from Kanto Chemicals Co., Inc. *n*-Butyl acrylate (*n*BA, >99.0%), methyl methacrylate (MMA, >99.8%), *N*,*N*-dimethylmethacrylamide (DMMAm, >98.0%), *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNTf_2, >95.0%), triisopropylsilyl trifluoromethanesulfonate (*i*-Pr_3SiOTf, >98.0%), methyl crotonate (>98.0%), isobutyryl chloride (>98.0%), 5-hexyn-1-ol (>95.0%), triisopropylsilyl chloride (*i*Pr_3SiCl), 4-(dimethylamino)pyridine (DMAP, >99.0%), *trans*-3-indoleacrylic acid (>98.0%), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, >98.0%), and tetrabutylammonium fluoride hydrate were purchased from Tokyo Kasei Kogyo Co., Ltd. (1*R*,2*S*,4*R*)-5-Norbornene-2-carboxylic acid (97%) and sodium trifluoroacetate (98%) were purchased from Sigma-Aldrich Chemicals Co. MMA, *n*BA, DMMAm, DMPU, and CH_2Cl_2 were distilled from CaH_2 and degassed by three freeze-pump-thaw cycles prior to use. Toluene and THF were distilled from sodium benzophenone ketyl. 1-Methoxy-1-triisopropylsiloxy-2-methyl-1-propene (MTS^{iPr}),[25,30] 2-hydroxyethyl isobutyrate,[19] (1*R*,2*S*,4*R*)-5-norborene-2-methanol,[31] and 1-methoxy-1-triisopropylsiloxy-1,3-butadiene (FI-CH=CH_2)[32] were synthesized by previously reported procedures. Spectra/Por® 6 membrane (molecular weight cutoff: 1000) was used for the dialysis. All other chemicals were purchased from available suppliers and

used without purification.

Instruments

The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a JEOL JNM-A400II, and a JEOL-ECS400. The polymerization solution was prepared in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere (H_2O, 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. Size exclusion chromatography (SEC) measurements for the end-functionalized P*n*BAs were performed at 40 °C using a Jasco GPC-900 system (Shodex® DU-2130 dual pump, Shodex® RI-71 RI detector, and Shodex® ERC-3125SN degasser) equipped with two Shodex KF-804 L columns (linear, 8 mm × 300 mm) in THF at the flow rate of 1.0 mL min^{-1}. The number average molecular weight ($M_{n,SEC}$) and polydispersity (M_w/M_n) of the P*n*BA were determined using PMMA standards with the M_w (M_w/M_n)s of 1.25 × 10^6 g mol^{-1} (1.07), 6.59 × 10^5 g mol^{-1} (1.02), 3.003 × 10^5 g mol^{-1} (1.02), 1.385 × 10^5 g mol^{-1} (1.05), 6.015 × 10^4 g mol^{-1} (1.03), 3.053 × 10^4 g mol^{-1} (1.02), and 1.155 × 10^4 g mol^{-1} (1.04), 4.90 × 10^3 g mol^{-1} (1.10), 2.87 × 10^3 g mol^{-1} (1.06), and 1.43 × 10^3 g mol^{-1} (1.15). The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed using an Applied Biosystems Voyager-DE STR-H mass spectrometer with a 25 kV acceleration voltage. The positive ions were detected in the reflector mode (25 kV). A nitrogen laser (337 nm, 3 ns pulse width, 106-107 W cm^{-2}) operating at 3 Hz was used to produce the laser desorption, and 200-500 shots were summed. The spectra were externally calibrated using narrow-dispersed polystyrene with a linear calibration. Samples for the MALDI-TOF MS measurements of the end-functionalized P*n*BAs were prepared by mixing

the polymer (1.5 mg mL^{-1}, 10 μL), the matrix (trans-3-indoleacrylic acid, 10 mg mL^{-1}, 90 μL), and the cationizing agent (sodium trifluoroacetate, 10 mg mL^{-1}, 10 μL) in THF.

Synthesis of 2-(Triisopropylsiloxy)ethyl Isobutyrate

iPr_3SiCl (8.82 mL, 41.6 mmol) was dropwise added to a solution of 2-hydroxyethyl isobutyrate (5.00 g, 37.8 mmol) and imidazole (2.95 g, 4.92 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature and sequentially washed with 1 mol L^{-1} HCl (100 mL × 2), conc. aq. $NaHCO_3$ (100 mL), and distilled water (100 mL). The organic phase was dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by distillation under reduced pressure to give 2-triisopropylsiloxyethyl isobutyrate as a transparent liquid. Yield, 9.67 g (88%). b.p., 81 °C / 0.08 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.16 (t, *J* = 4.8 Hz, 2H, -COOC*H*$_2$-), 3.89 (t, *J* = 5.2 Hz, 2H, -C*H*$_2$-O-Si-), 2.56 (sep, *J* = 6.8 Hz, 1H, -CO-C*H*$(CH_3)_2$), 1.17 (d, *J* = 6.8 Hz, 6H, -CO-CH(C*H*$_3)_2$), 1.01−1.13 (m, 21H, -OSi[C*H*$(CH_3)_2]_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 177.2, 65.7, 61.5, 34.0, 19.0, 17.9, 11.9. Anal. Calcd for $C_{15}H_{32}O_3Si$ (288.50): C, 62.45; H, 11.18. Found: C, 62.20; H, 11.32.

Synthesis of 1-(2-Triisopropylsiloxyethoxy)-1-triisopropylsiloxy-2-methyl-1-propene (FI-OH)

The following procedure (Method A) was used for the synthesis of FI-C≡CH and FI-NB: *n*-Butyl lithium (13.1 mL, 1.59 mol L^{-1} in *n*-hexane, 21.0 mmol) was dropwise added to a solution of diisopropylamine (2.81 mL, 20.0 mmol) in THF (50 mL) at 0 °C under an argon atmosphere, then the mixture was stirred for 30 min at 0 °C. DMPU (10.0 mL, 20.6 mmol) and 2-(triisopropylsiloxy)ethyl isobutylate (4.47 g, 15.5 mmol) were added to the mixture at

−78 °C. After stirring at −78 °C for 30 min, *i*-Pr_3SiOTf (4.03 mL, 30.7 mmol) was added to the reaction mixture at −78 ºC and stirred at room temperature for 12 h, then the reaction was quenched by adding a mixture of *n*-hexane and water. The organic phase was washed with conc. aq. NaCl (100 mL × 3), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was distilled under reduced pressure to give FI-OH as a yellow liquid. Yield, 2.09 g (30%). b.p., 125-130 °C / 0.020 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.86 (m, 2H, -SiOC*H*$_2$-), 3.83 (m, 2H, -C*H*$_2$-OC=), 1.58 (s, 3H, (^{E}C*H*$_3$)(^{Z}CH$_3$)C=), 1.54 (s, 3H, (^{E}CH$_3$)(^{Z}C*H*$_3$)C=), 1.11 (m, 21H, =COSi(C$_3$*H*$_7$)$_3$), 1.06 (m, 21H, -CH$_2$OSi(C$_3$*H*$_7$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 149.3, 91.0, 71.4, 62.1, 18.4, 17.5, 16.7, 16.1, 12.6, 11.7.

Synthesis of Hex-5-yn-1-yl Isobutyrate

Isobutyryl chloride (5.33 mL, 50.0 mmol) was dropwise added to a solution of 5-hexyn-1-ol (5.00 g, 50.9 mmol), triethylamine (5.40 mL, 36.0 mmol), and DMAP (184 mg, 1.50 mmol) in CH_2Cl_2 (150 mL) under a nitrogen atmosphere at 0 °C. After stirring at room temperature for 20 h, the reaction mixture was filtered and washed with conc. aq. $NaHCO_3$ (100 mL × 3) and distilled water (100 mL × 3). The organic layer was dried over anhydrous $MgSO_4$. The obtained crude product was distilled under reduced pressure to give hex-5-yn-1-yl isobutyrate as a colorless liquid. Yield, 6.95 g (89 %). b.p., 120 °C / 0.08 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.09 (t, *J* = 4.0 Hz, 2H, -OC*H*$_2$-), 2.54 (sep, *J* = 7.2 Hz, 1H, -C*H*(CH$_3$)$_2$), 2.24 (dt, ^{3}*J* = 7.2 Hz and ^{4}*J* = 2.8 Hz, 2H, HC≡CC*H*$_2$-), 1.96 (t, *J* = 2.8 Hz, 1H, -C≡C*H*), 1.76 (quin, *J* = 7.2 Hz, 2H, -OCH$_2$C*H*$_2$-), 1.61 (quin, *J* = 7.2 Hz, 2H, -OCH$_2$CH$_2$C*H*$_2$-), 1.17 (d, *J* = 8.0 Hz, 6H, -CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 177.2, 83.9, 68.7, 63.7, 34.0, 27.7, 24.9, 19.0, 18.1. Anal. Calcd. for $C_{10}H_{16}O_2$ (168.23): C, 71.39; H, 9.59. Found: C, 71.57; H, 9.75.

Synthesis of 1-(6-Triisopropylsilylhex-5-yn-1-yloxy)-1-triisopropylsiloxy-2-methyl-1-propene (FI-C≡CH)

Method A was used for the reaction of *n*-butyl lithium (25.0 mL, 1.59 mol L^{-1} in *n*-hexane, 40.0 mmol), diisopropylamine (5.54 mL, 39.5 mmol), THF (50 mL), DMPU (15.0 mL, 30.9 mmol), hex-5-yn-1-yl isobutylate (3.28 g, 19.5 mmol), and *i*-Pr_3SiCl (8.47 mL, 40.0 mmol) to give FI-C≡CH as a yellow liquid. Yield, 2.16 g (23%). b.p., 135-140 °C / 0.020 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.74 (t, *J* = 4.0 Hz, 2H, -OC*H*$_2$-), 2.29 (t, *J* = 4.0 Hz, 2H, ≡CC*H*$_2$-), 1.75 (m, 2H, -OCH_2CH_2-), 1.64 (m, 2H, -$OCH_2CH_2CH_2$-), 1.56 (s, 3H, (^{E}C*H*$_3$)(^{Z}CH_3)C=), 1.55 (s, 3H, (^{E}CH_3)(^{Z}C*H*$_3$)C=), 1.09 (m, 21H, -OSi(C_3H_7)$_3$), 1.06 (m, 21H, -C≡CSi(C_3H_7)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 149.6, 108.7, 91.4, 80.4, 70.0, 28.8, 25.6, 19.7, 18.6, 18.0, 17.8, 17.2, 16.6, 12.9, 12.0, 11.3.

Synthesis of (1*S*, 4*S*)-Norborn-5-en-2-ylmethyl Isobutyrate

Isobutyryl chloride (2.80 mL, 26.6 mmol) was dropwise added to a solution of 5-norbornene-2-methanol (3.00 g, 24.2 mmol), triethylamine (3.68 mL, 26.6 mmol), and 4-(dimethylamino)pyridine (0.148 g, 1.21 mmol) in CH_2Cl_2 (50 mL) at 0 °C under a nitrogen atmosphere. After 6 h of reaction at room temperature, the reaction mixture was washed with 1 mol L^{-1} HCl (50 mL), conc. $NaHCO_3$ (50 mL), and water (50 mL). The organic layer was dried over anhydrous $MgSO_4$ and filtered. The crude product was purified by distillation under reduced pressure to give (1*S*, 4*S*)-norborn-5-en-2-ylmethyl isobutyrate as a colorless liquid. Yield, 3.71 g (79%). b.p., 50 °C / 0.38 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm), 6.04-6.14 (m, 2H, -C*H*=C*H*-), 4.14 (dd, *J* = 6.4 Hz, *J* = 10.8 Hz, 1H, -OC*H*$_2$-), 3.97 (dd, *J* =

9.2 Hz, *J* = 10.8 Hz, 1H, -OC*H*$_2$-), 2.84-2.70 (br s, 2H, -C*H*-CH=CH-C*H*-), 2.57 (sep, *J* = 6.8 Hz, 1H, -C*H*(CH$_3$)$_2$), 1.71 (m, 1H, -CH-C*H*-CH$_2$-), 1.18, 1.17 (d, *J* = 6.8 Hz, 6H, -CH(C*H*$_3$)$_2$), 1.08-1.39 (m, 4H, bridgehead and -CH-CH-C*H*$_2$-). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 177.24, 136.89, 136.19, 68.33, 44.94, 43.57, 41.54, 37.96, 34.04, 29.48, 19.02, 19.00. Anal. Calcd for $C_{12}H_{18}O_2$ (194.27): C, 74.19; H, 9.37. Found: C, 74.00; H, 9.47.

Synthesis of 1-((1*S*,4*S*)-Norborn-5-en-2-ylmethoxy)-1-triisopropylsiloxy-2-metyl-1-propene (FI-NB)

Method A was used for the reaction of *n*-butyl lithium (8.86 mL, 1.60 mol L^{-1} in *n*-hexane, 14.2 mmol), diisopropylamine (1.95 mL, 13.9 mmol), THF (35.5 mL), DMPU (6.74 mL, 13.9 mmol), (1*S*, 4*S*)-norborn-5-en-2-ylmethyl isobutyrate (2.70 g, 13.9 mmol), and *i*-Pr$_3$SiOTf (3.73 mL, 14.2 mmol) to give FI-NB as a colorless liquid. Yield, 1.02 g (22%). b.p., 98 °C / 0.015 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.00-6.17 (m, 2H, -C*H*=C*H*-), 3.75 (dd, *J* = 6.0 Hz, *J* = 9.6 Hz, 1H, -OC*H*$_2$-), 3.60 (dd, *J* = 8.8 Hz, *J* = 9.6 Hz, 1H, -OC*H*$_2$-), 2.80 (br s, 2H, -C*H*-CH=CH-C*H*-), 1.35-1.14 (m, 4H, bridgehead and C*H*$_2$), 1.60 (s, 3H, =C(^{E}CH$_3$)(^{Z}CH$_3$)), 1.52 (s, 3H, =C(^{E}CH$_3$)(^{Z}C*H*$_3$)), 1.09 (s, 21H, -OSi(C$_3$*H*$_7$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 148.29, 136.75, 136.61, 91.35, 74.91, 45.02, 43.83, 41.60, 38.80, 29.75, 17.95, 17.30, 16.74, 12.97.

Synthesis of 4-Trimethylsilyl-3-butynyl 2-Phenylacrylate (FT-C≡CH)

The following procedure (Method B) was used for the synthesis of FT-OH, FT-CH=CH$_2$, and FT-Br. 2-Phenylacryloyl chloride (5.30 g, 31.8 mmol) was dropwise added to a solution of 4-trimethylsilyl-3-butyne-1-ol (4.11 g, 28.9 mmol), triethylamine (4.43 mL, 31.8 mmol), and DMAP (66.7 mg, 0.546 mmol) in CH_2Cl_2 (70 mL) at 0 °C under a nitrogen atmosphere.

After stirring at room temperature for 12 h, the reaction mixture was washed with 1N HCl (50 mL × 3), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 20/1, v/v, R_f = 0.3) and dried using molecular sieves 3A for 2 days. After removing the molecular sieves by filtration, the crude product was distilled under reduced pressure to give FT-C≡CH as a colorless liquid. Yield: 3.66 g (63.2 %), b.p., 110 °C / 0.015 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.15 (d, *J* = 0.8 Hz, 9H, -Si(C*H*$_3$)$_3$), 2.64 (t, J = 6.8 Hz, 2H, -COOC*H*$_2$-C*H*$_2$-), 4.28 (t, *J* = 6.8 Hz, 2H, -COO-C*H*$_2$-), 5.92 (s, 1H, =C*H*(H)), 6.40 (d, *J* = 1.2 Hz, 1H, =CH(*H*)), 7.30-7.48 (m, 5H, C$_6$*H*$_5$-). ^{13} C NMR (100 MHz, $CDCl_3$): δ (ppm) 0.11, 20.4, 62.9, 86.7, 102.4, 127.3, 128.2, 128.3, 128.4, 136.6, 141.3, 166.5. Anal. Calcd. for $C_{16}H_{20}O_2Si$ (272.12): C, 70.54; H, 7.40. Found: C, 70.25; H, 7.09.

Synthesis of 3-Butenyl 2-Phenylacrylate (FT-CH=CH$_2$)

Method B was used for the reaction of 2-phenylacryloyl chloride (5.62 g, 33.7 mmol), 3-butene-1-ol (2.68 g, 33.7 mmol), triethylamine (5.62 g, 33.7 mmol), and CH_2Cl_2 (50 mL). The crude product was distilled under reduced pressure to give FT-CH=CH_2 as a colorless liquid. Yield: 2.07 g (27.6 %), b.p., 71 °C / 0.030 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.46 (q, *J* = 6.8 Hz, 2H, -C*H*$_2$-CH=), 4.28 (t, *J* = 6.8 Hz, 2H, -COO-C*H*$_2$-), 5.11 (t, 2H, =C*H*$_2$), 5.75-5.87 (m, 1H, -C*H*=CH$_2$), 5.89 (d, *J* = 1.2 Hz, 1H, =C*H*(H)), 6.35 (d, *J* = 1.2 Hz, 1H, =CH(*H*)), 7.29-7.45 (m, 5H, C$_6$*H*$_5$-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 33.2, 64.2, 117.5, 126.9, 128.1, 128.2, 128.4, 134.1, 136.8, 141.5, 166.8. Anal. Calcd. for $C_{13}H_{14}O_2$ (202.10): C, 77.20; H, 6.98. Found: C, 76.76; H, 6.67.

Synthesis of 2-(*tert*-Butyldimethylsiloxy)ethyl 2-Phenylacrylate (FT-OH)

Method B was used for the reaction of 2-phenylacryloyl chloride (2.10 g, 10.9 mmol), (*tert*-butyldimethylsilyloxy)ethanol (4.80 g, 27.2 mmol), triethylamine (3.79 mL, 24.7 mmol), and CH_2Cl_2 (50 mL). The crude product was distilled under reduced pressure to give FT-OH as a colorless liquid. Yield: 1.98 g (52.0 %), b.p., 100 °C / 0.03 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.04 (s, 6H, -Si(C*H*$_3$)$_2$C(CH$_3$)$_3$), 0.89 (s, 9H, -Si(C*H*$_3$)$_2$C(CH$_3$)$_3$), 3.87 (t, *J* = 5.2 Hz, 2H, -COOCH$_2$-C*H*$_2$-), 4.30 (t, *J* = 5.2 Hz, 2H, -COOC*H*$_2$-CH$_2$-), 5.90 (d, *J* = 1.2 Hz, 1H, =C*H*(H)), 6.38 (d, *J* = 1.2 Hz, 1H, =CH(*H*)), 7.30-7.46 (m, 5H, C$_6$*H*$_5$-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 18.4, 26.0, 61.3, 66.5, 127.0, 128.2, 128.3, 128.5, 136.8, 141.5, 166.9. Anal. Calcd. for $C_{17}H_{26}O_3Si$ (306.17): C, 66.62; H, 8.55. Found: C, 66.13; H, 8.27.

Synthesis of 2-Bromoethyl 2-Phenylacrylate (FT-Br)

Method B was used for the reaction of 2-phenylacryloyl chloride (7.87 g, 47.2 mmol), 2-bromoethanol (3.75 g, 52.0 mmol), triethylamine (8.69 mL, 62.4 mmol), and CH_2Cl_2 (60 mL). The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate = 9/1, v/v, R_f = 0.37) and distilled under reduced pressure to give FT-Br as a colorless liquid. Yield: 4.83 g (40.0 %), b.p., 96 °C / 0.030 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.58 (t, *J* = 6.4 Hz, 2H, -C*H*$_2$-Br), 4.54 (t, *J* = 5.6 Hz, 2H, -COO-C*H*$_2$-), 5.96 (d, J = 0.92 Hz, 1H, =C*H*(H)), 6.44 (d, J = 0.96 Hz, 1H, =CH(*H*)), 7.31-7.48 (m, 5H, C$_6$*H*$_5$-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 28.8, 64.5, 127.8, 128.2, 128.5, 136.4, 141.0, 166.3. Anal. Calcd. for $C_{11}H_{11}BrO_2$ (253.99): C, 51.79; H, 4.35; Br, 31.32. Found: C, 51.72; H, 4.03; Br, 31.43.

Me_3SiNTf_2-Catalyzed GTP of *n*BA using Functional Initiator

A typical procedure is as follows: A stock solution of Me_3SiNTf_2 (25.0 μL, 2.50 μmol, 0.10

mol L^{-1} in CH_2Cl_2) was added to a solution of *n*BA (160 mg, 1.25 mmol) and FI-OH (22.2 mg, 50.0 μmol) in toluene (2.50 mL) under an argon atmosphere at room temperature. After stirring for 5 min, the polymerization was quenched by adding a small amount of methanol. Aliquots were removed from the reaction mixture to determine the conversion of *n*BA based on its ^{1}H NMR spectrum. The reaction mixture was purified by dialysis against acetone, followed by removal of the solvent to give the triisopropylsiloxy end-functionalized P*n*BA as a sticky solid. Yield, 158 mg (99 %). ^{1}H NMR: $M_{n,NMR}$, 3.41 kg mol^{-1}. SEC (RI): $M_{n,SEC}$, 4.10 kg mol^{-1}; M_w/M_n, 1.09. The GTPs of *n*BA using FI-C≡CH (24.0 mg, 50 μmol), FI-CH=CH_2 (12.8 mg, 50 μmol), and FI-NB (16.8 mg, 50 μmol) were carried out by a similar procedure to give the corresponding end-functionalized P*n*BAs as sticky solids.

Me_3SiNTf_2-Catalyzed GTP of *n*BA using Functional Terminator

The GTP of *n*BA with 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene (MTS^{iPr}; 12.9 mg, 50 μmol) as the initiator was carried out by a procedure similar to that using the functional initiator. After stirring for 3 min at room temperature, methyl 2-phenylacrylate (MPhA; 24.3 mg, 150 μmol) in toluene (c.a.100 μL) was sequentially added to the polymerization mixture and the mixture was reacted for 20 h at room temperature. The reaction mixture was purified by dialysis against acetone followed by removal of the solvent to give the ω-end-functionalized P*n*BA as a sticky solid. The termination reactions using *N*,*N*-dimethyl methacrylamide (DMMAm; 17.0 mg, 150 μmol), dimethyl itaconate (DMIt; 15.9 mg, 150 μmol), methyl methacrylate (MMA; 15.0 mg, 150 μmol), FT-C≡CH (40.9 mg, 150 μmol), FT-CH=CH_2 (30.3 mg, 150 μmol), FT-OH (52.3 mg, 150 μmol), and FT-Br (38.3 mg, 150 μmol) were carried out by a similar procedure to produce quantitative yields.

Deprotection of Trialkylsilyl Group from End-Functionalized Polymers

A typical procedure is as follows: Tetrabutylammonium fluoride hydrate (31.4 mg, 3 equiv. of an initiator or a terminator residue) was added to a solution of P*n*BA (100 mg) in THF (3 mL) at room temperature. After 1 h, the reaction mixture was passed through a short silica-gel column, filtered, and the solvent removed to give the end-functionalized P*n*BA in a quantitative yield.

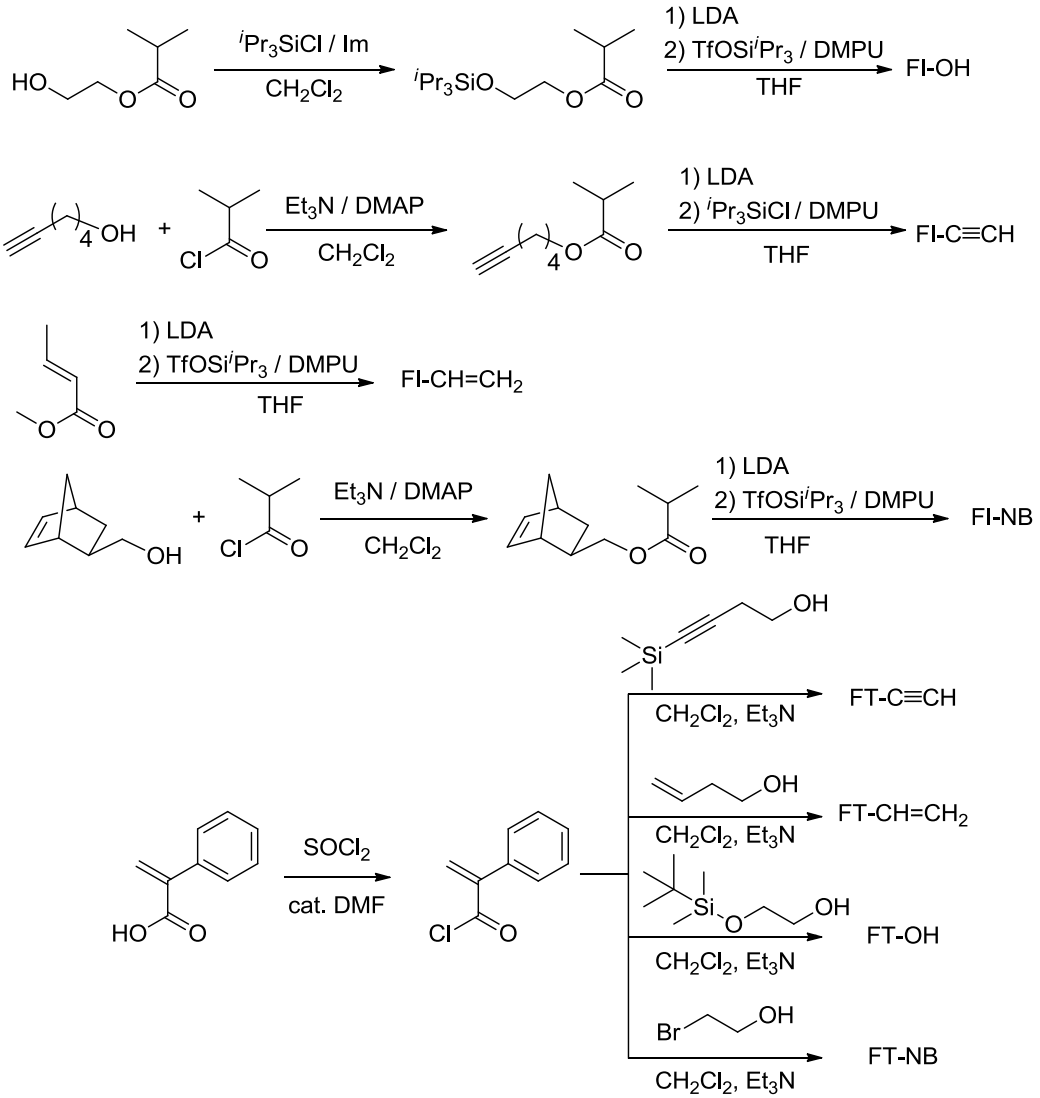
4.3 Results and Discussion

4.3.1 Synthesis of α-End-Functionalized P*n*BA using Functional Initiators

For the organocatalytic group transfer polymerization (GTP) of methyl acrylate, 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene (MTS^{iPr}) was used as the initiator because the bulky triisopropylsilyl group prevented any side reactions, such as the backbiting reaction, leading to well-defined poly(methyl acrylate)s.[26] Thus, we synthesized triisopropylsilyl ketene acetals as functional initiators (FIs), such as 1-(2-triisopropylsiloxyethoxy)-1-triisopropylsiloxy-2-methyl-1-propene (FI-OH), 1-(6-triisopropylsiloxy-5-yn-1-yloxy)-1-trimethylsiloxy-2-methyl-1-propene (FI-C≡CH), 1-methoxy-1-triisopropylsiloxy-2-methyl-1,3-butadiene (FI-CH=CH_2), and 1-((1*S*,4*S*)-norborn-5-en-2-ylmethoxy)-1-triisopropylsiloxy-2-metyl-1-propene (FI-NB). The synthetic procedures are illustrated in Scheme 4-2. Table 4-1 summarizes the results for the Me_3SiNTf_2-catalyzed GTP of *n*-butyl acrylate (*n*BA) using FI-OH, FI-C≡CH, FI-CH=CH_2, and FI-NB at the molar ratio of *n*BA and FI ($[n\text{BA}]_0/[\text{FI}]_0$) of 25 and 1000 in toluene at room temperature. All the polymerizations homogeneously proceeded and were quenched by adding methanol. For the polymers obtained using FI-OH and FI-C≡CH, the deprotection of the triisopropylsilyl group was carried out using tetrabutylammonium fluoride to prepare the hydroxyl- and ethynyl-functionalized P*n*BAs. The quantitative monomer conversions were confirmed by the ^{1}H NMR spectra of the crude polymerization mixtures. The polymerizations of *n*BA were well controlled to produce polymers with predicted molecular weights; the number average molecular weights ($M_{n,NMR}$s) determined using the ^{1}H NMR spectra were 3410 (run 1), 3690 (run 7), 3480 (run 13), and 3570 g mol^{-1} (run 19), which well agreed with the calculated values ($M_{n,calcd}$s) of 3330, 3370, 3300, and 3400 g mol^{-1}, respectively. In

addition, the molecular weight distributions (M_w/M_ns) of the obtained polymers were as low as 1.07 - 1.10.

Scheme 4-2. Synthesis of Functional Initiators and Terminators of FI-OH, FI-C≡CH, FI-CH=CH_2, FI-NB, FT-C≡CH, FT-CH=CH_2, FT-OH, and FT-Br



Im, imidazole; DMPU, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone; DMAP, 4-dimethylaminopyridine; LDA, lithium diisopropylamide; ^{i}Pr, *iso*-propyl group; Tf, trifluoromethanesulfonyl group.

Table 4-1. Synthesis of α-End-Functionalized P*n*BAs by GTP of *n*BA using FI-OH, FI-C≡CH, FI-CH=CH_2, and FI-NB [a]

run	functional initiator (FI)	$[n\text{BA}]_0/[\text{FI}]_0$	time / h	$M_{n,calcd}$ [b] / g mol^{-1}	$M_{n,SEC}$ [c] ($M_{n,NMR}$ [c]) / g mol^{-1}	M_w/M_n [c]
1	FI-OH	25	0.1	3 300	4 100 (3 400)	1.10
2	FI-OH	50	0.1	6 500	8 900	1.04
3	FI-OH	100	0.5	13 300	15 200	1.02
4	FI-OH	200	0.5	26 100	29 900	1.02
5	FI-OH	400	2	51 700	58 100	1.03
6	FI-OH	1000	6	128 600	142 700	1.05
7	FI-C≡CH	25	0.1	3 400	4 500 (3 700)	1.10
8	FI-C≡CH	50	0.1	6 600	9 000	1.06
9	FI-C≡CH	100	0.5	13 300	14 900	1.03
10	FI-C≡CH	200	0.5	26 100	30 600	1.03
11	FI-C≡CH	400	2	51 700	53 000	1.03
12	FI-C≡CH	1000	6	128 700	131 800	1.08
13	FI-CH=CH_2	25	0.1	3 300	4 000 (3 500)	1.03
14	FI-CH=CH_2	50	0.2	6 500	8 100	1.04
15	FI-CH=CH_2	100	0.2	12 900	14 000	1.02
16	FI-CH=CH_2	200	0.8	25 700	28 800	1.02
17	FI-CH=CH_2	400	4	51 400	52 100	1.06
18	FI-CH=CH_2	1000	6	128 300	129 300	1.03
19	FI-NB	25	0.1	3 400	4 500 (3 600)	1.10
20	FI-NB	50	0.1	6 600	7 900	1.05
21	FI-NB	100	0.2	13 000	15 300	1.03
22	FI-NB	200	1.5	25 800	30 000	1.03
23	FI-NB	400	3	51 500	56 100	1.02
24	FI-NB	1000	6	128 400	136 300	1.03

[a] Argon atmosphere; solvent, toluene; $[n\text{BA}]_0$, 1.0 mol L^{-1}; $[Me_3SiNTf_2]_0/[\text{FI}]_0$, 0.05; temperature, room temp.; monomer conversion, > 99 % (determined by ^{1}H NMR in $CDCl_3$). [b] Calculated by $[n\text{BA}]_0/[\text{I}]_0$ × conv × (MW of *n*BA, 128.17) + (MW of initiator residue: FI-OH, 132.16; FI-C≡CH, 168.23; FI-CH=CH_2, 100.12; FI-NB, 194.27). [c] Determined by SEC in THF using PMMA standards. [e] $[n\text{BA}]_0$, 2.0 mol L^{-1}; $[Me_3SiNTf_2]_0/[\text{FI}]_0$, 0.10. [f] Not determined due to the extremely small signals of terminal groups.

In the ^{1}H NMR spectrum of the polymer obtained using FI-OH (run 1), the characteristic signals due to the initiator residue of FI-OH were observed in the range from 4.19 to 3.81 ppm, which was attributed to the hydroxyl methylene (*i*) and the ester methylene (*h*) protons as shown in Figure 4-1(a). Furthermore, the signals due to the ester methylene (*c*), methylene (*b*), and methine (*a*) protons in the main-chain of P*n*BA were observed at 4.05, 2.30, and 1.90-1.30 ppm, respectively. Similarly, the initiator residues were also confirmed together with the main-chain of P*n*BA; the signals at 1.94 ppm due to the ethynyl methine proton (*j*) for FI-C≡CH, at 5.20 - 5.05 ppm due to the terminal olefin protons (*l* and *m*) for FI-CH=CH_2, and at 6.09, 2.85-2.68, and 1.15 ppm due to the methine protons (*p*) of the norbornenyl double bond, norbornenyl methine (*o*), and methyl (*g*) protons for FI-NB, as shown in Figures 4-1(b), (c), and (d), respectively. These results strongly indicated that every P*n*BA possessed the initiator residues that originated from FI-OH, FI-C≡CH, FI-CH=CH_2, and FI-NB.

In order to provide a more detailed insight into the polymer structure, we used matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). For the polymer obtained using FI-OH, the MALDI-TOF MS spectrum exhibited only one population of molecular ion peaks, as shown in Figure 4-2(a). The distance between two neighboring molecular ion peaks was 128.04 corresponding to the exact mass of *n*BA, 128.08, as the repeating unit. In addition, the *m*/*z* values of the observed molecular ion peaks corresponded to the calculated molecular weights of the P*n*BA bearing the hydroxyl moiety that originated from FI-OH ($C_{7n+6}H_{12n+12}O_{2n+3}Na$ = 128.08*n* + 132.08 + 22.99); for example, the observed value of 3356.02 agreed with the calculated value for the 25-mer structure of $[HOCH_2CH_2OC(O)C(CH_3)_2$-(*n*$BA)_{25}$-H + $Na]^+$ (3357.16). For the polymers obtained using FI-C≡CH, FI-CH=CH_2, and FI-NB, the observed *m*/*z* values were 3392.61, 3326.42, and

3421.07, respectively, which well agreed with the values calculated for the 25-mer of *n*BA with the ethynyl, vinyl, and norbornenyl groups in the α-chain end, respectively (Figure 4-2). The results definitely concluded that the obtained polymer structures were the α-hydroxyl-, α-ethynyl-, α-vinyl-, and α-norbornenyl-end-functionalized poly(*n*-butyl acrylate)s (HO-P*n*BA, HC≡C-P*n*BA, H_2C=CH-P*n*BA, and NB-P*n*BA, respectively). In addition, these functional groups together with their protecting groups retained their structures in the GTP process using Me_3SiNTf_2 from the organocatalyst.

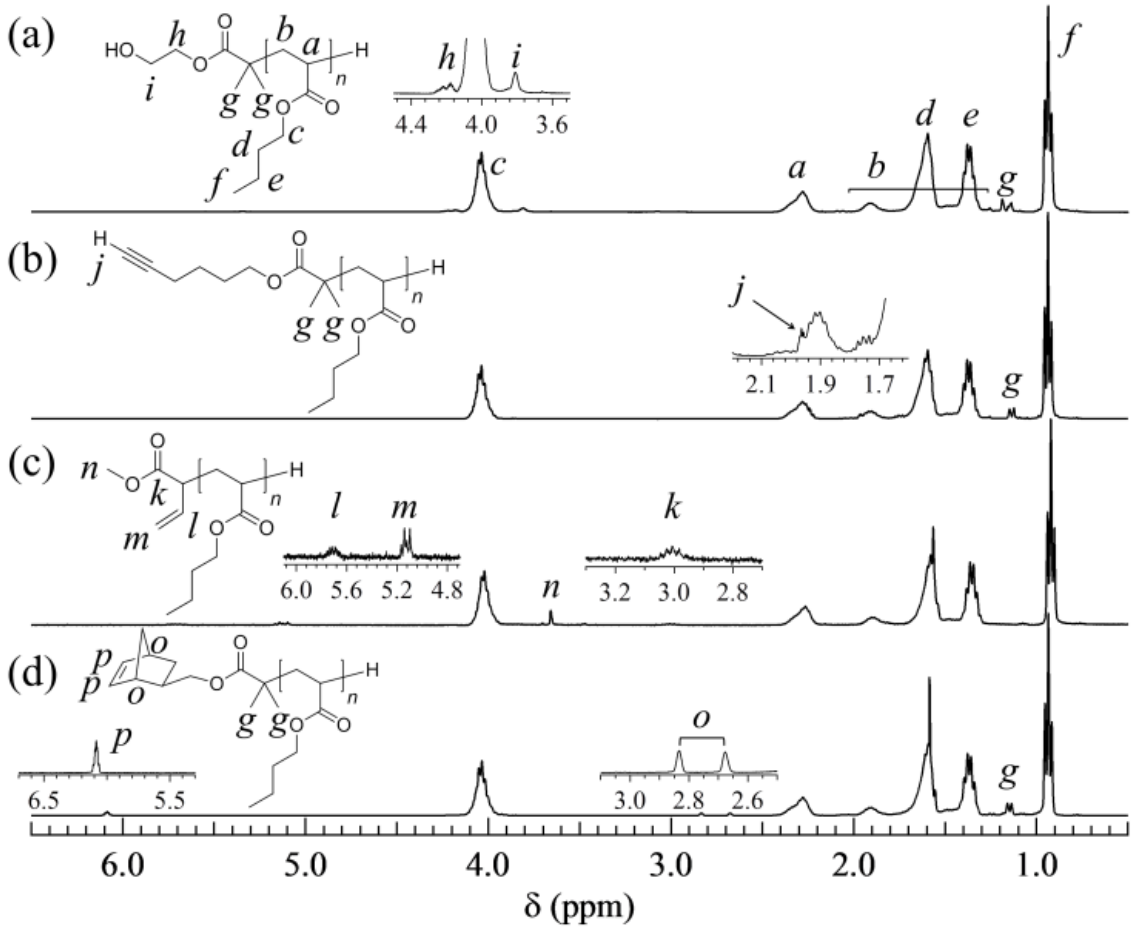


Figure 4-1. ^{1}H NMR spectra of (a) HO-P*n*BA, (b) HC≡C-P*n*BA, (c) H_2C=CH-P*n*BA, and (d) NB-P*n*BA prepared by the GTP of *n*BA using FI-OH, FI-C≡CH, FI-CH=CH_2, and FI-NB, respectively (solvent, $CDCl_3$).

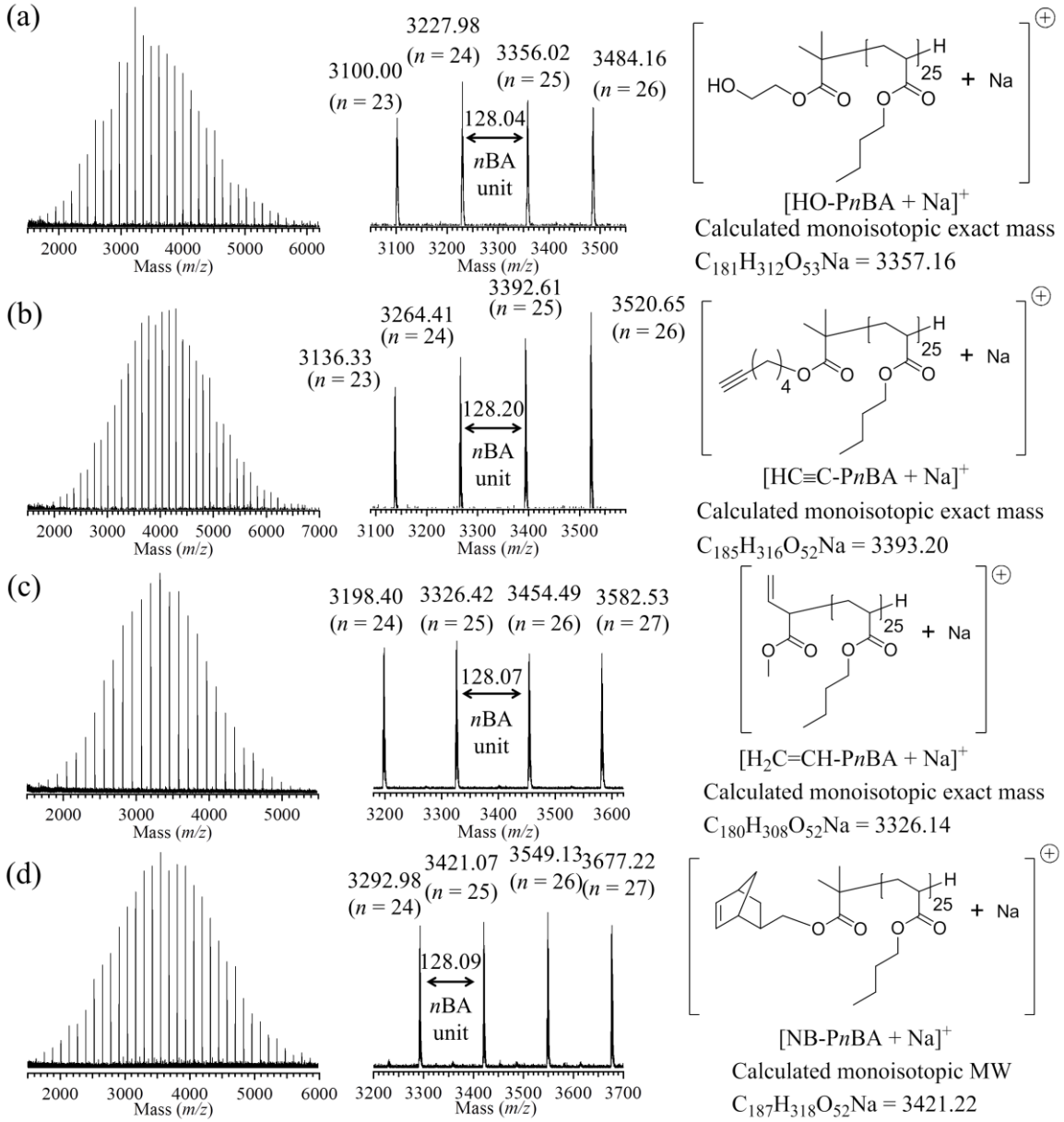


Figure 4-2. MALDI-TOF MS spectra of (a) HO-P*n*BA ($M_{n,NMR}$, 3.41 kg mol^{-1} and M_w/M_n, 1.10), (b) HC≡C-P*n*BA ($M_{n,NMR}$, 3.69 kg mol^{-1} and M_w/M_n, 1.10), (c) H_2C=CH-P*n*BA ($M_{n,NMR}$, 3.48 kg mol^{-1} and M_w/M_n, 1.07), and (d) NB-P*n*BA ($M_{n,NMR}$, 3.57 kg mol^{-1} and M_w/M_n, 1.10).

The Me_3SiNTf_2-catalyzed GTP of *n*BA initiated by FIs was utilized for preparing the α-end-functionalized *n*BAs with the targeted molecular weights. The polymerizations using FI-OH, FI-C≡CH, FI-CH=CH_2, and FI-NB were carried out under the conditions of $[n\text{BA}]_0/[\text{FI}]_0$s of 50, 100, 200, 400, and 1000. The polymerization results for the $[n\text{BA}]_0/[\text{FI}]_0$s of 50, 100, 200, and 400 and that of 1000 are listed in Table 4-1, respectively. The characteristic signals due to the α-end functional groups in the obtained P*n*BAs were confirmed by the ^{1}H NMR spectra. The SEC traces of the obtained polymers shifted to the higher molecular weight region with the increasing $[n\text{BA}]_0/[\text{FI}]_0$ ratio, as shown in Figure 4-3. In addition, all the obtained P*n*BAs showed monomodal molecular weight distributions and their polydispersities were as low as the M_w/M_ns of 1.02-1.05 for HO-P*n*BA, 1.03-1.08 for HC≡C-P*n*BA, 1.02-1.07 for H_2C=CH-P*n*BA, and 1.02-1.05 for NB-P*n*BA. The $M_{n,SEC}$s increased with the increasing $[n\text{BA}]_0/[\text{FI}]_0$ ratio, which agreed with the $M_{n,calcd.}$ values. Importantly, the polymerization time increased with the increasing $[n\text{BA}]_0/[\text{FI}]_0$ ratio, and the polymerizations with the $[n\text{BA}]_0/[\text{FI}]_0$ of 1000 required the polymerization time of 5 h. However, these polymerizations were well controlled to afford end-functionalized P*n*BAs with the high-molecular-weights of 119 000 − 142 700 g mol^{-1} and low polydispersities of 1.03-1.08 (Table 4-1; runs 6, 12, 18, and 24). These results indicated that the α-end-functional groups that originated from the FIs were tolerant throughout the Me_3SiNTf_2-catalyzed GTP process.

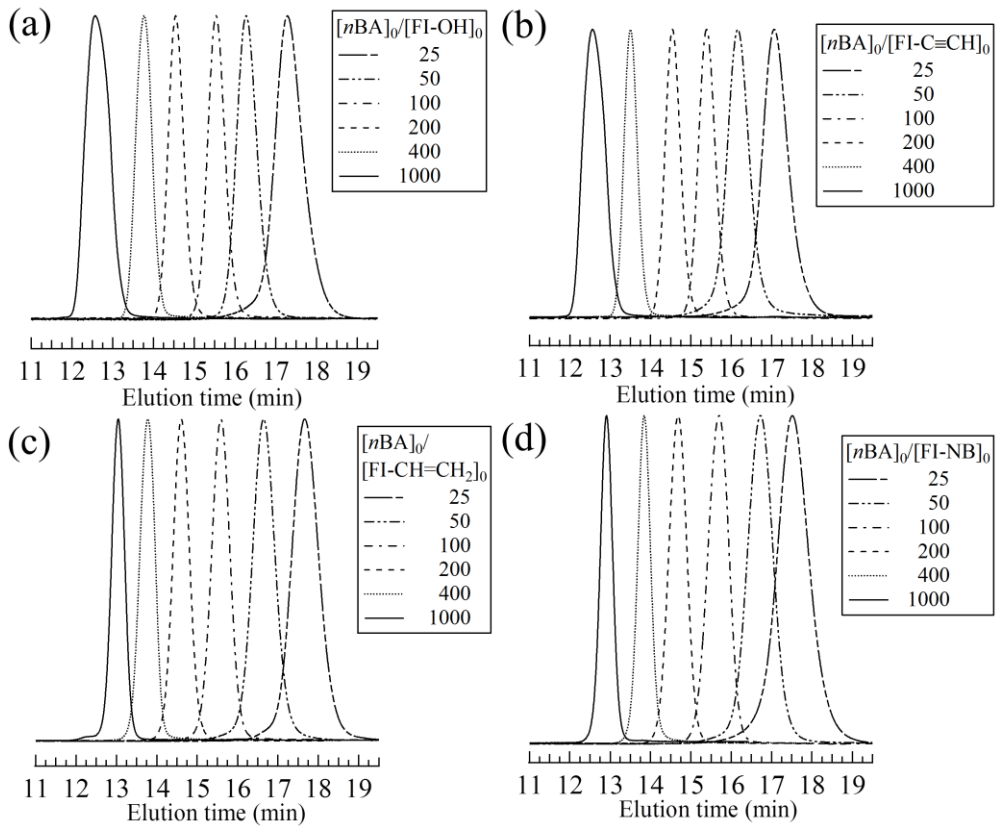


Figure 4-3. SEC traces of (a) HO-P*n*BA, (b) HC≡C-P*n*BA, (c) H_2C=CH-P*n*BA, and (d) NB-P*n*BA obtained from GTP of *n*BA using functional initiators (eluent, THF; flow rate, 1.0 mL min^{-1}).

4.3.2 Synthesis of ω-End-Functionalized P*n*BAs using Functional Terminators

In order to synthesize the ω-end-functionalized P*n*BA based on the termination approach, the termination reaction was examined using acrylic compounds for the Me_3SiNTf_2-catalyzed GTP of *n*BA. We utilized *N*,*N*-dimethylmethacrylamide (DMMAm), dimethyl itaconate (DMIt), methyl methacrylate (MMA), and methyl 2-phenylacrylate (MPhA) as the terminator (T), as shown in Chart 4-1, because the polymerization of these acrylic compounds hardly proceeded for the Me_3SiNTf_2-catalyzed GTP with 1-methoxy-1-triisopropylsiloxy-2-methy-1-propene (MTS^{iPr}) as the initiator, which was the

suitable system for alkyl acrylates. Table 4-2 summarizes the results for the termination reaction of the Me_3SiNTf_2-catalyzed GTP of *n*BA with initiator in toluene at room temperature for the $[n\text{BA}]_0/[\text{MTS}^{i\text{Pr}}]_0/[Me_3SiNTf_2]_0$ of 25/1/0.02. After all the monomer was consumed in 3 min, the polymerization was terminated by adding the terminators of DMMAm, DMIt, MMA, and MPhA with the $[\text{T}]_0/[\text{MTS}^{i\text{Pr}}]_0$ of 5. All the polymerizations were well controlled to produce polymers with predicted molecular weights and narrow polydispersities. For the obtained polymers, the degree of ω-end-functionalization (F_n) was determined using the ^{1}H NMR spectra, and the detailed structures involving their chain ends were estimated using the MALDI-TOF MS measurements. No termination reaction occurred using DMMAm, i.e., $F_n = 0$, because no characteristic signal due to the residue origining from DMMAm was observed in the ^{1}H NMR spectrum (Figure 4-4(a)) and the structure of the P*n*BA without any ω-end-functional group was also confirmed by the MALDI-TOF MS measurement (Figure 4-5(a)). This result indicated that none of DMMAm had reacted with the triisopropylsilyl ketene acetal unit in the polymer chain-end because the silyl ketene amide was the suitable initiator and propagating chain-end for the GTP of *N*,*N*-dialkylacrylamide compared with the silyl ketene acetal. DMIt acted poorly as the terminator to afford the mixture consisting of P*n*BAs with and without the terminator residues, which were estimated by the ^{1}H NMR spectrum (Figure 4-4(b)) and the MALDI-TOF MS spectrum (Figure 4-5(b)); the F_n was 0.29. The Me_3SiNTf_2-catalyzed GTP of DMIt using $\text{MTS}^{i\text{Pr}}$ insufficiently proceeded, which should cause the low F_n. Although the F_n was up to 0.99 using MMA based on the ^{1}H NMR spectrum (Figure 4-4(c)), the termination reaction proceeded with one and two units of MMA to afford the P*n*BAs with the monomeric and dimeric units of MMA as the ω-end groups, respectively, as shown in the MALDI-TOF MS spectrum (Figure 4-5(c)). On the other hand, the signals due to the phenyl protons of the

MPhA unit were clearly observed at 7.30-7.20 ppm in the ^{1}H NMR spectrum (Figure 4-4(d)), and the observed *m/z* value of 3362.69 well agreed with the predicted value of 3362.14 for the 24-mer of *n*BA possessing a MPhA unit as the ω-end functional group, as shown in the MALDI-TOF MS spectrum (Figure 4-5(d)). The results strongly indicated that MPhA had quantitatively terminated the Me_3SiNTf_2-catalyzed GTP of *n*BA, i.e., the F_n was up to 0.99. Quirk and coworkers previously reported that MPhA acted as the terminator for the conventional GTP of MMA at room temperature, which was caused by the low ceiling temperature of MPhA.[28,33] Similarly, we found that MPhA was also the suitable terminator for the organocatalytic GTP of the acrylate monomer to afford end-functionalized acrylate polymers with well-defined structures.

Chart 4-1. Terminators for the Me_3SiNTf_2-Catalyzed GTP of *n*BA

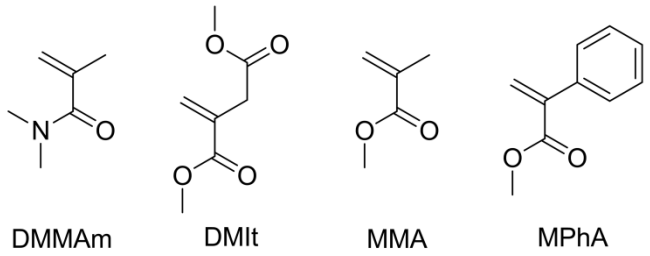


Table 4-2. Termination Reaction for the Me_3SiNTf_2-Catalyzed GTP of *n*BA with 1-Methoxy-1-triisopropylsiloxy-2-methy-1-propene (MTS^{iPr}) using DMMAm, DMIt, MMA, and MPhA [a]

run	terminator (T)	$M_{n,calcd.}$ [b] / g mol^{-1}	$M_{n,NMR}$ [c] / g mol^{-1}	$M_{n,SEC}$ [d] / g mol^{-1}	M_w/M_n [d]	F_n [e]
25	DMMAm	3 420	3 620	4 110	1.07	0
26	DMIt	3 460	3 800	4 480	1.08	0.29
27	MMA	3 410	3 460	4 080	1.08	> 0.99
28	MPhA	3 470	3 810	4 370	1.11	> 0.99

[a] Argon atmosphere; solvent, toluene; $[n\text{BA}]_0$, 1.0 mol L^{-1}; $[n\text{BA}]_0/[MTS^{iPr}]_0/[Me_3SiNTf_2]_0/[T]_0$, 25/1/0.02/5; temperature, room temp; polymerization time, 3min; monomer conversion, > 99 % (determined by ^{1}H NMR in $CDCl_3$); termination reaction time, 24 h. [b] Calculated by $[n\text{BA}]_0/[MTS^{iPr}]_0$ × conv × (MW of *n*BA, 128.17) + (MW of initiator residue, 102.13) + (MW of terminator residue; DMMAm, 113.16; DMIt, 158.15; MMA, 100.12; MPhA, 162.19). [c] Determined by ^{1}H NMR measurements. [d] Determined by SEC in THF using PMMA standards. [e] Determined by ^{1}H NMR and intensity of MALDI-TOF MS spectrum.

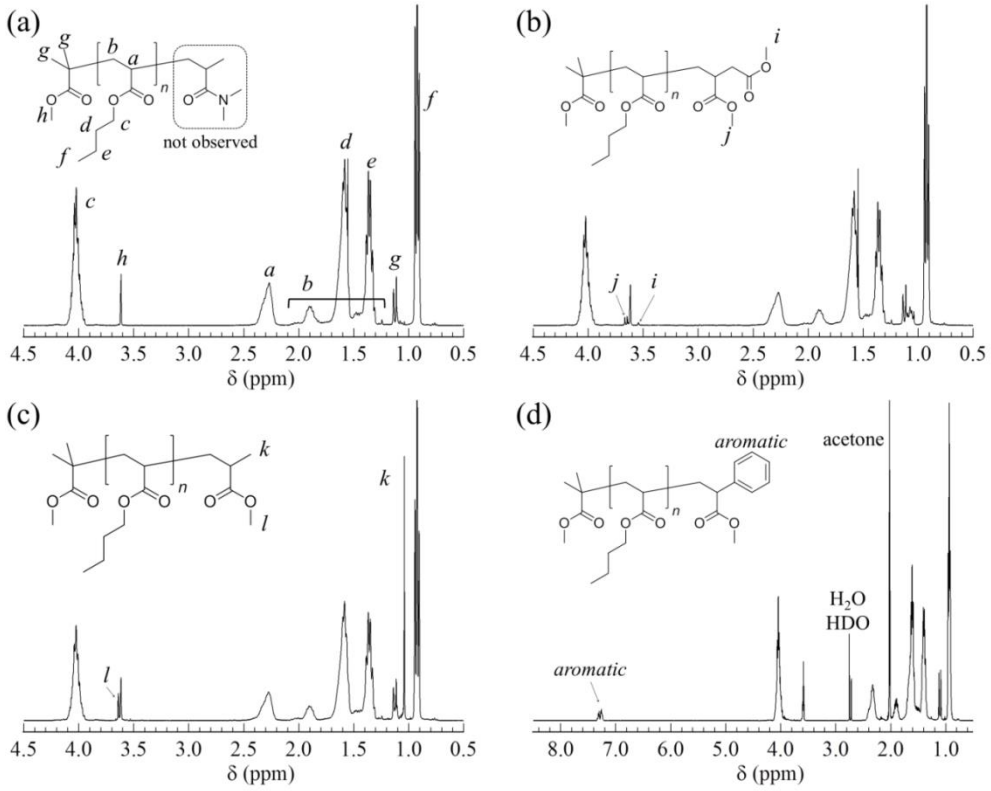


Figure 4-4. ^{1}H NMR spectra of the ω-functionalized P*n*BA obtained from termination with (a) DMMAm, (b) DMIt, (c) MMA, and (d) MPhA (solvent: (a), (b), and (d), $CDCl_3$; (d), acetone-d_6).

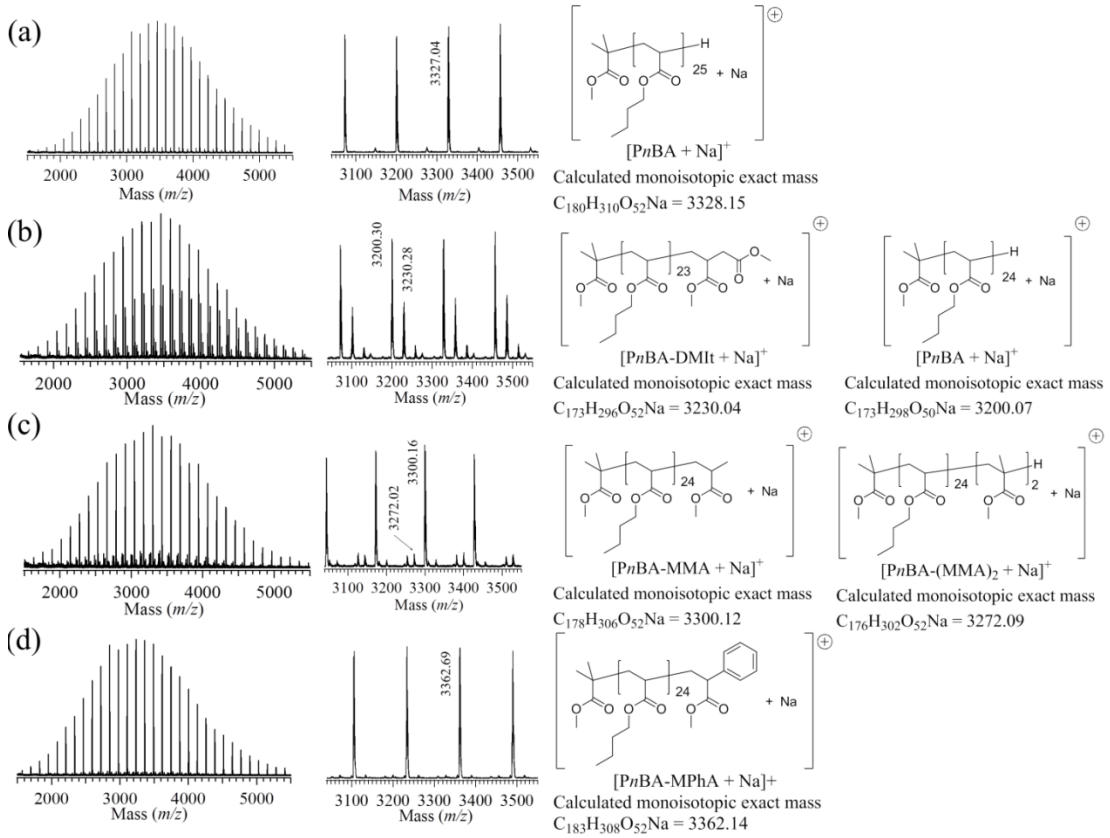


Figure 4-5. MALDI-TOF MS spectra of the obtained P*n*BA using (a) DMMAm, (b) DMIt, (c) MMA, and (d) MPhA as terminating agents for the Me_3SiNTf_2-catalyzed GTP of *n*BA.

For the synthesis of the ω-end-functionalized P*n*BAs based on the termination approach, 4-trimethylsilyl-3-butynyl, 3-butenyl, 2-(*tert*-butyldimethylsiloxy)ethyl, and 2-bromoethyl 2-phenylacrylates (FT-C≡CH, FT-CH=CH_2, FT-OH, and FT-Br, respectively) were used as the functional terminators (FTs) for the Me_3SiNTf_2-catalyzed GTP of *n*BA with MTS^{iPr} under the condition for $[n\text{BA}]_0/[MTS^{iPr}]_0/[Me_3SiNTf_2]_0/[FT]_0$ of 25/1/0.02/5 in toluene at room temperature. All the polymerizations produced well-defined P*n*BAs with predicted $M_{n,NMR}$s and narrow M_w/M_ns, as listed in Table 4-3. For all the obtained P*n*BAs, the characteristic

signals due to the phenyl protons that originated from the FTs were observed at 7.35-7.20 ppm along with the signals at 4.05, 2.35, 1.90-1.30 ppm due to the P*n*BA main chain, as shown in the ^{1}H NMR spectra (Figure 4-6). In addition, the signals attributed to the methylene protons (*i*) adjacent to the ethynyl group appeared at 2.51 ppm for the P*n*BA using FT-C≡CH (run 29), those to the vinyl protons (*j* and *k*) at 6.00-4.80 ppm using FT-CH=CH_2 (run 32), those to the hydroxyl methylene protons (*l*) at 3.65 ppm using FT-OH (run 35), and those to the ethylene proton of the ω-ester and the bromoethylene protons (*m* and *n*) at 4.22 and 3.62 ppm using FT-Br (run 38; Figure 4-6(a), (b), (c), and (d), respectively). For the MALDI-TOF MS spectra of the P*n*BAs obtained using FT-C≡CH, FT-CH=CH_2, and FT-OH (Figure 4-7), only one series of peaks was observed and the difference in the *m/z* value between two neighboring molecular ion peaks was 128.04, which corresponded to the exact mass of *n*BA. In addition, the observed *m/z* values of 3913.26, 3274.47, and 3633.56 well agreed with the calculated molecular weight for the 28-mer of *n*BA with FT-C≡CH, that for the 23-mer with FT-CH=CH_2, and that for the 25-mer of *n*BA with FT-OH before deprotection, respectively. For the P*n*BA obtained using FT-Br, two series of peaks denoted by ▲ and ∆ were assigned to the P*n*BAs with the bromoethyl and vinyl groups, respectively, which were produced by the elimination of hydrogen bromide from the bromoethyl groups during the MALDI-TOF MS measurement though both series had a regular interval of 128.04 corresponding to the *n*BA repeating unit.[34] In addition, the termination approach was efficient for preparing these ω-end-functionalized P*n*BAs with targeted molecular weights. Table 4-3 also summarizes the results for the Me_3SiNTf_2-catalyzed GTP of *n*BA with an initiator under the conditions with the $[n\text{BA}]_0/[\text{MTS}^{i\text{Pr}}]_0$s of 100 and 400. All the polymerizations were well controlled to produce P*n*BAs with molecular weights predicted by the $[n\text{BA}]_0/[\text{MTS}^{i\text{Pr}}]_0$ and narrow molecular weight distributions. The quantitative termination reaction for the GTP of

*n*BA was confirmed by the characteristic signals due to the ω-end functional groups in the ^{1}H NMR spectra of the obtained P*n*BAs. These results firmly indicated that the functional groups of the FTs caused no side reaction to quantitatively afford the ω-end-functionalized P*n*BAs with the ethynyl, vinyl, hydroxyl, and bromide groups, i.e., P*n*BA-C≡CH, P*n*BA-CH=CH_2, P*n*BA-OH, and P*n*BA-Br, respectively.

Table 4-3. Synthesis of ω-End-Functionalized P*n*BAs by GTP of *n*BA with 1-Methoxy-1-triisopropylsiloxy-2-methy-1-propene (MTS^{iPr}) using FT-C≡CH, FT-CH=CH_2, FT-OH, and FT-Br [a]

run	functional terminator (FT)	$[n\text{BA}]_0/[MTS^{iPr}]_0$ /$[Me_3SiNTf_2]_0$	time / min	$M_{n,calcd}$ [b] / g mol^{-1}	$M_{n,SEC}$ [c] ($M_{n,NMR}$)[b] / g mol^{-1}	M_w/M_n [c]
29	FT-C≡CH	25/1/0.02	3	3 400	4 900 (3 800)	1.06
30	FT-C≡CH	100/1/0.02	30	13 400	13 500	1.03
31	FT-C≡CH	400/1/0.10	60	51 800	58 100	1.03
32	FT-CH=CH_2	25/1/0.02	3	3 400	4 200 (3 600)	1.08
33	FT-CH=CH_2	100/1/0.02	30	13 300	13 900	1.03
34	FT-CH=CH_2	400/1/0.10	60	51 700	54 200	1.03
35	FT-OH	25/1/0.02	3	3 400	4 400 (3 700)	1.08
36	FT-OH	100/1/0.02	30	13 400	13 900	1.02
37	FT-OH	400/1/0.10	60	51 800	54 100	1.03
38	FT-Br	25/1/0.02	3	3 500	4 000 (3 800)	1.07
39	FT-Br	100/1/0.02	30	13 400	13 600	1.03
40	FT-Br	400/1/0.10	60	51 800	52 900	1.03

[a] Argon atmosphere; solvent, toluene; $[n\text{BA}]_0$, 1.0 mol L^{-1}; $[FT]_0/[MTS^{iPr}]_0$, 5; temperature, room temp; monomer conversion, > 99 % (determined by ^{1}H NMR in $CDCl_3$); termination reaction time, 24 hours; *Fn* > 99 % (determined by ^{1}H NMR and MALDI-TOF MS spectrum). [b] Calculated by $[n\text{BA}]_0/[MTS^{iPr}]_0$ × conv × (MW of *n*BA, 128.17) + (MW of initiator residue, 102.13) + (MW of terminator residue; FT-C≡CH, 200.23; FT-CH=CH_2, 202.25; FT-OH, 192.12; FT-Br, 255.11). [c] Determined by SEC in THF using PMMA standards.

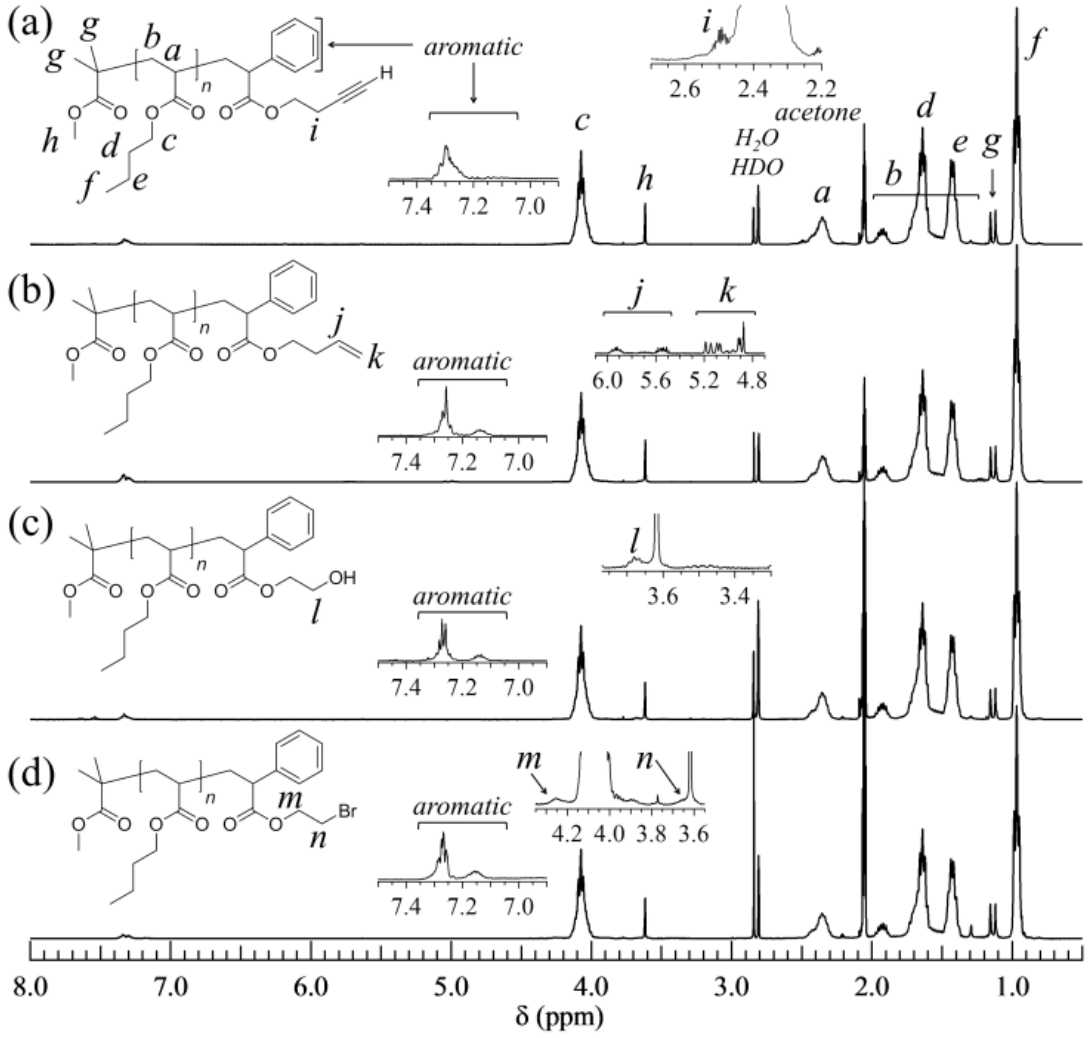


Figure 4-6. ^{1}H NMR spectrum of P*n*BAs obtained from GTP of *n*BA terminated by (a) FT-C≡CH, (b) FT-CH=CH_2, (c) FT-OH, and (d) FT-Br (solvent, acetone-d_6).

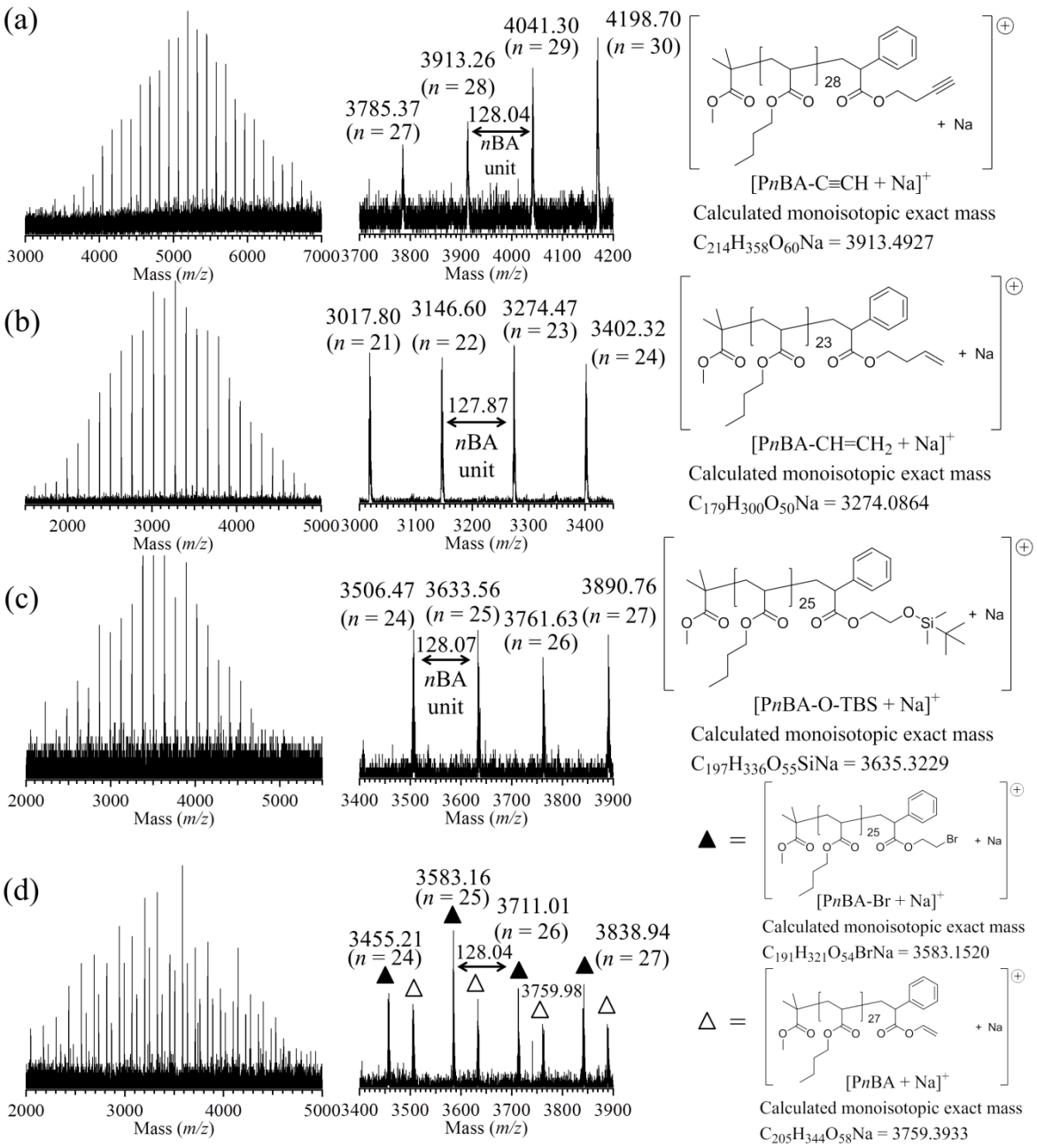


Figure 4-7. MALDI-TOF MS spectra of (a) P*n*BA-C≡CH ($M_{n,NMR}$, 3.76 kg mol^{-1} and M_w/M_n, 1.06), (b) P*n*BA-CH=CH$_2$ ($M_{n,NMR}$, 3.64 kg mol^{-1} and M_w/M_n, 1.10), (c) P*n*BA-OH with protecting group ($M_{n,NMR}$, 3.71 kg mol^{-1} and M_w/M_n, 1.07), and (d) P*n*BA-Br ($M_{n,NMR}$, 3.78 kg mol^{-1} and M_w/M_n, 1.10).

4.3.3 Synthesis of α,ω-End-Functionalized P*n*BAs using Functional Initiator and Terminator

We finally focused on the synthesis of the α,ω-end-functionalized P*n*BAs using the initiation approach coupled with the termination approach, i.e., telechelic and hetero telechelic P*n*BAs were synthesized by the Me_3SiNTf_2-catalyzed GTP of *n*BA using FIs and FTs, as shown in Scheme 4-3. The polymerizations were initiated by FI-C≡CH and FI-OH and sequentially terminated by FT-C≡CH and FT-OH to produce well-defined P*n*BAs, as listed in Table 4-4. For the polymerizations using the combinations of FI-C≡CH and FT-C≡CH (run 41) and FI-OH and FT-OH (run 42), the obtained polymers possessed the $M_{n,NMR}$s of 3790 and 3670 g mol^{-1} corresponding to the $M_{n,calcd.}$s 3570 and 3530 g mol^{-1}, respectively, and their polydispersities were narrow with the M_w/M_ns of 1.08 and 1.10, respectively. The characteristic signals due to the ethynyl and methylene protons adjacent to the ethynyl group appeared at 1.95 and 2.48 ppm for the polymer of run 41 and those due to the α-hydroxyl and ω-hydroxyl methylene protons at 3.70 and 3.65 ppm for the polymer of run 42 in their ^{1}H NMR spectra (Figures 4-8 (a) and (b), respectively). The polymer structures of the P*n*BAs with the diethynyl and dihydroxyl groups were also confirmed by the MALDI-TOF MS measurements, in which one series of peaks was observed and the *m/z* values of each observed peak corresponded to the molecular weights of the α,ω-diethynyl-functionalized P*n*BA (HC≡C-P*n*BA-C≡CH) and α,ω-dihydroxyl-functionalized P*n*BA (HO-P*n*BA-OH) in Figures 4-9(a) and (b), respectively. In addition, the polymerization using FI-OH and FT-C≡CH (run 43) was controlled to produce the P*n*BA with the predicted molecular weight of 3690 g mol^{-1} and the low polydispersity of 1.08, whose well-defined structure with the α-hydroxyl and ω-ethynyl functional groups was confirmed by the ^{1}H NMR and MALDI-TOF MS measurements; the

methylene protons (*l* and *m*) adjacent to the hydroxyl and ethynyl groups were observed at 3.70 and 2.50 ppm, respectively (Figure 4-8(c)), and one series of peaks consisted of the *m/z* values predicted by the structure of the α-hydroxyl, ω-ethynyl-functionalized P*n*BA (HO-P*n*BA-C≡CH) (Figure 4-9(c)). These results indicated that the functionalization of both chain ends in P*n*BA using FIs and FTs quantitatively proceeded to produce the α,ω-end-functionalized P*n*BAs as telechelic and hetero telechelic polymers.

Scheme 4-3. Synthesis of α,ω-End-Functionalized P*n*BAs by GTP of *n*BA using Functional Initiators (FIs) and Terminators (FTs)

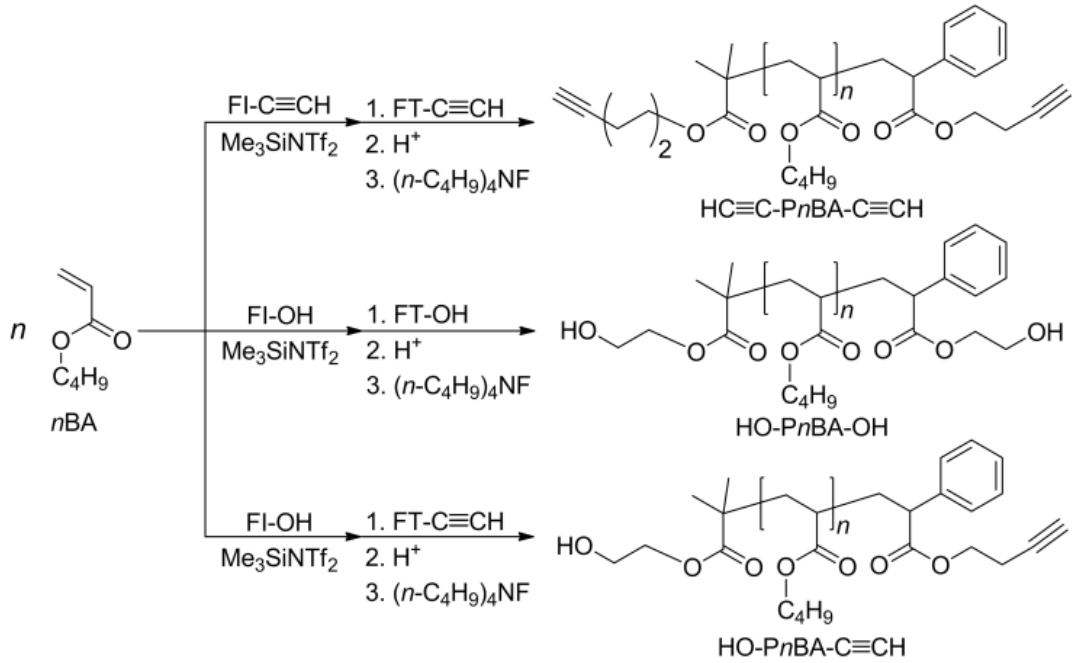


Table 4-4. Synthesis of α,ω-End-Functionalized P*n*BAs by Me_3SiNTf_2-Catalyzed GTP of *n*BA Initiated by FI-C≡CH and FI-OH and Terminated by FT-C≡CH and FT-OH [a]

run	functional initiator (FI)	functional terminator (FT)	$M_{n,calcd.}$ [b] / g mol^{-1}	$M_{n,NMR}$ [c] / g mol^{-1}	$M_{n,SEC}$ [d] / g mol^{-1}	M_w/M_n [d]
41	FI-C≡CH	FT-C≡CH	3 570	3 790	4 910	1.08
42	FI-OH	FT-OH	3 530	3 670	4 380	1.10
43	FI-OH	FT-C≡CH	3 540	3 690	4 240	1.08

[a] Argon atmosphere; solvent, toluene; temperature, room temp.; $[n\text{BA}]_0$, 1.0 mol L^{-1}; $[n\text{BA}]_0/[\text{FI}]_0/[Me_3SiNTf_2]_0/[\text{FT}]_0$, 25/1/0.05/5; polymerization time, 3 min; monomer conversion, > 99 % (determined by ^{1}H NMR in $CDCl_3$); termination time, 24 h. [b] Calculated by $[n\text{BA}]_0/[\text{FI}]_0$ × conv × (MW of *n*BA, 128.17) + (MW of initiator residue; FI-OH, 132.16; FI-C≡CH, 168.23) + (MW of terminator residue: FT-C≡CH, 200.23; FT-OH, 192.12). [c] Determined by ^{1}H NMR measurement. [d] Determined by SEC in THF using PMMA standards.

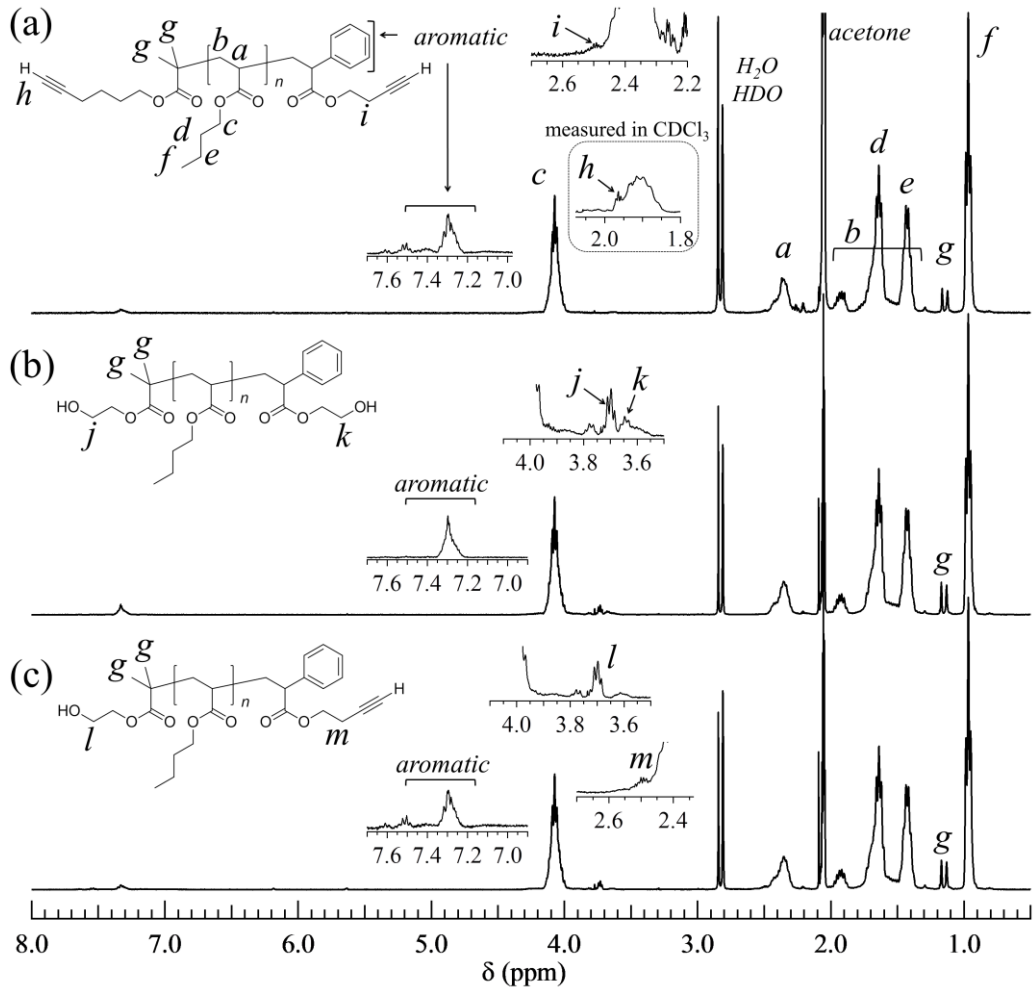


Figure 4-8. ^{1}H NMR spectrum of the P*n*BAs obtained from GTP of *n*BA using functional initiator and terminator (a) FI-C≡CH and FT-C≡CH, (b) FI-OH and FT-OH, and (c) FI-OH and FT-C≡CH, (solvent, acetone-d_6).

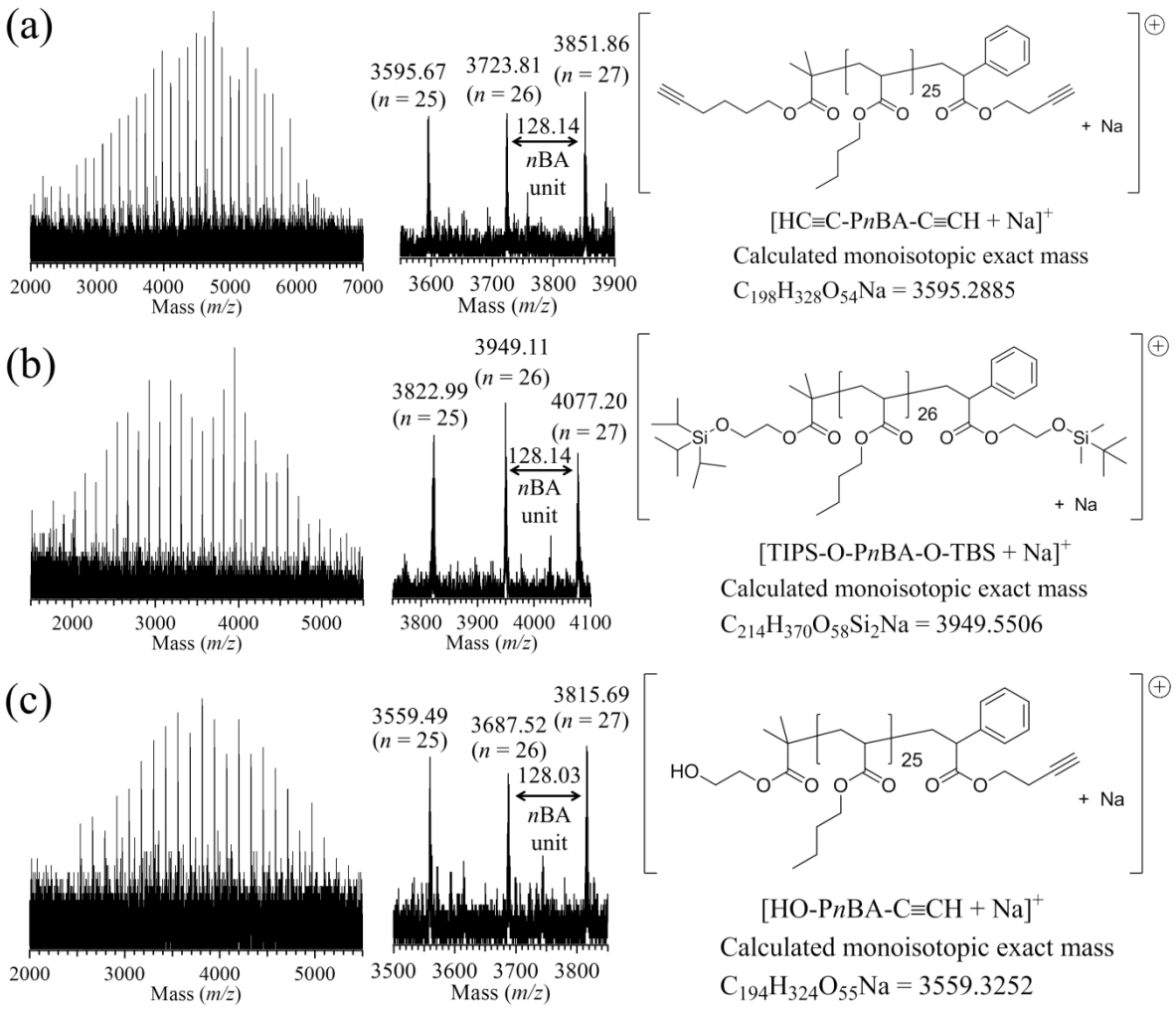


Figure 4-9. MALDI-TOF MS spectra of (a) HC≡C-P*n*BA-C≡CH, (b) HO-P*n*BA-OH with protecting group, and (c) HO-P*n*BA-C≡CH.

4.4 Conclusions

The precise syntheses of the α-, ω-, and α,ω-end-functionalized poly(*n*-butyl acrylate)s (P*n*BAs) have been accomplished by the initiation and termination approaches based on the group transfer polymerization (GTP) of *n*-butyl acrylate (*n*BA) using the organocatalyst of *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNT_2). For the initiation approach, the triisopropylsilyl ketene acetals with hydroxyl, ethynyl, vinyl, and norbornenyl groups acted as the suitable GTP initiator to produce the corresponding α-end-functionalized P*n*BAs. For the GTP using the functional terminators of the 2-phenylacrylates, the termination reaction quantitatively proceeded to produce the ω-end-functionalized P*n*BAs with ethynyl, vinyl, hydroxyl, and bromide groups. In addition, the simultaneous functionalizations of the α- and ω-polymer chain-ends were achieved by the GTP initiated by the functional initiators and subsequently terminated by the functional terminators. The efficiency of the initiation and termination reactions was extremely high, resulting in the production of well-defined polymers possessing desirable molecular weights predicted by the molar ratio of *n*BA and the initiator. The organocatalytic GTP is quite suitable for the controlled/living polymerization of alkyl acrylates, in which Me_3SiNT_2 efficiently activated the acrylate monomers, the triisopropylsilyl ketene acetal as the functional initiator, and the polymer chain-end is sufficiently stable to initiate and propagate with the activated acrylate monomers, and the stable polymer chain-end was definitely terminated by the 2-phenylacrylates. The telechelic and hetero telechelic polyacrylates possessing the hydroxyl, ethynyl, vinyl, norbornenyl, and bromo end-functional groups should be utilized as building blocks for constructing macromolecular architectures, such as block, cyclic, star-shaped, and dendritic polymers. Therefore, of great importance is to clarify the scope and limit of the synthetic method for the end-functionalization of the polymers based on the GTP process, thus the author have studied how to expand the applicable

functional initiators and terminators in relation to the applicable monomers and organocatalysts. To the best of our knowledge, these achievements showed the first reliable demonstration of the precise synthesis of end-functionalized acrylate polymers using the GTP process as one of the living anionic polymerization methods.

4.5 References and Note

(1) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921-2990.

(2) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661-3688.

(3) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93-146.

(4) Ouchi, M.; Terashima, T.; Sawamoto, M. *Chem. Rev.* **2009**, *109*, 4963-5050.

(5) Coessens, V.; Pintauer, T.; Matyjaszewski. K. *Plog. Polym. Sci.* **2001**, *26*, 337-377.

(6) Hayashi, M.; Hirao, A. *Macromol. Chem. Phys.* **2001**, *202*, 1717-1726.

(7) Mori, H.; Müller, A. H. E. *Prog. Polym. Sci.* **2003**, *28*, 1403-1439.

(8) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Mays, J. *Prog. Polym. Sci.* **2006**, *31*, 1068-1132.

(9) Higashihara, T.; Hayashi, M.; Hirao, A. *Prog.Polym. Sci.* **2011**, *36*, 323-375.

(10) Baskaran, D. *Prog. Polym. Sci.* **2003**, *28*, 521-581.

(11) Baskaran, D.; Müller, A. H. E. *Prog. Polym. Sci.* **2007**, *32*, 173-219.

(12) Janata, M.; Lochmann, L.; Müller, A. H. E. *Makromol. Chem.* **1990**, *191*, 2253-2260.

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

(14) Hertler, W. R.; Sogah, D. Y.; Webster, O. W. *Macromolecules* **1984**, *17*, 1415-1417.

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

(16) Janata, M.; Lochmann, L.; Vlček, P.; Dybal, J.; Müller, A. H. E. *Makromol. Chem.* **1992**, *193*, 101-112.

(17) Janata, M.; Lochmann, L.; Müller, A. H. E. *Makromol. Chem.* **1993**, *194*, 625-636.

(18) Ishizone, T.; Yoshimura, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1998**, *31*, 8706-8712.

(19) Ishizone, T.; Yoshimura, K.; Yanase, E.; Nakahama, S. *Macromolecules* **1999**, *32*, 955-957.

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

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

(22) Raynaud, J.; Gnanou, Y.; Taton, D. *Macromolecules* **2009**, 4*2*, 5996-6005.

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

(24) Raynaud, J.; Liu, N.; Fèvre, M.; Gnanou, Y. Taton, D. *Polym. Chem.* **2011**, *2*, 1706-1712.

(25) Takada, K.; Fuchise, K.; Chen, Y.; Satoh, T.; Kakuchi, T. *J. Polym. Sci., Part A, Polym. Chem.* **2012**, *50*, 3560-3566.

(26) Fuchise, K.; Chen, Y.; Satoh, T.; Kakuchi, T. *Polym. Chem.* **2013**, *4*, 4278-4291.

(27) Sogah, D. Y.; Webster, O. W. *J. Polym. Sci. Polym. Lett. Ed.***1983**, *21*, 927-931.

(28) Quirk, R. P.; Ren, J. *Polym. Int.* **1993**, *32*, 205-212.

(29) Gnaneshwar, R.; Sivaram, S. *J. Polym. Sci. Part A. Polym. Chem.* **2007**, *45*, 2514-2531.

(30) Liu, S.-Y.; Hills, I. D.; Fu, G. *J. Am. Chem. Soc.* **2005**, *127*, 15352-15353.

(31) Zha, Y; Disab-Miller, M. L.; Johnson, Z. D.; Hickner, M. A.; Tew, G. N. *J. Am. Chem. Soc.* **2012**, *134*, 4493-4496.

(32) Ratjen, L.; García-García, P.; Lay, F.; Beck, M. E.; List, B. *Angew. Chem. Int. Ed.* **2011**, *50*, 754-758.

(33) Hoppf, H.; Lussi, H.; Borla, L. *Makromol. Chem.* **1965**, *81*, 268.

(34) Kim, K.; Hasneen, A.; Paik, H.-J.; Chang, T. *Polymer*, **2013**, *54*, 6133-6139.

Chapter 5

Synthesis of Star-Shaped Acrylate Polymers by Core-First Group Transfer Polymerizaton using Organocatalyst

5.1 Introduction

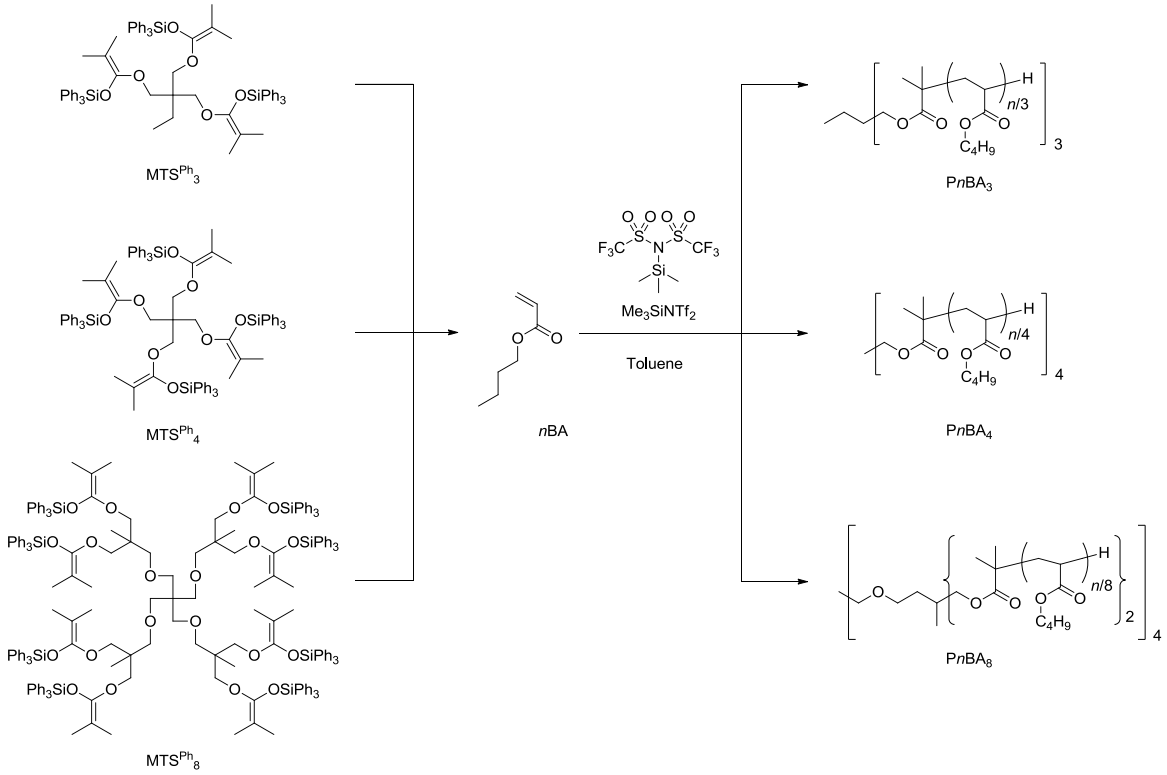
Star-shaped, dendritic, and hyperbranched polymers are famous for displaying a low hydrodynamic volume and low viscosity in solution which exhibit unique properties.[1,2] The star polymers consist of several identical linear chains linked to a central core, and the recent development in the controlled/living anionic and radical polymerization has enabled the preparation of well-defined polymers.[3-5] The synthesis of well-defined star polymers has been studied by the following three general synthetic methods: 1) the core-first living polymerization, 2) the arm-first living polymerization, and 3) the linking reaction with living polymers by radical/anionic polymerization processes. However, the anionic polymerization processes require severe reaction condition and complicated synthetic processes to prevent the interaction of each active chain end, backbiting reaction, and more. In addition, the synthesis of the star-shaped polymers by the living radical polymerization was disturbed by the coupling reaction of the inter/intra molecules based on the radical spiecies of the propagating chain ends. Thus, it is necessary to establish a method for the precise synthesis of star-shaped polymers by the controlled/living polymerization.

Group transfer polymerization (GTP) is a useful method for the polymerization of (meth)acrylate monomers which were reported by Webster and Sogah et al. in 1983.[6,7] Since they established the concept, there are many efforts to precisely control the polymerizations of (meth)acrylates,[8,9] acrylamides,[10] and (meth)acrylonitrile,[11] leading to well-defined polymers, and both Lewis bases and Lewis acids have been employed as catalysts.[12] The synthesis of star-shaped/branched methacrylate polymers was reported by several researchers.[13] For instance, Webster and Sogah et al. reported the star-shaped poly(ethyl acrylate) using three and four-armed initiators,[14] Wnek et al. investigated the core-first synthesis of the four-armed star-shaped poly(methyl methacrylates),[15] Patrikios et al. reported

the arm-first synthesis of various star-shaped methacrylate polymers using the bifunctional monomer, diacryloyl compound, as the linking agent,[16-20] and Kakuchi et al. reported the core-first synthesis of poly(methyl methacrylate) and poly(*N*,*N*-dimethylaminoethyl methacrylate) by organic superbases and acids.[21-23] However, the precise synthesis of the star-shaped acrylate polymer had never been reported using the GTP method. Thus, the precise synthesis of star-shaped acrylate polymers is a remaining task from the viewpoint of the living anionic polymerization involving the GTP method.

In this chapter, the author describes the synthesis of star-shaped acrylate polymers using the core-first approaches based on the organocatalytic GTP through the molecular design and synthesis of multifunctional initiators. The three-, four-, and eight-armed star-shaped poly(*n*-butyl acrylate)s (P*n*BAs) and various acrylate polymers were synthesized by the GTP of acrylates using polyvalent triphenylsilyl ketene acetals as the multifunctional initiators, in which *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNTf_2) is used as the organocatalyst, as shown in Scheme 5-1. The formation of star-shaped homo and copolymers were determined by size excretion chromatography measurements using THF. The obtained star-shaped polymer structures are confirmed based on the ^{1}H NMR measurements.

Scheme 5-1. Synthesis of Three-, Four-, and Eight-Armed Star-Shaped Poly(*n*-butyl acrylate)s, P*n*BA$_3$, P*n*BA$_4$, and P*n*BA$_8$ by the Me_3SiNTf_2-Catalyzed GTP of *n*BA Using Multifunctional Initiators



5.2 Experimental Section

Materials

Dichloromethane (CH_2Cl_2, >99.5%; water content, <0.001%), toluene (>99.5%; water content, <0.001%), tetrahydrofuran (THF, >99.5%; water content, <0.001%), triethylamine (>99.0%), methanol (>99.5%), and *tert*-butyl alcohol (>98.0%) were purchased from Kanto Chemicals Co., Inc. Methyl acrylate (MA, >99.8%), *n*-butyl acrylate (*n*BA, >99.0%), 2-ethylhexyl acrylate (EHA, 99.0%), 2-methoxyethyl acrylate (MEA, >98.0%), 2-hydroxyethyl acrylate (>95.0%), acrylic acid (>99.0%), acryloyl chloride (>95.0%), *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNTf_2, >95.0%), and triisopropylsilyl chloride (*i*PrSiCl) were purchased from Tokyo Kasei Kogyo Co., Ltd. MA, EA, *n*BA, MEA, and CH_2Cl_2 were distilled from CaH_2 and degassed by three freeze-pump-thaw cycles prior to their use. Toluene was distilled from sodium benzophenone ketyl. 1,1,1-Tris(isobutyryloxymethyl)propane (EtC(*i*Bu)$_3$), pentaerythritol tetraisobutyrate (C(*i*Bu)$_4$), 1-methoxy-1-triphenylsiloxy-2-methyl-1-propene (MTS^{Ph}), 2-(triisopropylsiloxy)ethyl acrylate (HEA-TIPS), and triisopropylsiloxy acrylate (TIPSA) were synthesized by previously reported procedures. A spectra/Por 6 membrane (molecular weight cutoff: 1000) was used for the dialysis. All other chemicals were purchased from available suppliers and used without purification.

Instruments

The ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a JEOL JNM-A400II, and a JEOL-ECS400. The polymerization solution was prepared in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves

and copper catalyst) in a dry argon atmosphere (H_2O, 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. Size exclusion chromatography (SEC) measurements for the end-functionalized P*n*BAs were performed at 40 °C using a Jasco GPC-900 system (Shodex® DU-2130 dual pump, Shodex® RI-71 RI detector, and Shodex® ERC-3125SN degasser) equipped with two Shodex KF-804 L columns (linear, 8 mm × 300 mm) in THF at the flow rate of 1.0 mL min^{-1}. The number average molecular weight ($M_{n,SEC}$) and polydispersity (M_w/M_n) of the obtained polymer were determined using PMMA standards with the M_w (M_w/M_n)s of 1.25 × 10^6 g mol^{-1} (1.07), 6.59 × 10^5 g mol^{-1} (1.02), 3.003 × 10^5 g mol^{-1} (1.02), 1.385 × 10^5 g mol^{-1} (1.05), 6.015 × 10^4 g mol^{-1} (1.03), 3.053 × 10^4 g mol^{-1} (1.02), and 1.155 × 10^4 g mol^{-1} (1.04), 4.90 × 10^3 g mol^{-1} (1.10), 2.87 × 10^3 g mol^{-1} (1.06), and 1.43 × 10^3 g mol^{-1} (1.15).

Synthesis of Tetrakis[{(2,2,5-trimethyl-1,3-dioxan-5-yl)methyl}oxymethyl]methane (C(HMEDD)$_4$)

In a three-neck flask equipped with a reflux condenser, a magnetic stirrer, and an addition funnel, potassium hydride (14.0 g, 249 mmol) and N,N-dimethylsulfoxyde (100 mL) were added under an argon atmosphere. 5-(Hydroxymethyl)-5-ethyl-2,2-dimethyl-1,3-dioxane (HMEDD, 7.98 g, 49.8 mmol) was added dropwise at 0 ºC, and the mixture was stirred for 3 h. Pentaerythritol tetrabromide (3.87 g, 9.96 mmol) was added dropwise. After the mixture was further refluxed for 12 h, a small amount of distilled water was added to stop the reaction. The mixture was then poured in ice water, and the precipitate is filtered, washed with water. The obtained solid was then dry in the high vaccume to give a pore yellow product. Yield, 5.57 g (79.3 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.45 (s, 12H, CH_3C-), 3.12 (s, 8H, C(CH_2OCH_2C-)$_4$), 3.21 (s, 8H, C(CH_2OCH_2C-)$_4$), 3.96 (s, 24H, CH_3C(CH_2O-)$_3$). ^{13}C NMR

(100 MHz, $CDCl_3$, δ): 23.1 (4C, $CH_3C(OCH_2)_3CCH_2$-), 35.0 (4C, $CH_3C(OCH_2)_3CCH_2$-), 45.8 (1C, $C(CH_2OCH_2C\text{-})_4$), 69.1 (12C, $CH_3C(OCH_2)_3CCH_2$-), 69.9 (4C, $CH_3C(OCH_2)_3CCH_2$-), 70.2 (4C, $C(CH_2OCH_2C\text{-})_4$), 108.7 (4C, CH_3C-).

Synthesis of Tetrakis[2-methyl-2,2-bis{(hydroxyl)methyl}ethyloxymethyl]methane ($C(OH)_8$)

In a 100 mL flask, $C(HMEDD)_4$ (10.23 g, 14.5 mmol), methanol (120 mL), and Dowex (15 g) were consequently added, and the mixture was stirred under room temperature for 2 days. The obtained mixture was filtered and dried to give the $C(OH)_8$. Yield, 7.90 g (99.9 %).^{1}H NMR (400 MHz, D_2O, δ): 3.40-3.50 (d, 16H, $C(CH_2OCH_2C\text{-})_4$), 3.12 (s, 24H, -CH_2OH).

Synthesis of Tetrakis{2-methyl-2,2-bis[(isobutyryloxy)methyl]ethyloxymethyl}methane ($C(i\text{Bu})_8$)

Method A: To a mixture of pentaerythritol (6.81 g, 50.0 mmol) and triethylamine (41.6 mL, 0.280 mol) in dry THF (150 mL), isobutyryl chloride (25.6 mL, 0.240 mol) in THF (50 mL) was slowly added at 0 ºC under argon atomosphere. After the reaction mixture was stirred at room temperature for 24 h, the resultant salt was removed by filtration and the filtrated organic layer was washed with saturated aqueous $NaHCO_3$, aqueous NaCl, and distilled water. The organic layer was dried over anhydrous Na_2SO_4 and then evaporated to remove the solvent. The residue was purified by the column chromatography (silicagel, *n*-hexane/ethyl acetate = 6/1(*v*/*v*), R_f = 0.26) to give tetrakis{2-methyl-2,2-bis[(isobutyryloxy)methyl]ethyloxymethyl}methane ($C(i\text{Bu})_8$) as a colorless liquid Yield, 4.46 g (26.2 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.16 (d, 24H, CH_3CH-), 2.57 (m, 4H, CH_3CH-), 4.13 (s, 8H, -CH_2O-). ^{13}C NMR (100 MHz, $CDCl_3$, δ):

19.0 (8C, *C*H_3CH-), 34.1 (4C, CH_3*C*H-), 42.4 (1C, *C*$(CH_2O)_4$-), 63.3 (4C, -*C*H_2O-), 176.6 (4C, *C*=O). Anal. Calcd for $C_{21}H_{36}O_8$ (416.51): C, 60.56; H, 8.71. Found: C, 60.61; H, 8.83.

Synthesis of 1-Methoxy-1-triphenylsiloxy-2-methyl-1-propene (MTS^{Ph})

Method B: A round-bottomed flask was charged with a solution of (*i*-Pr)$_2$NH (3.61 g, 5.00 mL, 35.7 mmol) in THF (100 mL) and then cooled to 0 °C. *n*-BuLi (1.6 mol L^{-1} in hexanes; 23.4 mL,37.5 mmol) was added to this solution dropwise at 0 °C, and the resulting mixture was stirred for 30 min. Methyl isobutyrate (4.09 mL, 3.64 g, 35.7 mmol) was added. After 30 min of stirring at 0 °C, a solid of chlorotriphenylsilane (10.8 g, 36.6 mmol) was added. The mixture was stirred for 30 min at 0 °C, then warmed to room temperature and stirred for 180 min. All volatiles (THF) were evaporated and *n*-hexane (50 mL) added. The resulting precipitates were filtered off under argon atmosphere;the filtrate was cooled to -30 °C inside a freezer of the gloveboxovernight, affording MTS^{Ph} as colorless crystals (yield, 8.67 g; 67.4%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65-7.37 (m, 15H, -Si(C_6H_5)$_3$), 3.18 (s, 3H, -OC*H*$_3$), 1.55 (s, 3H, =C(^{E}C*H*$_3$)(^{Z}CH_3)), 1.54 (s, 3H, =C(^{E}CH_3)(^{Z}C*H*$_3$)).

Synthesis of 1,1,1-Tris([2-methyl-1-(triphenylsiloxy)prop-1-enyloxy]methyl)propane (MTS^{Ph}_3)

Method B: A round-bottomed flask was charged with a solution of (*i*Pr)$_2$NH (4.12 mL, 29.3 mmol) in THF (100 mL) and then cooled to 0 °C. *n*-BuLi (1.6 mol L^{-1} in hexanes; 18.4 mL, 29.5 mmol) was added to this solution dropwise at 0 °C, and the resulting mixture was stirred for 30 min. EtC(*i*Bu)$_3$ (3.00 g, 8.71 mmol) and 1,3-dimethyl-3,4,5,6,-tetrahydro-2(*H*)-pyrimidinone (DMPU, 3.19 mL, 26.4 mmol) were added to a reaction mixture. After 30 min of stirring at 0 °C, a solid of chlorotriphenylsilane

(7.78 g, 26.4 mmol) was added. The mixture was stirred for 30 min at 0 °C, then warmed to room temperature and stirred for 180 min. All volatiles (THF) were evaporated and *n*-hexane (50 mL) added. The resulting precipitates were filtered off under argon atmosphere, the filtrate was reprecipitated to methanol at -80 °C, affording MTS^{Ph}_3 as colorless crystals. (1.20 g, 12.3 %). Yield, 3.12 g (66 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60-7.20 (m, 45H, [-Si(C_6H_5)$_3$]$_3$), 3.19 (s, 6H, [-OCH_2-]$_3$), 1.37 (s, 9H, [=C(^{E}CH_3)(^{Z}CH_3)]$_3$), 1.38 (s, 9H, [=C(^{E}CH_3)(^{Z}CH_3)]$_3$), 0.79 (q, 2H, -CCH_2CH$_3$), 0.24 (t, 3H, -CCH$_2$CH_3).

Synthesis of Tetrakis[{2-methyl-1-(triphenylsiloxy)prop-1-enyloxy}methyl]methane (MTS^{Ph}_4).

Method B was applied to dry THF (ca. 100 mL), diisopropylamine (5.60 mL, 36.6 mmol), *n*-butyllithium (23.1 mL, 37.0 mmol; 2.50 mol L^{-1} in *n*-hexane), C(*i*Bu)$_4$ (3.40 g, 8.16 mmol), DMPU (3.96 mL, 33.0 mmol), and chlorotriphenylsilane (9.72 g, 33.0 mmol). The crude product was reprecipitated in methanol at 0 ºC to give tetrakis[{2-methyl-1-(triphenylsiloxy)prop-1-enyloxy}methyl]methane (MTS^{Ph}_4) as a white crystal. Yield, 5.53 g (46.7 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57-7.23 (br, 60H, [-Si(C_6H_5)$_3$]$_4$), 3.18 (s, 8H, [-OCH_2-]$_4$), 1.29 (s, 12H, [=C(^{E}CH_3)(^{Z}CH_3)]$_4$), 1.20 (s, 12H, [=C(^{E}CH_3)(^{Z}CH_3)]$_4$).

Synthesis of Tetrakis{2-methyl-2,2-bis[(2-methyl-1-(triphenylsiloxy)prop-1-enyloxy)methyl]ethyloxy methyl}methane (MTS^{Ph}_8)

Method B was applied to dry THF (ca. 80 mL), diisopropylamine (2.95 mL, 20.1 mmol), *n*-butyllithium (13.2 mL, 21.2 mmol; 2.50 mol L^{-1} in *n*-hexane), C(*i*Bu)$_8$ (2.59 g, 2.34 mmol),

DMPU (3.96 mL, 18.9 mmol) and chlorotriphenylsilane (5.58 g, 18.9 mmol). The crude product was reprecipitated in methanol to give tetrakis{2-methyl-2,2-bis[(2-methyl-1-(triphenylsiloxy)prop-1-enyloxy)methyl]ethyloxymethyl}methane (MTS^{Ph}_8) as a white crystal. Yield, 2.05 g (27.6 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60-7.20 (br, 120H, [-Si(C_6H_5)$_3$]$_8$), 3.16 (s, 16H, [-C(CH_3)CH_2OC=]$_8$), 3.01 (s, 8H, C(CH_2-)$_4$), 2.69 (s, 8H, C(CH_2OCH_2C-)$_4$), 1.38 (s, 24H, [=C(^{E}CH_3)(^{Z}CH_3)]$_8$), 1.31 (s, 24H, [=C(^{E}CH_3)(^{Z}CH_3)]$_8$), 0.41 (s, 12H, (-CCH_3)$_4$).

Me_3SiNTf_2-Catalyzed GTP of *n*BA using Multifunctional Initiator

A typical procedure is as follows: A stock solution of Me_3SiNTf_2 (5.00 μL, 0.50 μmol, 0.10 mol L^{-1} in CH_2Cl_2) was added to a solution of *n*BA (320 mg, 2.50 mmol) and MTS^{Ph}_4 (36.3 mg, 25.0 μmol) in toluene (2.50 mL) under an argon atmosphere at room temperature. After stirring for 5 min, the polymerization was quenched by adding a small amount of methanol. Aliquots were removed from the reaction mixture to determine the conversion of *n*BA based on its ^{1}H NMR spectrum. The reaction mixture was purified by dialysis against acetone, followed by removal of the solvent to give the four-armed star-shaped P*n*BA as a sticky solid. Yield, 315 mg (98.4 %). ^{1}H NMR: $M_{n,NMR}$, 3410 g mol^{-1}. SEC (RI): $M_{n,SEC}$, 4100 g mol^{-1}; M_w/M_n, 1.09. The GTPs of *n*BA using MTS^{Ph} (24.0 mg, 50 μmol), MTS^{Ph}_3 (12.8 mg, 50 μmol), and MTS^{Ph}_8 (16.8 mg, 50 μmol) were carried out by a similar procedure to give P*n*BAs as sticky solids with quantitative yields.

5.3 Results and Discussion

5.3.1 Synthesis of Three-, Four-, and Eight-armed Star and Linear Acrylate Polymers

For the core-first synthesis of the star-shaped polyacrylate by group transfer polymerization (GTP), the initiators of the multifunctional silyl ketane acetals were synthesized, such as 1,1,1-tris([2-methyl-1-(triphenylsiloxy)prop-1-enyloxy]methyl)propane (MTS^{Ph}_3), tetrakis[{2-methyl-1-(triphenylsiloxy)prop-1-enyloxy}methyl]methane (MTS^{Ph}_4), and tetrakis{2-methyl-2,2-bis[(2-methyl-1-(triphenylsiloxy)prop-1-enyloxy)methyl]ethyloxymethyl}methane (MTS^{Ph}_8) for the synthesis of the three-, four, and eight-armed star-shaped polyacrylate. 1-Methoxy-1-triphenylsiloxy-2-methyl-1-propene (MTS^{Ph}) was synthesized according to the literature in order to synthesize the linear acrylate polymers.[24] Tetrakis[2-methyl-2,2-bis{(hydroxyl)methyl}ethyloxymethyl]methane ($C(OH)_8$) was synthesized from a pentaerythritol core by an esterization reaction of pentaerythritol with 5-(hydroxymethyl)-5-methyl-2,2-dimethyl-1,3-dioxane (HMDD) according to a previous report.[25] Trimethylolpropane, pentaerythritol, and $C(OH)_8$ were reacted with isobutyryl chloride to give their tris-, tetrakis-, and octakis-isobutylate, i.e., 1,1,1-tris(isobutyryloxymethyl)propane ($EtC(i\text{Bu})_3$), tetrakis(isobutyryloxymethyl)methane ($C(i\text{Bu})_4$), and tetrakis[2-methyl-2,2-bis(isobutyryloxymethyl)ethyloxymethyl]methane ($C(i\text{Bu})_8$), respectively. These esters were reacted with lithium diisopropylamide (LDA), followed by chlorotriphenylsilane (Ph_3SiCl) to afford 1,1,1-tris([2-methyl-1-(triphenylsiloxy)prop-1-enyloxy]methyl)propane (MTS^{Ph}_3), tetrakis[{2-methyl-1-(triphenylsiloxy)prop-1-enyloxy}methyl]methane (MTS^{Ph}_4), and tetrakis{2-methyl-2,2-bis[(2-methyl-1-(triphenylsiloxy)prop-1-enyloxy)methyl]ethyloxymeth

yl}methane (MTS^{Ph}_8), respectively.

The Me_3SiNTf_2-catalyzed GTPs of *n*BA were carried out using the obtained multifunctional initiators, MTS^{Ph}_3 MTS^{Ph}_4, and MTS^{Ph}_8, to synthesize the well-defined star-shaped poly(*n*-butyl acrylate) (P*n*BA) with a high-molecular-weight and narrow dispersity. First, the polymerization of *n*BA using MTS^{Ph} to indicate that the triphenylsilyl group could control the polymerization reaction. As a result, the molecular weights and distribution of the linear P*n*BA were 4700 g mol^{-1} and 1.12, respectively. Based on this result, the triphenylsilyl group controlled the polymerization by preventing the side reaction along with the triisopropylsilyl group. In the case of the GTP initiated by MTS^{Ph}_3, the values of $M_{n,SEC}$ and M_w/M_n were 8700 and 1.13, respectively. Similarly, MTS^{Ph}_4 also produced the P*n*BA with the controlled $M_{n,SEC}$ (M_w/M_n) of 13 200 (1.08). Using the MTS^{Ph}_8, the M_w/M_n of the obtained polymer was as low as 1.09, however, the $M_{n,SEC}$ of 18 000 was lower than the calculated value ($M_{n,calcd}$) of 26 700. This difference was caused by the differences in the sizes of the polymers between the star-shaped P*n*BA and linear poly(methyl methacrylate) standards for the SEC in THF. Thus, the molecular weight, which was determined by the SEC measurement using multiangle light scattering (SEC-MALS) ($M_{w,MALS}$) of P*n*BA obtained from run 3 was 15 800 which agreed with the calculated value. Based on these results, it was clarified that the multi-armed star-shaped P*n*BAs, such as the three-, four-, and eight-armed, could be synthesized via the Me_3SiNTf_2-catalyzed GTP using triphenylsilyl ketene acetals.

Table 5-1. Me_3SiNTf_2-Catalyzed GTP of *n*BA using MTS^{Ph}, MTS^{Ph}_3, MTS^{Ph}_4, MTS^{Ph}_8 as Initiators in Toluene [a]

run	initiator (I)	$[M]_0/[I]_0$	time / min	conv / % [b]	$M_{n,calcd.}$ / g mol^{-1} [c]	$M_{n,SEC}$ / g mol^{-1} [d]	M_w/M_n [d]
1	MTS^{Ph}	25	5	> 99	3 300	4 700	1.12
2	MTS^{Ph}_3	60	15	> 99	8 000	8 700	1.13
3	MTS^{Ph}_4	100	15	> 99	13 200	13 200	1.08
4	MTS^{Ph}_8	200	300	> 99	26 700	18 000	1.09

[a] Argon atmosphere; catalyst, Me_3SiNTf_2; solvent, toluene; $[M]_0$, 1.0 mol L^{-1}; $[catalyst]_0/[initiator]_0$, 0.02; temperature, room temperature. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([M]_0/([I]_0)$ × (conv) × (MW of *n*BA, 128.17) + (MW of initiator residue MTS^{Ph}, 102.13; MTS^{Ph}_3, 344.44; MTS^{Ph}_4, 416.51; MTS^{Ph}_8, 1105.39). [d] Determined by SEC in THF using poly(methyl methacrylate) standards.

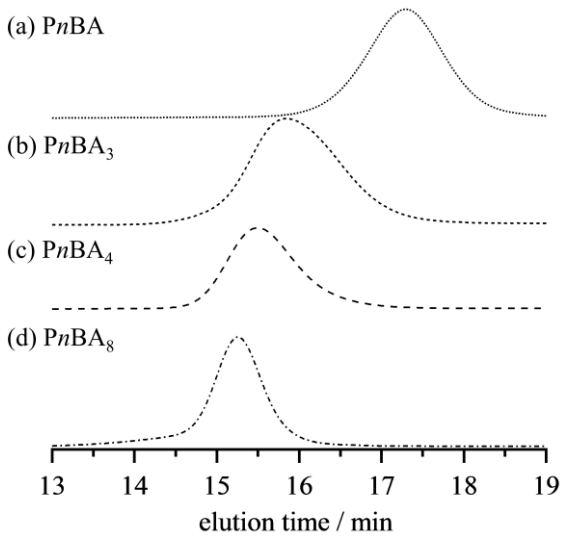


Figure 5-1. SEC traces (a) linear P*n*BA, (b) P*n*BA$_3$, (c) P*n*BA$_4$, and (d) P*n*BA$_8$ (eluent, THF; flow rate, 1.0 mL min^{-1}).

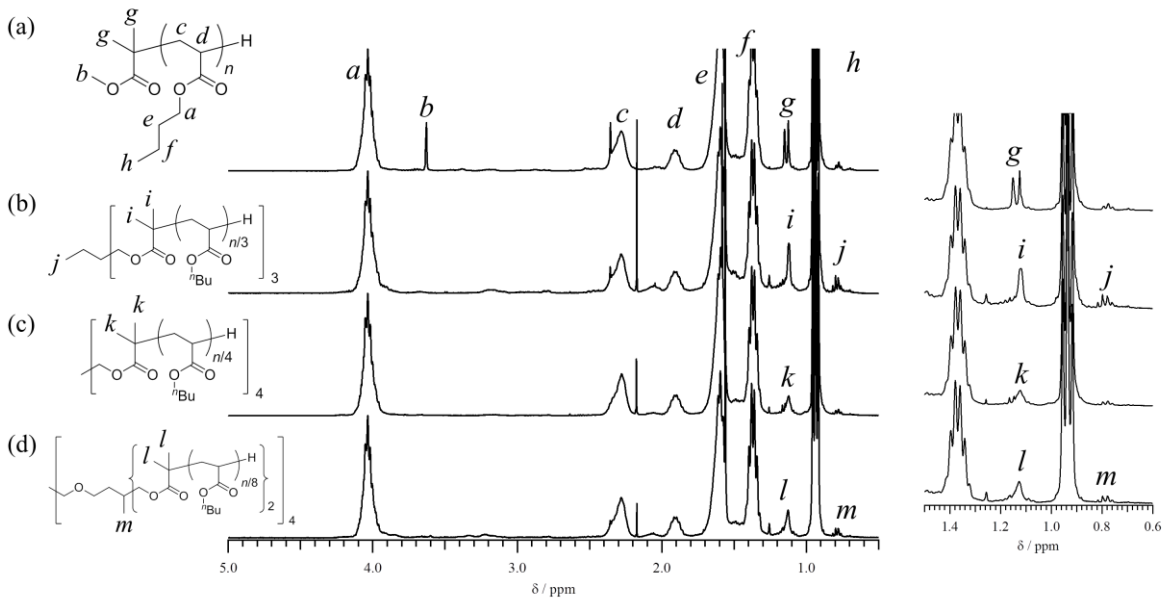


Figure 5-2. ^{1}H NMR spectra of (a) linear P*n*BA, (b) P*n*BA$_3$, (c) P*n*BA$_4$, and (d) P*n*BA$_8$ obtained from GTP (solvent, $CDCl_3$).

5.3.2 Living Nature for Group Transfer Polymerization of *n*BA using Multifunctional Initiator

In order to confirm the living nature for the polymerization of the acrylate using a multifunctional initiator, the kinetic experiment and control of the molecular weight of the polymer were carried out under the condition of the $[\text{monomer}]_0$ of 1.0 mol L^{-1} in toluene at room temperature. In the kinetic experiment, the additional condition was the $[n\text{BA}]_0/[\text{MTS}^{i\text{Pr}}{}_4]_0/[\text{Me}_3\text{SiNTf}_2]_0$ of 800/1/0.05, and the first-order kinetic plots of the polymerization displayed a straight line, which proved the constant number of the active chain ends and constant rate of propagation during the entire stage of the polymerization (Figure 5-3a). In addition, the molecular weight ($M_{\text{n,SEC}}$), determined by SEC measurement, of the obtained four-armed P*n*BA ((P*n*BA)$_4$) linearly increased from 17 500 to 101 000 with

the increasing conversion, and the M_w/M_n values of the obtained polymers were in the low range of 1.02 to 1.05 (Figure 5-3b). The control of the molecular weight of acrylate polymer was carried out under the condition of changing the initial-ratio of $[n\text{BA}]_0/[\text{I}]_0$ from 100 to 2400. All of the polymerizations homogeneously proceeded and were quenched by a small amount of methanol. The monomer conversions were determined by the ^{1}H NMR measurement of the crude polymerization mixtures using deuterium chloroform ($CDCl_3$). The values of $M_{w,MALS}$s increased from 15 800 to 425 100, which well agreed with the caluculated values from the $[n\text{BA}]_0/[\text{I}]_0$ for each polymer (Table 5-2). Henece, the Me_3SiNTf_2-catalyzed GTPs of *n*BA using a multifunctional initiator were capable of providing the PMA and P*n*BA with a narrow MWD and wide range of molecular weights. These results led to the conclusion that the GTP of acrylate monomers using a multifunctional initiator was found to possess a living nature and produced well-defined star-shaped acrylate polymers.

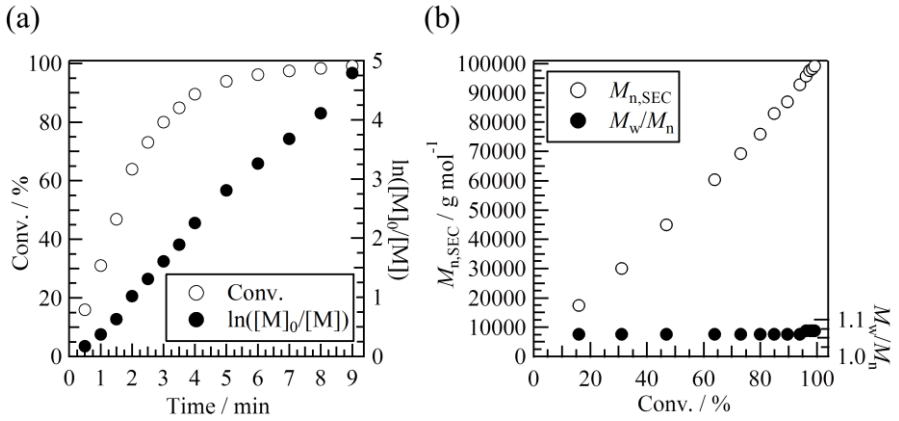


Figure 5-3. (a) Zero–order (○) and first–order (●) kinetic plots of Me_3SiNTf_2-catalyzed GTP of *n*BA in toluene at 27 °C under conditions of $[n\text{BA}]_0/[\text{MTS}^{\text{Ph}}_4]_0/[Me_3SiNTf_2]_0$, 800/1/0.05 and $[n\text{BA}]_0$, 1.0 mol L^{-1} and (b) relationship among the monomer conversion (Conv.), number average molecular weight ($M_{n,SEC}$) (○) and molecular weight distributions (M_w/M_n) (●).

Table 5-2. Me_3SiNTf_2-Catalyzed GTP of *n*BA using MTS^{Ph}_4 as an Initiator in Toluene [a]

run	$[n\text{BA}]_0/[MTS^{Ph}_4]$ /$[Me_3SiNTf_2]_0$	time / min	$M_{n,calcd.}$ / g mol^{-1} [b]	$M_{n,SEC}$ / g mol^{-1} [c]	$M_{w,calcd.}$ / g mol^{-1} [d]	$M_{w,MALS}$ / g mol^{-1} [e]	M_w/M_n [c]
5	100/1/0.02	15	13 200	13 200	14 300	15 800	1.08
6	200/1/0.02	15	26 100	24 800	27 700	27 100	1.06
7	400/1/0.05	15	51 700	47 800	54 300	53 900	1.05
8	800/1/0.05	15	103 000	95 500	109 200	148 300	1.06
9	1600/1/0.10	60	205 500	194 700	236 300	268 500	1.15
10	2400/1/0.20	60	308 000	333 600	378 000	425 100	1.23

[a] Ar atmosphere; $[n\text{BA}]_0$, 1.0 mol L^{-1}; temperature, 27 °C, conversion > 99 %. [b] Calculated from ($[n\text{BA}]_0/([MTS^{Ph}_4]_0)$ × (conv) × (MW of *n*BA, 128.17) + (MW of MTS^{Ph}_4 residue, 416.51). [c] Determined by SEC in THF using poly(methyl methacrylate) standards. [d] Calculated from ($M_{n,calcd.}$) × (M_w/M_n). [e] Determined by SEC equipped with MALS in THF.

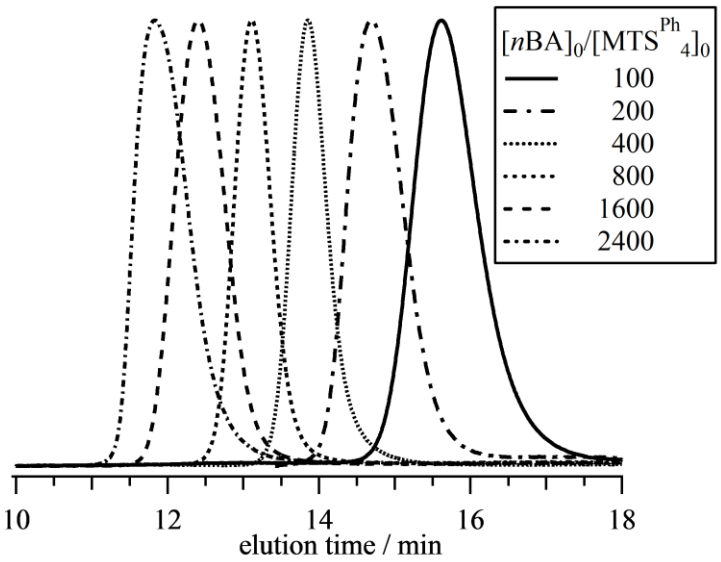


Figure 5-4. SEC traces of the obtained P*n*BA$_4$s (eluent, THF; flow rate, 1.0 mL min^{-1}).

5.3.3 Synthesis of Star-Block Copolymers via Group Transfer Polymerization

Star-block copolymers were synthesized by two routes, i.e., the linking reaction of a living diblock copolymer with the suitable linking agents and sequential polymerization of two or more kinds of monomers. The sequential block copolymerizations of *n*BA with vatious acrylate monomers were carried out with different monomer additions, i.e., the polymerization of *n*BA followed by methyl acrylate (MA), 2-ethylhexyl acrylate (EHA), 2-methoxyethyl acrylate (MEA) and triisopropylsilyl acrylate (TIPSA) (Table 5-3). Figures 5-5a and 5-5b show the SEC traces for both of the block copolymerizations. After the first polymerization of *n*BA under the condition of $[n\text{BA}]_0/[\text{I}]_0/[\text{Me}_3\text{SiNTf}_2]_0$ of 100/1/0.02, 100 equivalents of the monomer was added to the reaction mixture as the second polymerization. The product of the first polymerization showed a monomodal distribution in the SEC trace, which shifted to a higher molecular weight region in the SEC trace for the product of the

second polymerization, while maintaining a narrow distribution, as shown in Figure 5-5a. The $M_{n,SEC}$ of the obtained polymers increased from 13 200 to 21 000 and the M_w/M_ns ranged from 1.08 to 1.09 after the block copolymerization (run 11). For the block copolymerization with EHA, it formed the star-shaped P*n*BA-*b*-PEHA with the $M_{n,SEC}$ of 26 000, and M_w/M_ns of 1.09 (run 12). The first polymerization of TIPSA was carried out under the condition for the $[TIPSA]_0/[I]_0/[Me_3SiNTf_2]_0$ of 100/1/0.05 to produce the polymerization of TIPSA. The subsequent second polymerization of *n*BA was started by adding 100 equivalents of *n*BA to produce the star-shaped PTIPS-*b*-P*n*BA with the $M_{n,SEC}$ of 25 100 and M_w/M_n of the reratively low value of 1.19 (run 13). In addition, the block copolymerizations of *n*BA and MEA and *vice versa* were carried out in order to synthesize amphiphilic block copolymers. The first polymerization of *n*BA produced the P*n*BA with the $M_{n,SEC}$ (M_w/M_n) of 13 200 (1.08) and second polymerization of MEA gave the star-shaped P*n*BA-*b*-PMEA with the $M_{n,SEC}$ (M_w/M_n) of 25 100 (1.08) (run 14). Alternatively, the polymerization of MEA and *n*BA produced well-defined homo and block copolymers with the $M_{n,SEC}$ (M_w/M_n) of 12 900 (1.10) and 23600 (1.07) (run 15), respectively.

Based on these results, the well-defined star-block acrylate polymers, such as P*n*BA-*b*-PMA, P*n*BA-*b*-PEHA, PTIPS-*b*-P*n*BA, P*n*BA-*b*-PMEA, and *vise versa* were synthesized by the sequential addition of acrylate monomers by applying the living nature of the GTP using a multifunctional initiator. Importantly, the triphenylsilyl group in the initiator or propagating end could prevent the side reaction such as the backbiting reaction in the polymer side-chain.

Table 5-3. Me_3SiNTf_2-Catalyzed Block Copolymerization of *n*BA with MA, EHA, MEA, and TIPSA Using $MTS^{Ph}{}_4$ in Toluene [a]

run	monomer (M)		$[M_{first}+M_{second}]_0/[MTS^{Ph}{}_4]$ /$[Me_3SiNTf_2]_0$	time / min	$M_{n,calcd.}$ / g mol^{-1} [b]	$M_{n,SEC}$ / g mol^{-1} [c]	M_w/M_n [c]
11	first	*n*BA	100+100/1	15	13 200	13 200	1.08
	second	MA	/0.02	15	21 800	21 000	1.09
12	first	EHA	100+100/1	15	18 800	15 300	1.09
	second	*n*BA	/0.02	15	32 000	26 000	1.09
13[d]	first	TIPSA	100+100/1	60	23 300	12 000	1.10
	second	*n*BA	/0.05	120	36 100	25 100	1.19
14	first	*n*BA	100+100/1	60	13 200	13 200	1.08
	second	MEA	/0.05	120	26 200	25 100	1.08
15	first	MEA	100+100/1	60	13 400	12 900	1.10
	second	*n*BA	/0.05	120	26 200	23 600	1.07

[a] Ar atmosphere; $[M]_0$, 1.0 mol L^{-1}; $[Me_3SiNTf_2]_0/[MTS^{Ph}{}_4]_0$, 0.02; temperature, 27 °C monomer conversion, > 99% (determined by ^{1}H NMR in $CDCl_3$). [b] Calculated from $([M]_0/([MTS^{Ph}{}_4]_0)$ × (conv) × (MW of monomer; *n*BA, 128.17; MA, 86.09; EHA, 184.28; TIPSA, 228.40; MEA, 130.14) + (MW of $MTS^{Ph}{}_4$ residue, 416.51). [c] Determined by SEC in THF using poly(methyl methacrylate) standards. [d] Solvent; CH_2Cl_2.

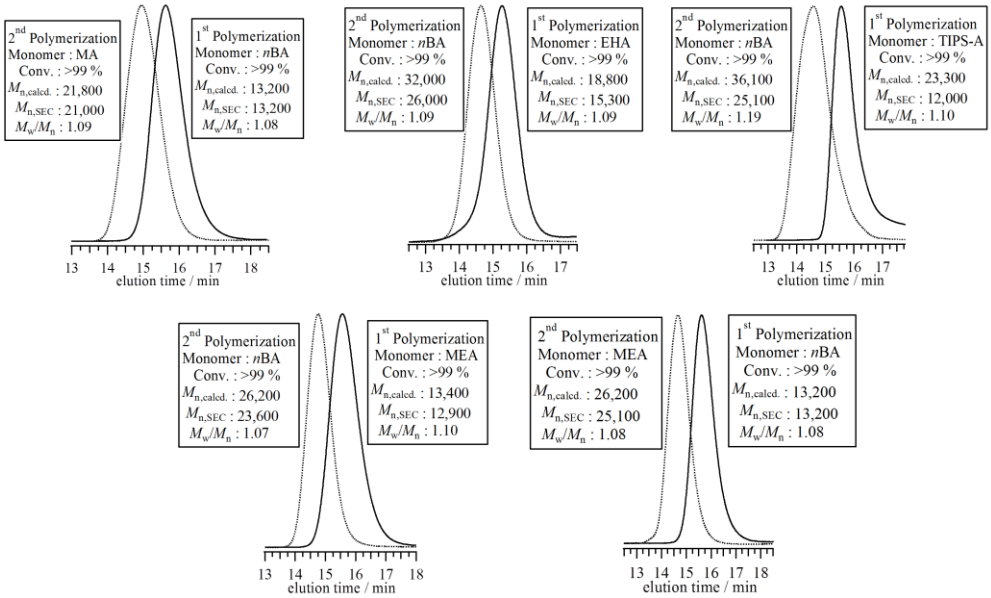


Figure 5-5. SEC traces of the polymers obtained from the first polymerization (solid line) and the second polymerization (dotted line) in the block copolymerization of various monomers (eluent, THF; flow rate, 1.0 mL min^{-1}).

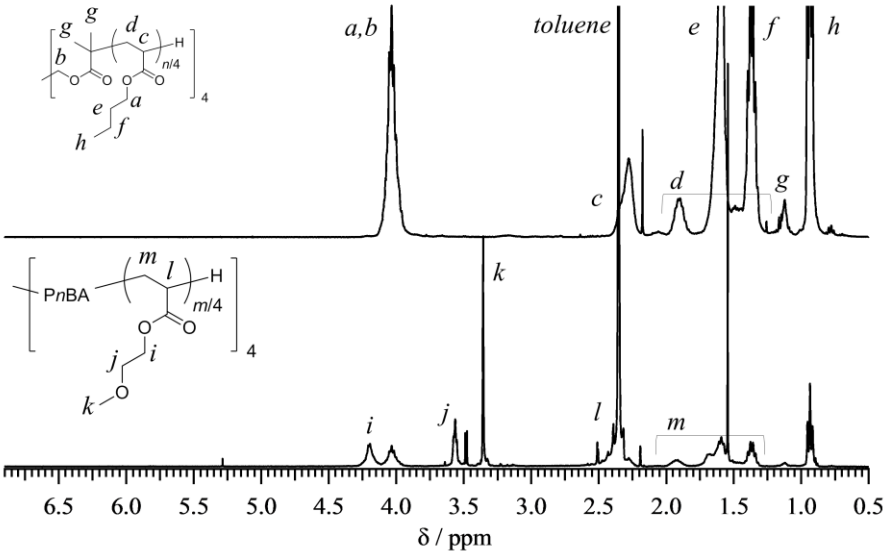


Figure 5-6. ^{1}H NMR spectra of the star-shaped P*n*BA (upper) and P*n*BA-*b*-PMEA (loweer) in $CDCl_3$ at room temperature.

5.4 Conclusions

The three-, four-, and eight-armed star-shaped polyacrylates with predictable molecular weights and very low dispersity were obtained from the Me_3SiNTf_2-catalyzed GTP based on the core-first polymerization method using a multifunctional initiator, such as a dendritic initiator bearing three-, four-, and eight-triphenylsilyl-ketene-acetal groups, i.e., MTS^{Ph}_3, MTS^{Ph}_4, and MTS^{Ph}_8, respectively. The living natures for the GTP using the multifunctional initiator, MTS^{Ph}_4, were confirmed by a kinetic experiment and control of the molecular weight of the four-armed star-shaped P*n*BAs. Furthermore, the high-molecular-weight star-shaped P*n*BA was obtained in this chapter which had the predicted $M_{w,MALS}$ (M_w/M_n) of 425 100 (1.25). The star-block copolymers were synthesized by the sequential GTP method to produce the P*n*BA-*b*-PMA and P*n*BA-*b*-PEHA. In addition, PTIPS-*b*-P*n*BA, which could produce polyacrylate-*b*-P*n*BA, and P*n*BA-*b*-PMEA, amphiphilic block copolymers, were also synthesized by a similar procedure. To the best of our knowledge, this is the first reliable method for the synthesis of high-molecular-weight star-shaped homo acrylate polymers and star-block acrylate polymers by the GTP method.

5.5 References and Notes

(1) (a) Szwarc, M. *J. Polym. Sci. Part: A Polym Chem.* **1998**, *36,* v-xiii; (b) Szwarc, M. *Science* **1970**, *170*, 23; (c) Lee, L.; Adams, R.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1971**, *93*, 4149-4154. (d) Szwarc, M. *Polym. Eng. Sci.* **1973**, *13*, 1-9; (e) Szwarc, M. *Acc. Chem. Res.* **1972**, *5*, 169-176.

(2) Mishra, M. K.; Kobayashi, S. editors. *Star and hyperbranched polymers*. New York, Basel: Marcel Dekker, Inc.; **1999**.

(3) Hadjichristidis, N. ; Pitsikalis, M.;Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747-3792.

(4) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Mays, J. *Prog. Polym. Sci.* **2006**, *31*, 1068-1132.

(5) Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317-350

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

(7) Webster, O. W. *J. Polym. Sci. Part A: Polym. Chem.* **2000,** *38*, 2855-2860.

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

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

(10) Raynaud, J.; Liu, N.; Févre, M.; Gnanou, Y.; Taton, D. *Polym. Chem.* **2011**, *2*, 1706-1712.)

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

(12) Webster, O. W. *Adv. Polym. Sci.* **2004,** *167*, 1-34.

(13) Sakamoto, K.; Aimiya, T.; Kira, M. *Chem. Lett.* **1997**, 1245-1246.

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

1473-1488

(15) Zhu, Z.; Rider, J.; Yang, C.-Y.; Gilmartin, M. E.; Wnek, G. E. *Macromolecules* **1992**, *25*, 7330-7333.

(16) Simmons, M. R.; Yamasaki, E. R.; Patrickios, C. S. *Polymer* **2000**, *41*, 8523-8529.

(17) Lang, P.; Burchard, W.; Wolfe, M. S.; Spinello, H. J.; Page, L. *Macromolecules* **2004**, *37*, 6734-6743.

(18) Kali, G.; Georgiou, T. K.; Iván, B.; Patrickos, C. S.; Loizou, E.; Thomann, Y.; Tiller, J. C. *Macromolecules* **2007**, *40*, 2192-2200.

(19) Georgiou, T. K.; Patrickios, C. S.; Groh, P. W.; Iván, B. *Macromoleceles* **2007**, *40*, 2335-2343.

(20) Kassi, E.; Patrickios, C. S. *Macromolecules* **2010**, *43*, 1411-1415.

(21) Chen, Y; Fuchise, K.; Narumi, A.; Kawaguchi, S.; Satoh, T.; Kakuchi, T. *Macromolecules* **2011**, *44*, 9091-9098.

(22) Chen, Y.; Takada, K.; Fuchise, K.; Satoh, T.; Kakuchi, T. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 3277-3285.

(23) Kikuchi, S.; Chen, Y.; Fuchise, K.; Takada, K.; Kitakado, J.; Sato, S.; Satoh, T.; Kakuchi, T. *Polym. Chem.* **2014**, *5*, 4701-4709.

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

(25) Ouchi, M.; Inoue, Y.; Wada, K.; Iketani, S.; Hakushi, T.; Weber, E. *J. Org. Chem.* **1987**, *52*, 2420-2427.

Chapter 6

Conclusions

In this thesis, the author describes the precise synthesis of acrylate polymers via the organocatalyzed group transfer polymerization (GTP) of various acrylate monomers, such as methyl acrylate (MA), ethyl acrylate (EA), *n*-butyl acrylate (*n*BA), 2-ethylhexyl acrylate (EHA), cyclohexyl acrylate (*c*HA), and dicyclopentanyl acrylate (d*c*PA) as alkyl acrylates and 2-methoxyethyl acrylate (MEA), 2-(2-ethoxyethoxy)ethyl acrylate (EEA), allyl acrylate (AlA), propargyl acrylate (PgA), 2-(triisopropylsiloxy)ethyl acrylate (TIPS-HEA), and triisopropylsilyl acrylate (TIPSA) as functional acrylate monomers with the specially-structured acrylate polymers. Pentafluorophenylbis(triflyl)methane ($C_6F_5CHTf_2$), one of the Brønsted acids, and *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNTf_2), one of the Lewis acids, promoted/catalyzed the GTP of the acrylate monomers using 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene (MTS^{iPr}) and its derivatives (functional initiators and star-shaped initiators) that proceeded a living manner. Furthermore, acrylate polymers with the degree of polymerization more than 1000 were synthesized by the organocatalyzed GTP methods. In addition, the multiblock polymers, AB-, BA-, $(ABC)_4$-, $(ABCD)_3$-, and ABCDEF-types, were synthesized by the sequential GTP method using the stability of the propagating chain end as the MTS^{iPr}. Furthermore, the α-, ω-, and α,ω-end-functionalized acrylate polymers, bearing the hydroxyl, vinyl, ethynyl, norboronenyl, and bromoethyl groups, were also synthesized by the GTP system using functional initiators and functional terminators. Finally, star-shaped acrylate polymers were precisely synthesized by fixing the structure of the silyl ketene acetals.

A summary of this thesis is as follows:

Chapter 2 "Optimization of Organic-Acid-Catalyzed GTP of Acrylate Monomers"

The strong organic acid and bulky initiator, such as $C_6F_5CHTf_2$, and 1-methoxy-1-triisopropylsiloxy-2-methyl-1-propene (MTS^{iPr}) were found to act as an effective promoter and initiator, respectively, for the GTP of MA. All the homopolymerizations, the postpolymerization, and the block copolymerization with *n*-butyl acrylate proceeded through a living manner to produce the well-defined poly(methyl acrylate) (PMA) and its block copolymers. In particular, the living polymerization for the $C_6F_5CHTf_2$-promoted GTP of MA and *n*BA using MTS^{iPr} produced PMA and P*n*BA with a high molecular weight and low molecular weight distribution. The fundamental synthetic strategy for acrylate monomers was achieved using a strong organic acid and highly bulky silyl ketene acetals, MTS^{iPr}, in this chapter.

Chapter 3 "Expand the Scope of Organocatalyzed GTP to Synthesize the Multiblock Acrylate Polymers"

The syntheses of the AB and BA diblock, $(ABC)_4$, $(ABCD)_3$, and ABCDEF multiblock acrylate polymers of which the blocks were composed of different types of acrylate monomer units including methyl, ethyl, *n*-butyl, 2-ethylhexyl, cyclohexyl, dicyclopentanyl, 2-methoxyethyl, 2-(2-ethoxyethoxy)ethyl, allyl, and propargyl acrylates, were based on the sequential *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (Me_3SiNTf_2)-catalyzed group transfer polymerization (GTP) method using the appropriate initiator of triisopropylsilyl ketene acetal (MTS^{iPr}). It was found that the stability of the propagating chain end of the acrylate polymer, i.e., the MTS^{iPr} structure, had a high livingness although nine and eleven postpolymerizations of various acrylate monomers were required. These GTP characteristics were caused by the living nature such that the triisopropylsilyl ketene acetal of the initiator

and the propagating chain-end efficiently reacted with the acrylate monomer activated by the strong organic Lewis acid, which was proved by the sequential GTP leading to the polymer chain extension.

Chapter 4 "Quantitative End-Functionalization of Acrylate Polymers using Functional Initiators and Terminators for GTP"

The end-functionalization of acrylate polymers was demonstrated by the organocatalyzed GTP of *n*BA using the functional initiators (FIs) and the functional terminators (FTs) as an effective method to produce the end-functionalized poly(*n*-butyl acrylate)s (P*n*BAs) with well-defined structures, i.e., the α-hydroxyl-, α-ethynyl-, α-vinyl-, and α-norbornenyl-functionalized P*n*BAs were synthesized by the Me_3SiNT_2-catalyzed GTP of *n*BA using the FIs of the triisopropylsilyl ketene acetals with the respective functional groups, and ω-ethynyl, ω-vinyl-, ω-hydroxyl-, and ω-bromo-functionalized P*n*BAs using the FTs of the 2-phenylacrylates with the respective functional groups. In addition, the α,ω-diethynyl-, α,ω-dihydroxyl-, and α-hydroxyl-ω-ethynyl-functionalized P*n*BAs were synthesized by the GTP of *n*BA initiated by the FIs and subsequently terminated by the FTs. The results described in this chapter showed the first reliable demonstration for the synthesis of the end-functionalized acrylate polymers with high-molecular-weights and low polydispersities based on the GTP as one of the living anionic polymerizations.

Chapter 5 "Synthesis of Star-Shaped Acrylate Polymers using Multifunctional Initiators"

The star-shaped polymers, three-, four-, and eight-armed P*n*BAs, were precisely synthesized by the Me_3SiNTf_2-catalyzed GTP using multifunctionalized silyl ketene acetals such as MTS^{Ph}_3, MTS^{Ph}_4, and MTS^{Ph}_8. The triphenylsilyl group could produce not only a

multifunctionalized initiator, but also well-defined polyacrylates. The obtained polymers had predictable molecular weights and narrow molecular weight distributions up to M_n (M_w/M_n) of 425 100 (1.25). In addition, the star-block copolymers were also obtained from the sequential block copolymerizations of MA, *n*BA, EHA, MEA, and TIPSA. Thus, these results indicated that the Me_3SiNTf_2-catalyzed GTP using a multifunctionalized initiator is one of the suitable methods for the synthesis of well-defined star-shaped acrylate polymers. This GTP process will be a versatile method for the synthesis of star-shaped acrylate polymers with high-molecular-weights and low dispersities including the star-block polymers.

Above all, the author revealed the methodology for the precise synthesis of acrylate polymers including the multiblock, end-functionalized, and star-shaped structure with a high-molecular-weight and narrow dispersity. The GTP had been considered as an intractable polymerization method because the silyl ketene acetals of the initiator were unstable compounds, and the GTP was the “quasi-living polymerization method” since Webstar et al. reported the concept of polymerization. However, by combining of the strong-organic-acid-catalyzed GTP and stable initiator bearing the bulky silyl group, the GTP has become the “truly-living polymerization method” and the most suitable technique for the synthesis of acrylate polymers. Importantly, all of the obtained polymers were first synthesized through the controlled/living anionic polymerization method. The author expects that the GTP of acrylate monomers will attract much interest by not only polymer scientists, but also the researchers in different fields.