Organoheteroatom-Mediated Living Vinyl Polymerization under Acidic Condition

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Acknowledgement

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Contents

General Introduction

In the modern, advanced industrial and information-oriented society, role of polymer materials has been dramatically increasing. Polymers are processed to commodities and specialities ranging from household goods to electrotic materials, which are now essential materials for our modern life. Significant scientific efforts have been made to improve the properties of existing polymer materials and/or to discover new properties of polymers. One of the most efficient and challenging way for such efforts is to control the structure of polymers in terms of molecular weight, polydispersity (PDI), monomer sequence, end-group structure, and stereoregularity (tacticity). Living polymerization, especially living anionic and cationic polymerizations, significantly contributes to the control the polymer structure, and, therefore, development of new living polymerization methods has been a significant challenge in synthetic polymer chemistry.

Acids, especially Lewis acids often play a crucial role in living polymerization methods. For example, Lewis acids work as powerful activators for living cationic polymerization.[1] While the first report of living cationic polymerization by Higashimura and Sawamoto utilized I_2 as an activator with the combination of organoiodine dormant species,[2] the following studies extensively utilized Lewis acid as activator with the combination of various heteroatom dormant species, as exemplified in organic halides and esters (Scheme 1).[1]

Scheme 1. Living cationic polymerization.

X = halogen, $OCOR$, OSO_2R, $OP(O)(OR)_2$, OR, ...
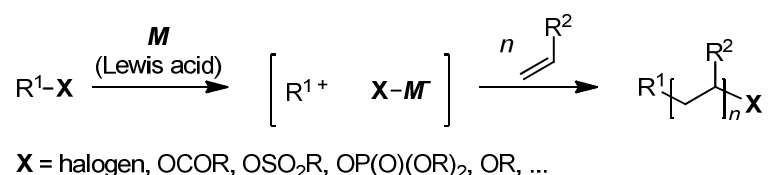
Significant progresses have been recently made to increase the scope of living cationic polymerization. For example, Aoshima and coworkers developed a binary initiation system consisting of Lewis acid and Lewis base, which enables ultrafast living cationic polymerization of vinyl ethres; the polymerization completed within few seconds and showed higher PDI control than that without Lewis base.[3-15] Kamigaito and coworkers have achieved the use of a trithiocarbonate, which is used for the reversible addition fragmentation chain transfer polymerization (RAFT), for a dormant species for living cationic polymerization by the activation of Lewis acid. They also applied this method for the synthesis of block copolymers by sequential living radical and living cationic polymerization (Scheme 2).[16]

Scheme 2. Cationic polymerization by using a trithiocarbonate as a dormant species.
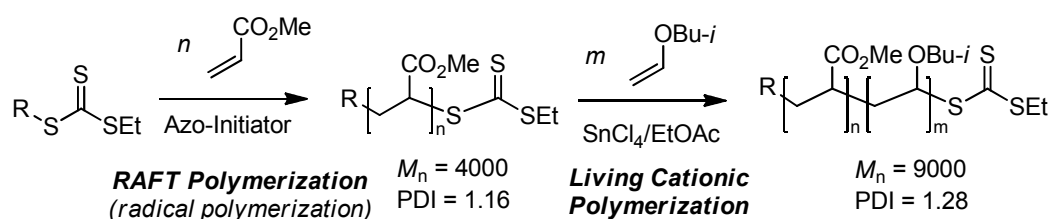
Lewis acids also play important role in the control of stereoregularity. For example, living anionic polymerization of methacrylates initiated by strong Lewis acidic organometallic reagents, such as *t*-BuMgBr and *t*-BuLi/alkylaluminum gave highly stereospecific polymethacrylates with meso triad (mm) = 97%.[17-19] In contrast, although cationic polymerization uses Lewis acid, there is no general stereospecific polymerization conditions. For example, Sawamoto and coworkers attempted stereospecific cationic polymerization of IBVE by changing Lewis acids and obtained the highly isotactic poly(isobutyl ether) (PIBVE) with a meso dyad (m) = 92% by employing sterically bulky titanium-based Lewis acid (Scheme 3).[20] However, further improvement of this result has been so far unachieved. Okamoto and coworkers reported the control of tacticity in radical

polymerization of acrylates and acrylamides by Lewis acids, but their generality has been limited.[21-26]

Scheme 3. Highly isotactic living cationic polymerization of IBVE.
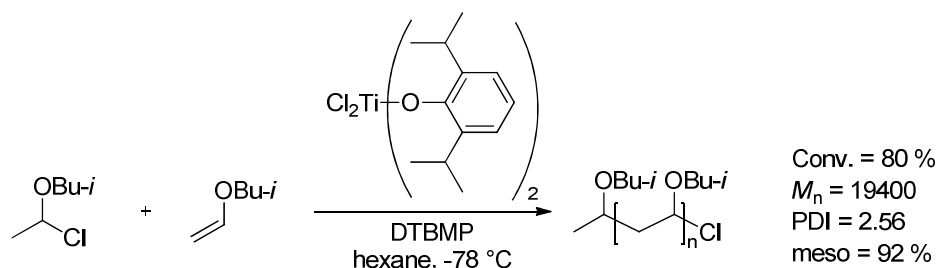
Lewis acids are also utilized as an additive for radical copolymerization of acrylates and α-alkenes.[27,28] By coordination of a Lewis acid to an acrylate-derived polymer-end radical species, insertion of α-alkene increases due to the increase of electrophilic character of the polymer-end radical species. Several efforts have been made to control of the copolymerization with high α-alkene insertion ratio by carring out living radical polymerization in the presence of Lewis acid. Structurally well controlled copolymers with low PDIs (<1.5) were obtained under nitroxide-mediated radical polymerization (NMP),[29,30] atom-transfer radical polymerization (ATRP),[30-35] and RAFT[37,3816] without Lewis acid when targeted molecular weights were low (M_n < 10000; M_n refers to number average molecular weight). However, mole fractions of α-alkene in the resulting copolymers were low (MF_{alkene} = 0.08-0.26). Addition of Lewis acids such as AlCl$_3$[30] and Sc(OTf)$_3$[36] dramatically improved the MF_{alkene} to 0.50 (Scheme 4), but PDI control could not be unachieved (PDI > 2.0) even the polymerization was carried out under RAFT conditions. This is due to the incompatibility of the Lewis basic RAFT reagents to Lewis acid. ATRP is also known incompatible to Lewis acid,[37] and polymerization of NMP which usually requires high temperature is unsuitable for the presence of Lewis acid for many functional monomers. Therefore, development of new living radical polymerization method which can be compatible with Lewis acid has been

awaited.

Scheme 4. Living radical copolymerization under RAFT conditions.

No AlCl₃	*AlCl₃* *
Conv. of MA = 16%	Conv. of MA = 53%
M_n = 4400, PDI = 1.07, MF$_{alkene}$ = 0.20	M_n = 66200, PDI = 2.19, MF$_{alkene}$ = 0.50
	* No RAFT agent was added.
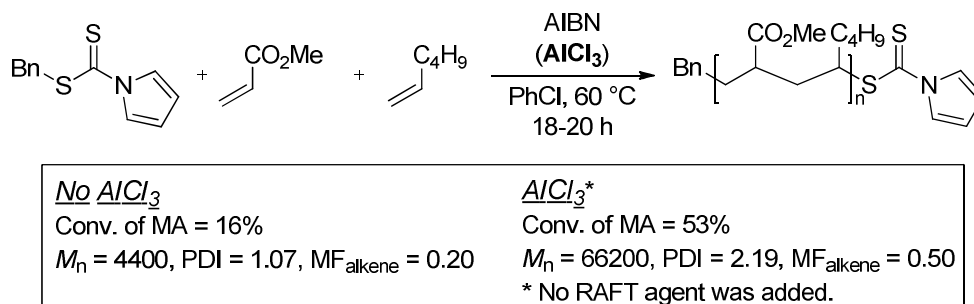
Recentry, Kamigaito and coworkers reported the effects of fluoroalcohols, such as $(CF_3)_2CHOH$ and $(CF_3)_3COH$, as protic acids on the MF$_{alkene}$ in the copolymerization of acrylates and α-alkene under iodine-mediated living radical copolymerization (IRP, Scheme 5).[38] While they achieved altenating copolymerization by employing excess amount of 1-hexene against methyl acrylates in the presence of the fluoroalcohol, the PDI control of the resulting altenating copolymer was low (1.87).

Scheme 5. Living radical copolymerization under IRP.

Conv. of MA = 85-95 %

No Fluoroalcohol	*Fluoroalcohol*
M_n = 6200-37800, PDI = 1.46-2.83,	M_n = 3900, PDI = 1.87,
MF$_{alkene}$ = 0.13-0.25	MF$_{alkene}$ = 0.50
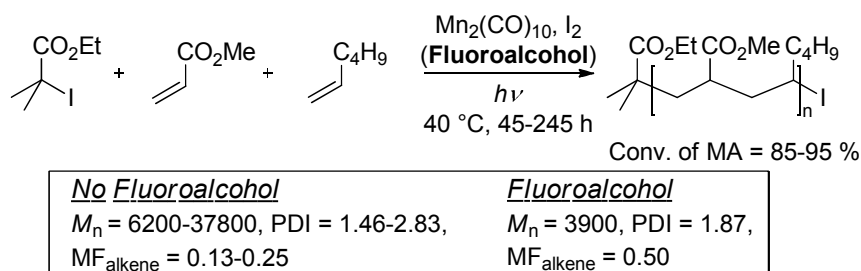
Our group have recently developed new living radical polymerization methods using organotellurium, organostibine, and organobismuthine compounds, which are designated as TERP, SBRP, and BIRP (organo<u>te</u>llurium-, organo<u>sti</u>bine, and organo<u>bis</u>muthine-mediated living <u>r</u>adical

polymerization), respectively (Scheme 6).[39-4539,40,46-49] They are one of the most synthetically valueable methods for living radical polymerization,[43,44,50] such as high versatility of monomer families, high compatibility towards functional groups and solvents,[39,51-54] and ease of the living-end transformation for the synthesis of block copolymers[41,55-58] and end-functionalized polymers.[59-62] However, these methods have never been carried out in the presence of Lewis acids. Furthremore, since chalcogens and pnictgens are recognized as congeners of halogens, organotellurium, stibine, and bismuthine compounds would be activated by Lewis acid and thus serve as controlling agents for living cationic polymerization. However, these possibilities have been never tested.

Scheme 6. Organoheteroatom-mediated living radical polymerization.
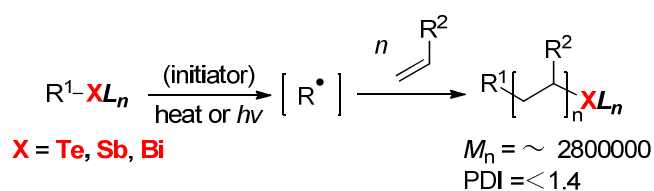
Outline of this thesis.

On the basis of above mentioned current status of living polymerization, we considered that TERP, SBRP, BIRP, and related polymerization conditions under acidic conditions would significantly increase the availability of structurally well controlled new polymers. These polymers would be useful for processing new functional polymer materials for various applications. This thesis entitled in "**Organoheteroatom-Mediated Living Vinyl Polymerization under Acidic Condition**" consists of five chapters and emphasizes to the development of new methods to control macromolecular structrure based on heteroatom-mediated living polymerization under acidic conditions.

Chapter 1 describes the development of new Lewis acidic activator of organotellurium

compounds (Scheme 7). Phenyltellanyl triflate (PhTeOTf) prepared in situ from dibromophenyl(phenyltellanyl)telluride and AgOTf efficiently activated various organotellurium compounds generating corresponding carbocations and their equivalents. When the activation was carried out in the presence of aromatic compounds, the Friedel–Crafts reaction took place in good to excellent yields. Application to polymer-end organotellurium compounds afforded the corresponding end-functionalized polymers.

Scheme 7. Electrophilic activation of organotellurium compounds by PhTeOTf.
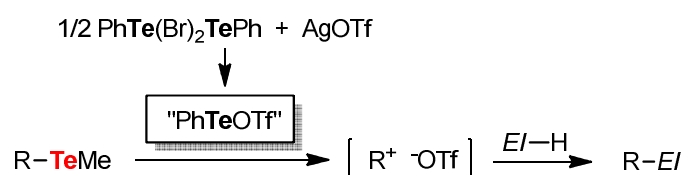
Chapter 2 describes on the development of living cationic polymerization using organotellurium compound as an initiator and its application to the synthesis of "hybrid" block copolymers (Scheme 8). Polymerization of vinyl ethers in the presence of organotellurium initiator and Lewis acid, such as In(OTf)$_3$ and BF$_3$·OEt$_2$, proceeded in a living manner and afforded well controlled poly(vinyl ether)s with predetermined molecular weights and narrow PDIs. Poly (meth)acrylates possessing organotellurium group at the ω-polymer end, which were prepared by using TERP, were also used for macro initiators for living cationic polymerization after tellurium-group transfer radical addition to vinyl ether. One-pot, two-step reaction of the macro initiator with vinyl ether under radical and cationic conditions gave well controlled AB diblock and ABA triblock copolymers.

Scheme 8. Synthesis of hybrid block copolymers by sequential living radical and cationic polymerizations.
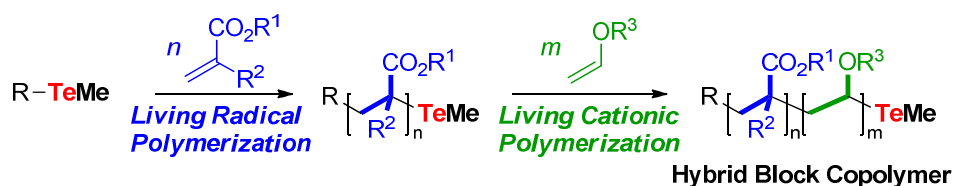
Chapter 3 describes random and alternating copolymerizations of (meth)acrylates and vinyl ethers under TERP, SBRP, and BIRP conditions (Scheme 9). Structurally well-controlled random and alternating copolymers with controlled molecular weights and polydispersities were synthesized. Syntheses of new block copolymers with controlled macromolecular structures by combining living copolymerization and living radical or living cationic polymerization were also discussed.

Scheme 9. Synthesis of random and alternating copolymerization.
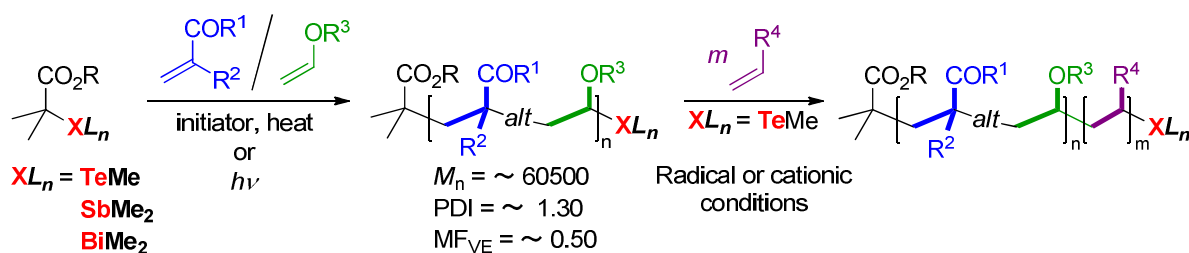
Chapter 4 describes controlled copolymerizations of (meth)acrylates with α-alkyl or α, α-dialkylolefins under TERP condition (Scheme 10). Structurally well-controlled random and alternating copolymers with controlled molecular weights and low PDIs were synthesized. Addition of Brønsted acids, such as $1,3\text{-}C_6H_4[C(CF_3)_2OH]_2$ and $(CF_3)_2CHOH$, increased the insertion rate of alkylethylenes in the copolymer with keeping low PDIs. The copolymers were successfully used as macro initiators for block copolymer synthesis.

Scheme 10. Copolymerization of (meth)acrylates and alkylolefins under TERP and its application to the synthesis of block copolymer.
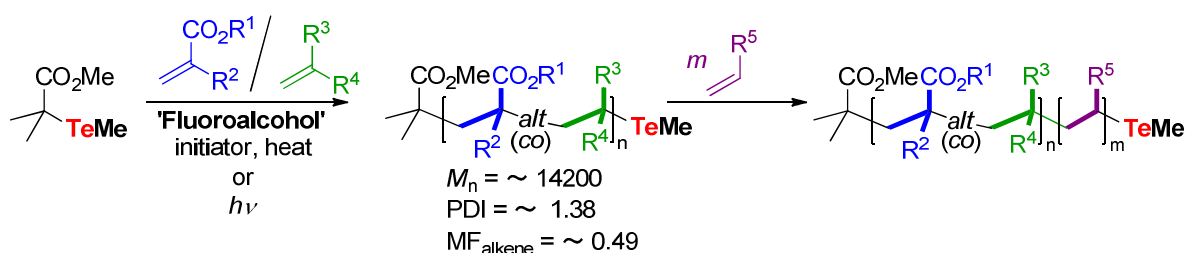
Chapter 5 describes model reactions for the control of stereoregularity in cationic polymerization by using intramolecular participation. Vinyl ethrer **1** which bears ester group was synthesized, and it was used as a precursor of α-alkoxy carbocation **2**, which is the polymer end reactive species in cationic polymerization of vinyl ethers, upon activation by Lewis acid (Scheme 11). The reaction of the cation with allyltrimethylsilane, which is a model monomer of vinyl ether, gave allylated product with up to 96% diastereoselectivity. Several control experiments suggest the involvement of cyclic intermediate **3**, which determined the stereoselectivity by controlling the trajectory of incoming allylsilane, by the intramolecular participation of the ester group to the cation.

Scheme11. Diastereoselectie allylation through α-alkoxy cation intermediate.
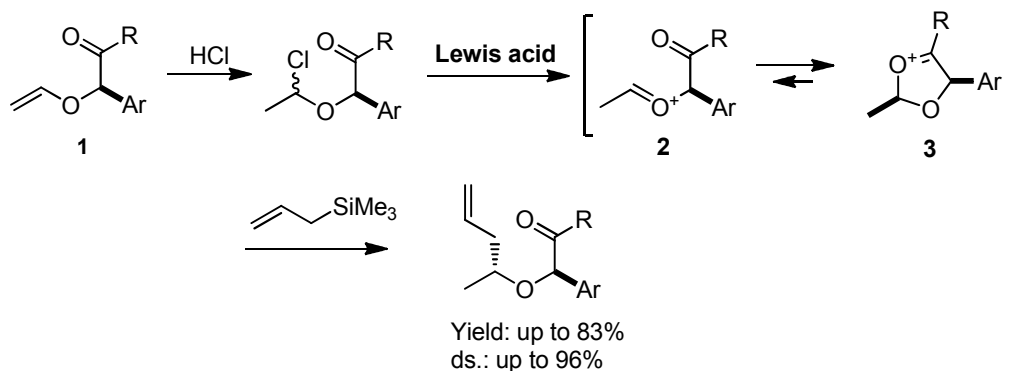
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Chapter 1

Formation of Cationic Species from Organotellurium Compounds in Friedel-Crafts reaction.

Abstract

A powerful electrophilic activator for organotellurium compounds was developed. Phenyltellanyl triflate (PhTeOTf) prepared in situ from dibromophenyl(phenyltellanyl)telluride and AgOTf selectively activated various organotellurium compounds in the presence of aromatic compounds yielding the corresponding Friedel–Crafts reaction products. Polymer-end organotellurium compounds were also activated by PhTeOTf providing the corresponding end-functionalized polymers.

Introduction

Organoheteroatom compounds have been widely used as the precursors for reactive carbon species, such as carbanions, carbocations, and carbon-centered radicals, which are essential intermediates in organic synthesis. Among these, organotellurium compounds have been recognized as some of the most versatile precursors due to their simple preparation methods, considerable stabilities, and high reactivities.[1-3] For example, various organometallic reagents are prepared from organotellurium compounds by the tellurium–metal exchange reaction.[4-6] Carbon-centered radicals generated from organotellurium compounds are also used for the controlled synthesis of small molecules[7,8] and macromolecules.[9-12] We recently showed that a dual use of organotellurium compounds as the precursors of both carboncentered radicals and carbanions offered unique synthetic transformations, which were unattainable with a single carbon-reactive species.[13,14] By contrast, the generation of carbocations from organotellurium compounds has been limited,[15-21] especially in applications with carbon–carbon bond-formation reactions.[22] These results prompted us to investigate the use of organotellurium compounds as the precursors of carbocationic species. We hypothesized that this situation could be attributed to the lack of a suitable activator of organotellurium compounds, and that the development of an efficient activator would open new possibilities for their use in electrophilic reactions. Here, we report on a new and efficient tellurophilic activator, and its utilization in the Friedel–Crafts reaction.

Result and discussions

Friedel-Crafts acylation of acryltelluride 2. We focused on dibromophenyl(phenyltellanyl) -telluride (**1**)[23] as a precursor of an electrophilic activator. A recent study indicated that **1** reversibly generated PhTeBr at ambient temperature. Thus, **1** prepared by mixing an equimolar amount of diphenylditelluride and bromine was treated with **2** equivalent of AgOTf at 0 °C in CH_2Cl_2 for 0.5 h,

and a mixture of acyl telluride **2** and 1,3,5-trimethoxybenzene (**3**) was added to this solution at 0 °C. After aqueous workup, the Friedel–Crafts product was identified in 66% yield by ^{1}HNMR analysis (Table 1, run 1). The yield increased to 91% when the acylation was carried out at room temperature (Table 1, run 2). As neither **1** nor AgOTf activated **2** under similar conditions (<6% yield), PhTeOTf generated from these reagents must be the real activating species (see below). The synthetic advantages of acyl tellurides are also worth mentioning, because they are more hydrolytically stable and easier to purify than acyl halides, which are routinely used as substrates in the Friedel–Crafts reaction.

Activators in situ prepared from **1** and AgNTf$_2$, AgSbF$_6$, and AgB(C$_6$F$_5$)$_4$ also served as the activators (Table 1, runs 3–5), but their efficiency was lower than that of PhTeOTf. PhSeOTf[24] and

Table 1. Friedel-Crafts acylation of acryltelluride **2** and 1, 3, 5-trimethoxybenzene (**3**) with a tellurophilic activator.[a]
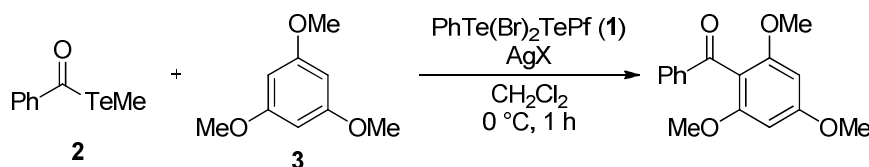
run	Activator	Yield (%)[b]
1	**1**/AgOTf	66
2[c]	**1**/AgOTf	91
3	**1**/AgNTf$_2$	53
4	**1**/AgSbF$_6$	49
5	**1**/AgB(C$_6$F$_5$)$_4$	24
6	PhSeOTf	50
7[e]	PhSOTf	44

[a]The activator prepared from **1** (0.15 mmol) and AgOTf (0.41 mmol) was added to a CH$_2$Cl$_2$ solution of **2** (0.26 mmol) and **3** (0.29 mmol) at 0 °C. [b]Determined by ^{1}H NMR based on **2**. [c]The reaction was carried out at room temperature.

PhSOTf[25] also activated **2** with moderate efficiency (Table 1, runs 6 and 7). Conventional activators, such as $BF_3 \cdot OEt_2$,[22] NIS, NIS/TMSOTf, *t*-BuOCl, MeOTf,[16] and Br_2,[21] were inefficient (<14% yield in all cases) under similar reaction conditions.

The generality of the new activator was examined by employing various organotellurium compounds and electrophiles, and the results are summarized in Table 2. The reaction of acyl telluride **2** with substituted benzene derivatives proceeded smoothly to give the desired products in excellent yields (Table 2, runs 1–3). The 1,4-disubstituted product predominantly formed over the 1,2-disubstituted product in the reaction with methoxybenzene (Table 2, run 2). Heteroaromatic

Table 2. Phenyltellanyl triflate mediated the Friedel-Crafts reaction.[a]

a: R^1, R^2 = OMe, R^3 = H   d: R^4 = TeBu-*n*
b: R^1, R^3 = H, R^2 = OMe   e: R^4 = TeMe
c: R^1, R^2 = Me, R^3 = H   f: R^4 = TePh
   g: R^4 = 2, 4, 6-$(MeO)_3C_6H_2$
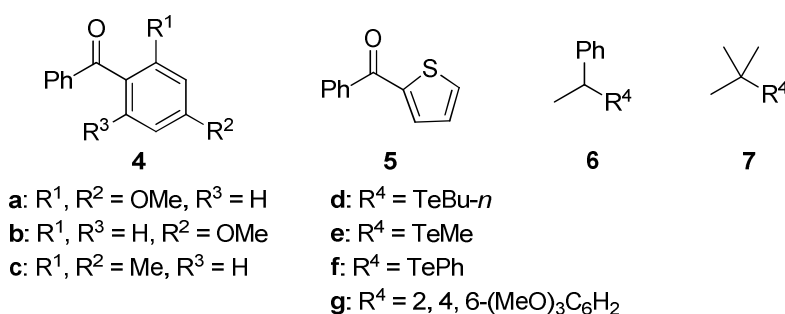
run	Substrate	Nucleophile	Product	Yield (%)
1	**2**	1, 3-$(MeO)_2C_6H_4$	**4a**	92
2	**2**	$MeOC_6H_5$	**4b**	91[b]
3	**2**	1, 3-$Me_2C_6H_4$	**4c**	94
4[c]	**2**	Thiophene	**5**	74
5	**6e**	**3**	**6g**	63[d]
6	**7f**	**3**	**7g**	74
7[e]	**8e**	**3**[e]	**8g**	100[f]

[a]A substrate and a nucleophile (1.5 equiv) were treated with the activator prepared from **1** (0.55 equiv) and AgOTf (1.1 equiv) in CH_2Cl_2 at room temperature for 1 h. [b]The product formed as a 96 : 4 mixture of 1, 4-isomers and 1, 2-isomers. [c]2, 6-Di-*tert*-butyl-4-methylpyridine (1.5 equiv) was added to avoid decomposition of **5**. [d]Dialkylated product formed in 14% yield. [e]10 equiv of **3** was used. [f]Polystylene with M_n = 3400, M_w/M_n = 1.14. See text for details for the efficiency of the end functionalization.

compounds, such as thiophene, also reacted with **2** to give the 3-substituted product in good yield (Table 2, run 4). The observed regioselectivities were consistent with those in the conventional Friedel–Crafts reaction, suggesting that the reaction indeed generated carbocationic species from organotellurium compounds. Alkyl tellurides **6e** and **7f** were also activated with PhTeOTf in the presence of **3** to give the desired products in moderate-to-good yields (Table 2, runs 5 and 6).

Synthesis of end-functionalized polystyrene. The synthetic efficiency was further examined in the polymer-end functionalization using polystyrene **8e**, which was prepared by living radical polymerization of styrene (30 equiv) with **6e** (Entry 7).[13] Thus, **8e** was treated with PhTeOTf in the presence of **3** (10 equiv). The gel permeation chromatography of the purified polymer **8g** indicated the formation of a monodisperse polystyrene with a number-averaged molecular weight (M_n) of 3440 and a molecular weight distribution (M_w/M_n, where M_w is the weight-averaged molecular weight) of 1.14. The ^{1}HNMR analysis revealed the nearly quantitative efficiency (97%) of the
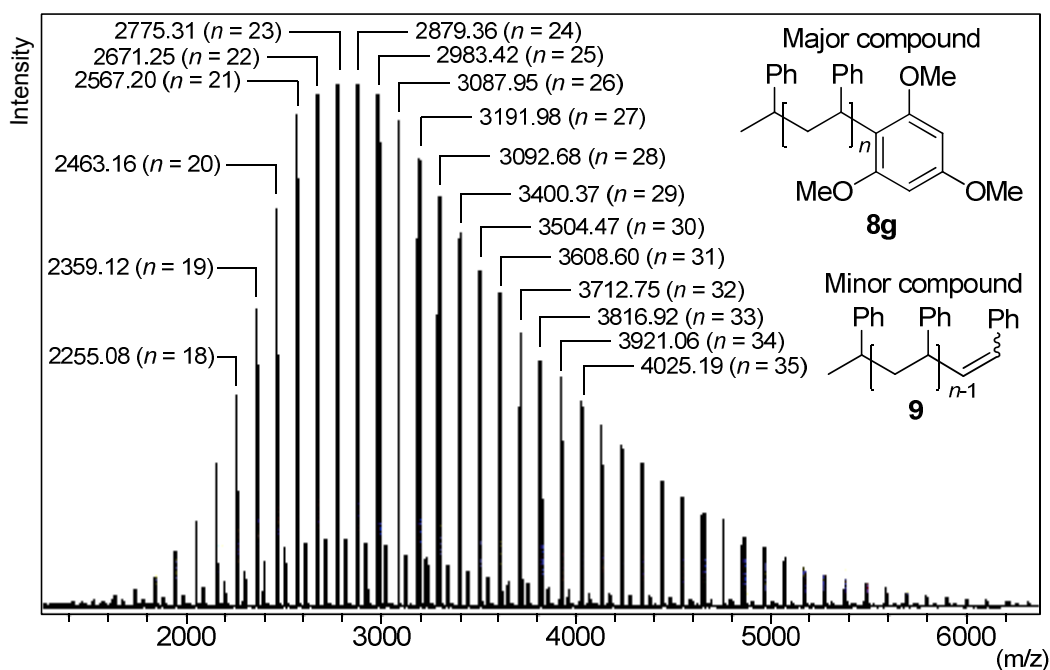
Figure 1. MALDI-TOF-mass spectrum of polystyrene **8g** and **9** (= 93: 7). A series of peaks, as indicated by the average mass number, was observed in the silver ion added form $(M + Ag)^+$.

end-group transformation. MALDI-TOF mass spectrometry also indicated the predominant formation of **8g** together with a small amount of **9** as judged from a series of molecular ion peaks (Figure 1, **8g**:**9** = 93:7). The formation of **9** is also consistent with the generation of carbocationic species at the polymer-end.

To confirm the activating species, the intermediate was analyzed by [125]Te NMR spectroscopy. While **1** did not show [125]Te NMR resonance in CD_2Cl_2 at room temperature,[23] a new signal at 1119 ppm appeared upon treatment of **1** with 2 equivalents of AgOTf at 0 °C. The signal at 1155 ppm was also observed when dichlorophenyl(phenyltellanyl)telluride was treated with AgOTf. The marginal difference of the chemical shift might be due to the interaction of PfTeOTf with AgX (X = Br or Cl). These results, combined with the established protocol for the halogen–triflate exchange reaction using AgOTf, strongly suggest the formation of PhTeOTf as the activating species. However, attempts to isolate the intermediate have so far been unsuccessful. Further synthetic and mechanistic studies are underway, and will be reported in due course.

Conclusions

We showed that phenyltellanyl triflate (PhTeOTf) prepared in situ from dibromophenyl(phenyltellanyl)telluride and AgOTf selectively activated various organotellurium compounds in the presence of aromatic compounds yielding the corresponding Friedel–Crafts reaction products. This powerful electrophilic activator could also activate polymer-end organotellurium compounds and provided the corresponding end-functionalized polymers.

Experimental Section

General. All reaction conditions dealing with air- and moisture sensitive compounds were carried out in a dry reaction vessel under nitrogen or argon atmosphere. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured for a CDCl$_3$ or CD$_2$Cl$_2$ solution of a sample. ^{1}H NMR spectra are reported in parts per million (δ) from internal tetramethylsilane (0 ppm), ^{13}C NMR from CDCl$_3$ (77.0 ppm), ^{125}Te NMR from external PhTeTePh (+422 ppm). IR spectra (absorption) are reported in cm^{-1}. MALDI-TOF mass spectra were recorded on a spectrometer equipped with a 337 nm N$_2$ laser in the reflection mode and at 20 kV acceleration voltage. Samples were prepared from a tetrahydrofuran (THF) solution by mixing sample (1 mg/mL), dithranol (10 mg/mL), and silver trifluoroacetate (1 mg/mL) in a ratio of 5:1:1. Gel permeation chromatography (GPC) was performed on a liquid chromatography equipped with two linearly connected polystyrene (PSt) mixed gel columns (300 x 8.0 mm; bead size = 7 μm, pore size = 20–200 Å). Preparative HPLC was performed with GPC column (JAIGEL 1H and 2H columns with CHCl$_3$ as eluant).

Materials. Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. CH$_2$Cl$_2$ was distilled successively from P$_2$O$_5$ and K$_2$CO$_3$ and stored over molecular sieves. Organotellurium compounds **2**,[25] **6e**,[13] and **7f**[18] were prepared as reported.

General procedure for the preparation of "phenyltellanyl triflate". Dibromophenyl (phenyltellanyl) telluride (**1**) was prepared by mixing diphenylditelluride (61.4 mg, 0.15 mmol) and bromine (7.7 μL, 0.15 mmol) in 0.3 mL of CH$_2$Cl$_2$ at 0 °C for 0.5 h. The resulting solution was added to AgOTf (106 mg, 0.41 mmol) at 0 °C, and the resulting mixture was stirred for 15 min at this temperature. This mixture was used for the next step without further purification. ^{125}Te NMR (CD$_2$Cl$_2$) 1119.

"Phenyltellanyl trilfate" prepared from dichlorophenyl(phenyltellanyl)telluride.
Sulfuryl chloride (8.1 μL, 0.10 mmol) was added to a solution of diphenylditelluride (40.9 mg, 0.10 mmol) in 0.6 mL of CD_2Cl_2 at 0 °C, and the resulting solution was stirred at this temperature for 0.5 h to generate dichlorophenyl(phenyltellanyl)telluride [^{1}H NMR (CD_2Cl_2) 7.35~7.48 (m, 3 H), 8.06 (br d, J = 7.0 Hz)]. This solution was added to AgOTf (77.1 mg, 0.30 mmol) in a NMR tube at 0 °C, and the reaction mixture was warmed to room temperature. ^{1}H NMR (400 MHz) 7.53~7.73 (m, 3 H), 7.92 (distorted dd, J = 8.0, 1 5 H, 2 H); ^{13}C NMR (CD_2Cl_2) 119.46 (q, J = 319 Hz, $CF3$), 131.17 (CH x 2), 132.96 (C), 133.60 (CH), 134.17 (CH x 2); ^{125}Te NMR (CD_2Cl_2) 1155.

General Procedure for the Fridel-Crafts reaction: Synthesis of phenyl 2,4,6-trimethoxyphenyl ketone.[26] A solution of acyltelluride **2** (64.3 mg, 0.26 mmol) and 1,3,5-trimethoxybenzene (**3**, 48.8 mg, 0.29 mmol) in 0.2 mL of CH_2Cl_2 was added to the above prepared "PhTeOTf" solution at 0 °C. After being stirred at room temperature for 1 h, the reaction was quenched by addition of Et_3N (100 μL) followed by saturated aqueous $NaHCO_3$ solution. The organic phase was separated, and the aqueous phase was extracted with ethyl acetate. The combined organic extracts were washed with saturated aqueous NaCl solution, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a crude oil. Purification by flash column chromatography (elution with 20 % ethyl acetate in hexane) afforded the titled compound in 92 % yield (66.0 mg, 0.24 mmol). ^{1}H NMR (400 MHz, CDCl3) 3.68 (s, 6 H), 3.86 (s, 3 H), 6.17 (s, 2 H), 7.38-7.44 (m, 2 H), 7.53 (tt, J = 7.2, 2.0 Hz, 1 H), 7.82-7.87 (m, 2 H); ^{13}C NMR (100 MHz, CDCl3) 55.43, 55.74, 90.53, 110.75, 128.24, 129.39, 132.91, 138.09, 158.65, 162.32, 195.02.

2,4-Dimethoxyphenyl phenyl ketone (4a).[27] ^{1}H NMR (400 MHz, $CDCl_3$) 3.70 (s, 3 H), 3.87 (s, 3 H), 6.50-6.57 (m, 2 H), 7.38-7.44 (m, 4 H), 7.52 (tt, J = 7.4, 2.0 Hz, 1 H), 7.75-7.79 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) 55.46, 98.67, 104.38, 121.33, 127.94, 129.62, 132.18, 132.30, 138.69, 159.83, 163.25, 195.53; HRMS (EI) *m/z*: Calcd for $C_{15}H_{14}O_3$ (M+), 242.0943; Found 242.0940.

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Phenyl 4-methoxyphenyl ketone (4b).[28] ^{1}H NMR (400 MHz, CDCl$_3$) 3.89 (s, 3 H), 6.96 (dt, J = 9.6, 2.5 Hz, 2 H), 7.47 (tt, J = 7.6, 1.4 Hz, 2 H), 7.56 (tt, J = 7.6, 2.0 Hz, 1 H), 7.73-7.78 (m, 2 H), 7.83 (dt, J = 9.3, 2.4 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) 55.46, 113.52, 128.15, 129.69, 130.11, 131.86, 132.53, 138.24, 163.18, 195.57.

2,4-Dimethylphenyl phenyl ketone (4c).[29] 1H NMR (400 MHz, CDCl3) 2.33 (s, 3 H), 2.38 (s, 3 H), 7.04 (d, J = 7.4 Hz, 1 H), 7.11 (s, 1 H), 7.23 (d, J = 8.0 Hz, 1 H), 7.41-7.47 (m, 2 H), 7.56 (tt, J = 7.4, 1.2 Hz, 1 H), 7.75-7.80 (m, 2 H); 13C NMR (100 MHz, CDCl3) 20.06, 21.34, 125.73, 128.31, 129.22, 130.85, 131.85, 132.81, 135.55, 137.24, 138.17, 140.61, 198.53.

Phenyl 2-thienyl ketone (5).[30,31] ^{1}H NMR (400 MHz, CDCl$_3$) 7.17 (dd, J = 5.2, 3.6 Hz, 1 H), 7.46-7.54 (m, 2 H), 7.60 (tt, J = 7.4, 2.2 Hz, 1 H), 7.65 (dd, J = 4.0, 1.2 Hz, 1 H), 7.73 (dd, J = 4.8, 1.2 Hz, 1 H), 7.84-7.90 (m, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) 127.94, 128.40, 129.16, 132.25, 134.20, 134.84, 138.13, 143.62, 188.24.

1-Phenyl-1-(2,4,6-trimethoxyphenyl)ethane (6g). IR (KBr) 3010, 1610; ^{1}H NMR (400 MHz, CDCl$_3$) 1.63 (d, J = 7.2 Hz, 3 H), 3.68 (s, 6 H), 3.78 (s, 3 H), 4.74 (q, J = 7.2 Hz, 1 H), 6.12 (s, 2 H), 7.09 (t, J = 7.2 Hz, 1 H), 7.21 (t, J = 7.6 Hz, 2 H), 7.24-7.30 (m, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) 17.73 (CH3), 32.91 (CH), 55.20 (CH3), 55.70 (CH3, 2 C), 91.38 (CH, 2 C), 115.83 (C), 124.80 (CH), 127.23 (CH, 2 C), 127.46 (CH, 2 C), 146.60 (C), 158.96 (C, 2 C), 159.38 (C); HRMS (EI) *m/z*: Calcd for C$_{17}$H$_{20}$O$_3$ (M+), 272.1412; Found 272.1405.

2-*Tert*-butyl-1,3,5-trimethoxybenzene (7g). IR (KBr) 3010, 1595; ^{1}H NMR (400 MHz, CDCl$_3$) 1.44 (s, 9 H), 3.75 (s, 6 H), 3.78 (s, 3 H), 6.14 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) 31.98 (CH3, 3C), 35.80 (C), 55.08 (CH3), 55.93 (CH3, 2 C), 92.93 (CH, 2 C), 118.64 (C), 158.47 (C), 160.26 (C, 2C); HRMS (EI) *m/z*: Calcd for C$_{13}$H$_{20}$O$_3$ (M+), 224.1412; Found 224.1409.

2,4,6-Trimethoxybenzene-substituted polystyrene 8g. Polystyrene was prepared by heating a mixture of **8e** (30.5 μL, 0.20 mmol) and styrene (0.69 mL, 6.0 mmol) at 100 °C for 20 h under nitrogen atmosphere in a glove box. Dichloromethane (0.7 mL) and 1,3,5-trimethoxybenezene (336 mg, 2.0 mmol) was added, and the resulting mixture was shaken until the solution became homogeneous at room temperature. "Phenyltellanyl trilfate" solution, which was prepared according to the procedure shown above from diphenylditelluride (61.4 mg, 0.15 mmol), bromine (7.7 μL, 0.15 mmol), and AgOTf (106.4 mg, 0.414 mmol) in 0.6 mL of CH_2Cl_2, was added to the polymer solution at room temperature. After being stirred for 2 h at this temperature, the solution was poured into a vigorously stirring methanol. Precipitate was collected, washed with methanol repeatedly, dried under reduced pressure, and purified by preparative GPC to give 684.7 mg of **8g** (100%).

^{1}H NMR of 8g.
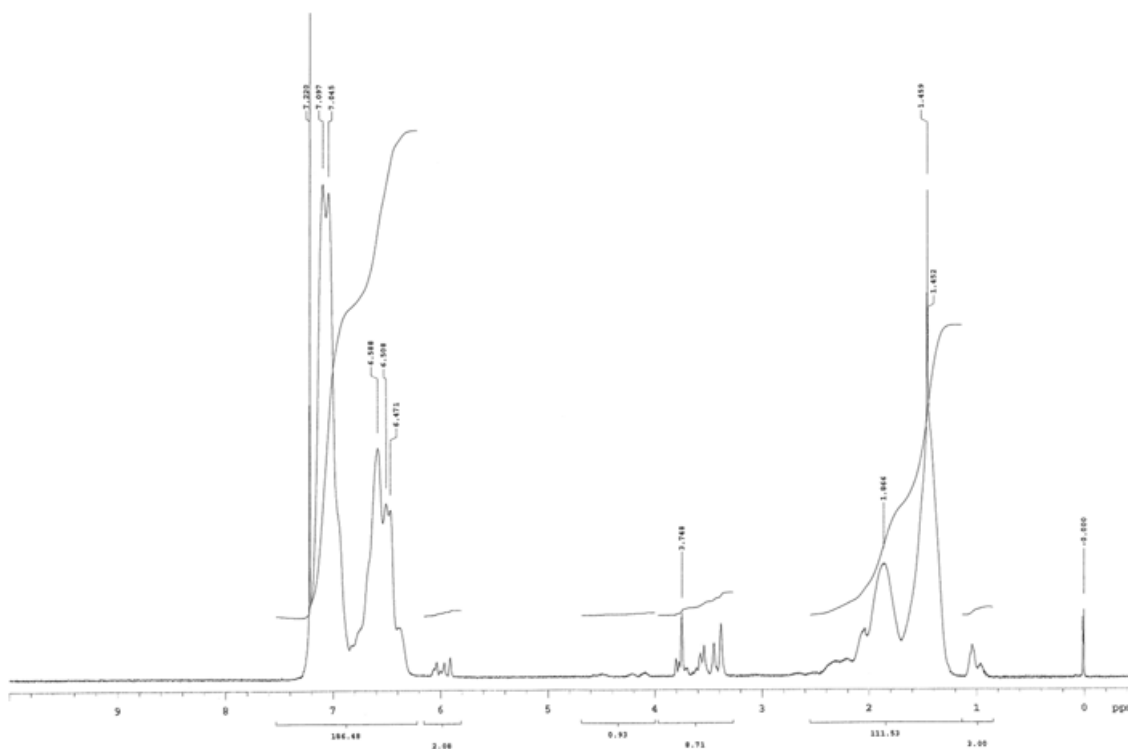
MALDI TOF MS spectra of 8g.
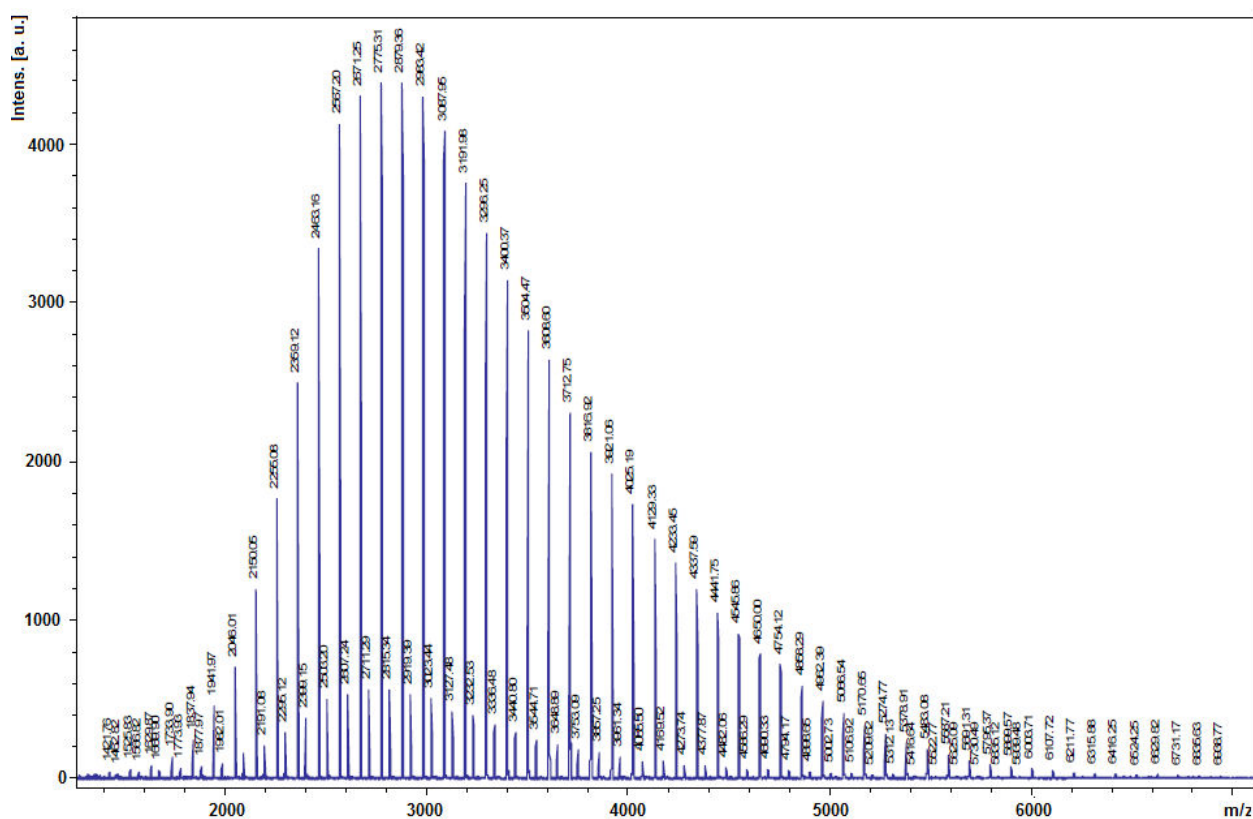
Expanded MALDI TOF MS spectra of 8g.
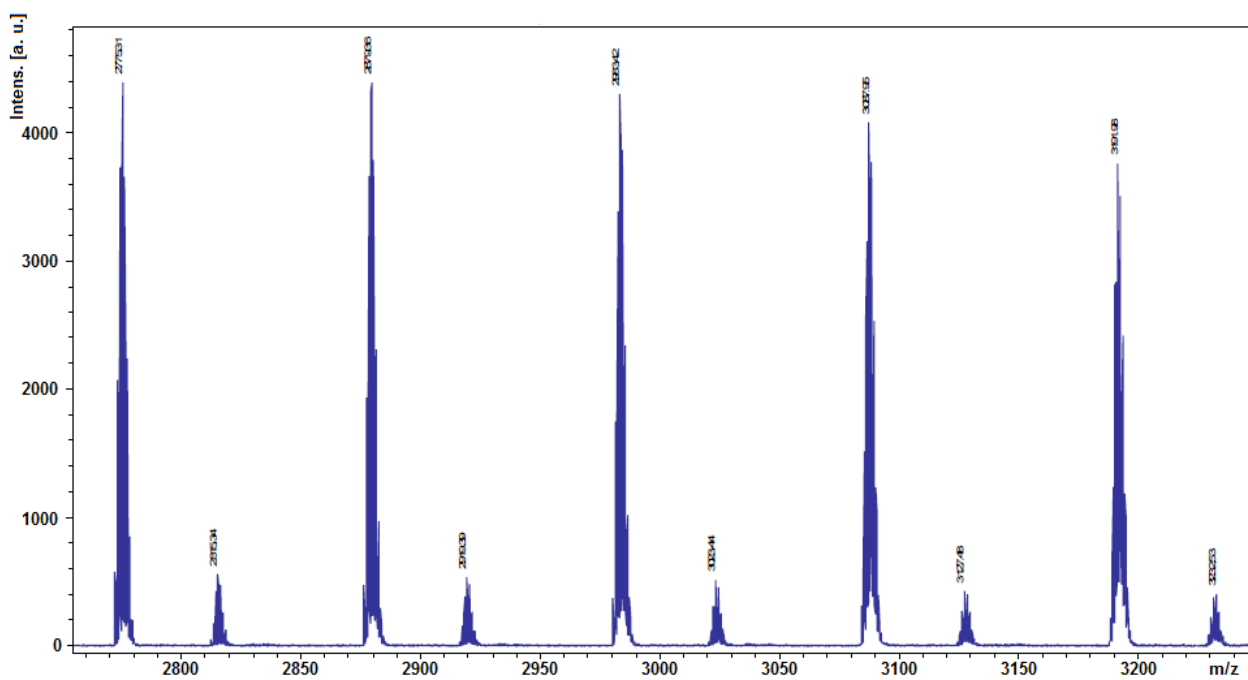
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Chapter 2

Precision Synthesis of Hybrid Block Copolymers by Organotellurium-Mediated Successive Living Radical and Cationic Polymerizations.

Abstract

Living cationic polymerization reactions using organotellurium compounds as initiators are reported. Polymerization of vinyl ethers in the presence of an organotellurium initiator and a Lewis acid, such as In(OTf)$_3$ and BF$_3$·OEt$_2$, afforded well-controlled poly(vinyl ether)s with predetermined molecular weights and narrow molecular weight distributions. Poly (meth)acrylates possessing organotellurium group at the ω-polymer end, which were prepared by organotellurium-mediated living radical polymerization (TERP), were used as macroinitiators for living cationic polymerization. The one-pot, two-step reaction of the macroinitiator with vinyl ether under radical and cationic conditions gave well-controlled AB diblock copolymers, poly{([meth]acrylate)-*block*-(vinyl ether)}s. ABA triblock copolymers, poly{(vinyl ether)-*block*-([meth]acrylate)-*block*-(vinyl ether)}s, with controlled structures were also synthesized from bifunctional organotellurium initiator. (Meth)acrylates and vinyl ethers are orthogonal monomer families under radical and cationic polymerization conditions, and thus, they cannot be polymerized under cationic and radical conditions, respectively. However, a selective chain end transformation via a radical-mediated tellurium-group transfer addition reaction of poly(meth)acrylate macroinitiator to vinyl ethers alternates the reactivity of ω–polymer end group, which is suitable for living cationic polymerization.

Introduction

Atom or group transfer addition reactions of organoheteroatom compounds (R-X) to alkenes and alkynes forming adduct **1**, as shown in Scheme 1, have been widely used in organic synthesis.[1-3] Repetition of this reaction under appropriate cationic or radical conditions leads to the formation of polymer **2**, which possesses X functionality at the polymer end.[4-6] If the repetition is controlled, living polymers with controlled macromolecular structures are obtained.[7-13] Therefore, this type of reaction has attracted a great deal of attention from both academic and industrial viewpoints. The addition of second alkenes to **2** would generate block copolymer **3**, which has been regarded as the next-generation functional material for a variety of applications, such as photonic, magnetic, and electronic materials, thermoplastic elastomers, adhesives, dispersants, and so forth.[14-16]

Scheme 1. Mono- and multi-addition reactions of organoheteroatom compounds to alkenes.
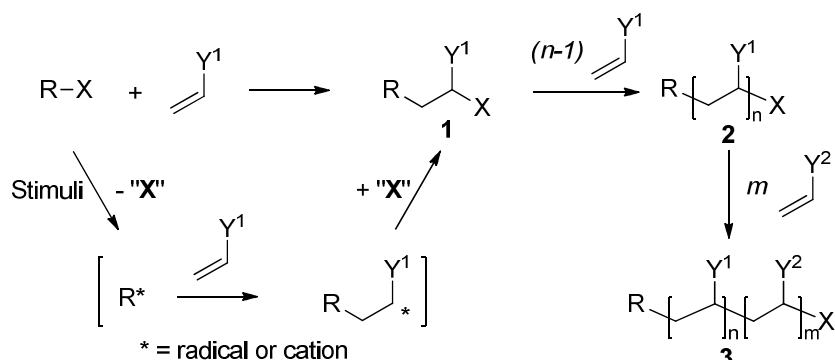
Despite the similarity in the formal transformation shown in Scheme 1, applicable monomer families under cationic or radical polymerization conditions are orthogonal except for styrene derivatives. Polymer end cations are electrophilic and tend to react with electron-rich monomers, such as vinyl ethers. However, vinyl ethers do not polymerize under radical conditions. Electron-deficient monomers, such as (meth)acrylates, are excellent monomers for radical

polymerization but not for cationic polymerization. Furthermore, generation of cationic species from poly(meth)acrylate polymer ends is electronically unfavourable. Therefore, the synthesis of block copolymers by successive living cationic and radical polymerization reactions, or vice versa, with orthogonal monomer families has been a formidable challenge. There are several reports on the synthesis of block copolymers with blocks made by using living cationic and radical polymerizations in this manner. However, these methods require transformation of the polymer end group before performing the blocking reaction[17] or utilization of polystyrene as a block[18-20] or a "buffer" block in between two orthogonal polymer blocks.[21-23] Moreover, the isolation of macroinitiator is required to remove protic or Lewis acids used for living cationic polymerization before carrying out living radical polymerization.

While investigating the selective transformation of polymer end groups prepared by using organoheteroatom-mediated living radical polymerization,[12,24-27] we became intrigued with the idea of using organoheteroatom compounds as common initiators in living cationic polymerization to synthesize new block copolymer **4** by the successive addition of monomers with orthogonal reactivities (Scheme 2). We anticipated that poly(meth)acrylate **5** would undergo a heteroatom transfer radical addition reaction with a vinyl ether to give mono-addition adduct **6** because the radical generated from **5** has amphiphilic character and reacts with both electron-deficient and electron-rich alkenes.[28] The radical generated from **6** does not react with vinyl ethers sufficiently, but the ω–alkoxytellanyl group in **6** is suitable for the formation of carbocations. Therefore, it should be possible to use **6** as a macroinitiator for living cationic polymerization. Cationic polymerization is usually less tolerant of polar functional groups than radical polymerization. However, recent progress in the area of living cationic polymerization has shown that various Lewis bases are compatible under the polymerization conditions, and that they even increase the control of the polymerization.[13,29-33] Therefore, polar functional groups on the macroinitiators prepared by

living radical polymerization would be compatible under living cationic polymerization conditions. However, to the best of our knowledge, there are no reports on the synthesis of block copolymers using this route.

Scheme 2. Working hypothesis of the synthesis of hybrid block copolymer by successive living radical and cationic polymerization.
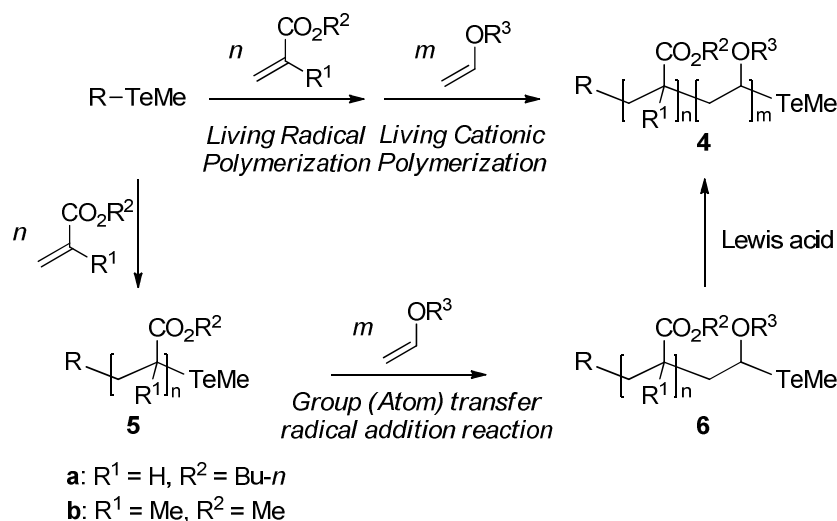
We report here a one-pot synthetic method for block copolymers consisting of poly(meth)acrylate and poly(vinly ether) blocks by sequential addition of (meth)acrylate and vinyl ether through selective transformation of a living radical polymer end into a living cationic polymer end. We selected organotellurium compounds as common initiators because they are excellent precursors for both radical and cationic species.[34-37] Although organotellurium compounds have been used as precursors of carbocations,[38-46] there are no reports on their use in living cationic polymerization. Therefore, we first investigated living cationic polymerizations using organotellurium compounds as initiators. Then, we examined the synthesis of block copolymers starting from macroinitiators that were prepared by organotellurium-mediated living radical polymerization (TERP). During our investigation, Sawamoto and co-workers reported the

transformation of chlorine-functionalized living poly(methyl methacrylate) polymer end to a macroinitiator for living cationic polymerization using styrenic monomers and Kamigaito and co-workers reported the successive use of trithiocarbonyl polymer end group for RAFT polymerization (living radical polymerization) of acrylates and living cationic polymerization.[47]

Result and discussions

Structural effects of organotellurium initiatnors. We first examined the structural effects of organotellurium initiators for cationic polymerization (Scheme 3). α-Alkoxytelluride **7**, which mimics polymer end structure of poly(vinyl ether)s and possesses a cation-stabilizing group, was prepared and was activated by PhTeOTf[48] in the presence of *iso*-butyl vinyl ether (IBVE, 50 equiv) in dichloromethane at 0 ℃ to room temperature for 1.5 h. IBVE was completely consumed and poly(*iso*-butyl vinyl ether) (PIBVE) was isolated after routine workup. Gel permeation chromatography (GPC) analysis indicated the formation of monodisperse polymer with a number average molecular weight (M_n) = 3000 and polydispersity index (PDI) = 1.57 (Table 1, run 1). While the level of control was low with M_n(exp) significantly deviated from the theoretical value [M_n(theo) = 5300] and high PDI value, the result clearly indicate the potential of organotellurium compounds as initiators for living cationic polymerization.

Scheme 3. Organotellurium-mediated living cationic polymerization of vinyl ether.
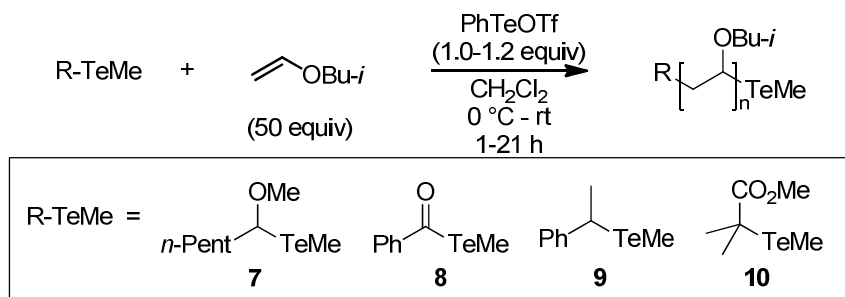
Acyltelluride **8** which generates acylinium ion was next examined. While it was activated by PhTeOTf, the polymer with bimodal distribution was obtained (Table 1, run 2). While phenylethyltelluride **9** generates stable benzilic cation, it turned out to be an inefficient initiator (Table 1, run 3). We also examined ester-substituted organotellurium compound **10**, which is an excellent initiator for living radical polymerization,[24,25,49,50] but it did not control the cationic polymerization (Table 1, run 4). This result is consistent with the fact that **10** have electron-withdrawing ester groups adjacent to the C-Te bond, which is electronically unfavorable for the generation of a carbocation.

Table 1. Effect of initiators.[a]

Run	Initiator (equiv)	Conv (%).[b]	M_n(theo)	M_n(exp)[c]	PDI[c]
1	**7**	100	5300	3000	1.57
2	**8**	100	5300	1049900	1.64
				15900	1.91
3	**9**	100	5300	1100	8.41
4	**10**	100	5300	1700	2.23

[a]A mixture of **7-10** (1.0 equiv), IBVE (50 equiv), and PhTeOTf (1.0-1.2 equiv) in CH_2Cl_2 was stirred at 0 °C to room temperature. Complete monomer conversion was observed in all cases. [b]Monomer conversion determined by ^{1}H NMR spectroscopy. [c]Number-average molecular weight (M_n) and polydispersity index (PDI) obtained by GPC calibrated with polystyrene standards.

Optimization of polymerization conditions. Next, effects of Lewis acid was examined by using α-alkoxy organotellurium compound **7** as an initiator and IBVE (50 equiv) as a monomer. When In(OTf)$_3$ (1.1 equiv) was used, structurally well controlled PIBVE with M_n close to the theoretical value [M_n (theo) = 5300 and M_n (exp) = 6100] and a low PDI = 1.24 was obtained (Table

2, run 1). Polymerization of IBVE proceeded with In(OTf)$_3$ in the absence of **7**, but the resulting polymer had a high PDI of 3.95 (Table 2, run 2). Various Lewis acids, such as Bi(OTf)$_3$, Ga(OTf)$_3$,[51] Ag(OTf), Cu(OTf)$_2$, BF$_3$·OEt$_2$, and Hf(OTf)$_4$ also promoted controlled polymerization with M_ns close to the theoretical value [M_n(exp) = 4100–5100] and low PDIs (= 1.22–1.50). Though Y(OTf)$_3$, Sn(OTf)$_2$, Bu$_2$Sn(OTf)$_2$, Sc(OTf)$_3$, and Zn(OTf)$_2$ promoted polymerization, the control of the resulting polymers was low [M_n(exp) = 1300–5400, PDI = 1.50-1.65] (See Table 4 in the experimental section). Other Lewis acids, such as TMSOTf, Au(OTf)$_3$, AuCl$_3$, Yb(OTf)$_3$, Sm(OTf)$_2$, Ti(OiPr)$_4$, and Mg(OTf)$_2$ were also examined, but they were inefficient promoters and gave polymers with low M_n and/or high PDI. Since In(OTf)$_3$ exhibited the best control, we employed this Lewis acid to the following investigations. Note that we did not use metal halides, such as metal iodide and bromide, besides BF$_3$·OEt$_2$ as Lewis acids in this study, because they potentially undergo halogen-tellurium exchange reactions at the polymer end.

The polymerization conditions were optimized further by using In(OTf)$_3$ or BF$_3$·OEt$_2$ as an activator. The PDI control increased by lowering the temperature to −25 ºC (Table 2, run 3), decreasing the amount of Lewis acid to 0.1 equivalents (Table 2, runs 4 and 11), and addition of 0.1 equivalents of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) as a proton scavenger (Table 2, run 5). Although several Lewis bases, such as ethyl acetate, THF, and 1,4-dioxane, are effective for increasing the PDI control,[13,29] the current conditions were insensitive to the Lewis bases. Other vinyl ethers, such as *n*-butyl vinyl ether (NBVE) and dodecyl vinyl ether (DVE), were polymerized in a controlled manner using **7** in the presence of 0.1 equivalents of In(OTf)$_3$ (Table 2, runs 6 and 7).

Table 2. Cationic polymerization of vinyl ethers by using **7** in the presence of Lewis acid.[a]

Run	Monomer[b] (equiv)	Lewis Acid (equiv)	Condns.[c] (ºC/h)	M_n(theo)	M_n(exp)[d]	PDI[d]
1	IBVE (50)	In(OTf)$_3$ (1.1)	0/1	5300	6100	1.24
2[e]	IBVE (50)	In(OTf)$_3$ (1.1)	0/1	5300	3500	3.95
3[f]	IBVE (50)	In(OTf)$_3$ (1.1)	-25/1	5300	6000	1.21
4	IBVE (50)	In(OTf)$_3$ (0.1)	-25/0.5	5300	6000	1.15
5[f]	IBVE (50)	In(OTf)$_3$ (0.1)	-25/1	5300	5800	1.10
6[f]	NBVE (50)	In(OTf)$_3$ (0.1)	-25/0.5	5300	4500	1.18
7[f]	DVE (50)	In(OTf)$_3$ (0.1)	-25/1	10900	11100	1.24
8[f]	IBVE (200)	In(OTf)$_3$ (0.1)	–40~ –25/4	20300	22400	1.20
9[f]	IBVE (500)	In(OTf)$_3$ (0.1)	–40 ~–25/4	50300	49600 (46500)[g]	1.24
10	IBVE (50)	BF$_3$·OEt$_2$ (1.1)	0/1	5300	4800	1.46
11	IBVE (50)	BF$_3$·OEt$_2$ (0.1)	-25/0.5	5300	5500	1.25

[a]A mixture of **7** (1.0 equiv), IBVE, and a Lewis acid in CH$_2$Cl$_2$ was stirred under the conditions indicated in the table. Complete monomer conversion was observed in all cases. [b]Monomer abbreviations: IBVE = *iso*-butylvinyl ether, NBVE = *n*-butylvinyl ether, DVE = dodecylvinyl ether. [c]Monomer conversion determined by ^{1}H NMR spectroscopy. [d]Number-average molecular weight (M_n) and polydispersity index (PDI) obtained by GPC calibrated with polystyrene standards. [e]Polymerization was carried out without **7**. [f]2,6-Di-*tert*-butyl-4-methylpyridine (0.1 equiv) was added. [g]M_n estivated from M_w obtained by multi-angle laser light scattering in THF and PDI value.

Living character was first confirmed on the basis of the linear increase in M_n of the resulting polymers by increasing the monomer/**7** ratio (Table 2, runs 8 and 9, Figure 1). Second, it was further confirmed by a chain extension experiment. Thus, after polymerization of IBVE (50 equiv) under optimized conditions to give PIBVE with M_n = 6100 and PDI = 1.09, 200 equivalents of

IBVE was added. In the GPC analysis, the peak corresponding to the initially formed PIBVE disappeared, and a new unimodal peak corresponding to a chain-extended PIBVE with $M_n = 22200$ and PDI = 1.36 formed (Figure 2).

Figure 1. Correlation of M_n on monomer equivalent for the cationic polymerization of IBVE in the presence of **7**, In(OTf)$_3$, and DTMBP.
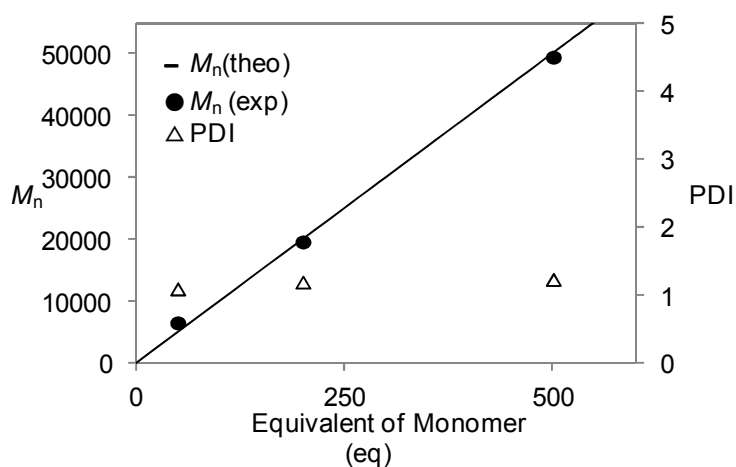
Figure 2. GPC traces before and after the chain-extension.
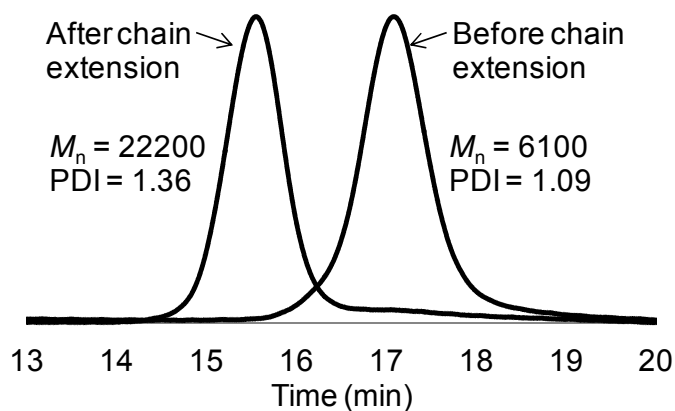
Group transfer radical addition reaction. We next examined the selective transformation of poly(meth)acrylate **11** to macro initiator **13** for living cationic polymerization (Scheme 4).

Scheme 4. Synthesis of hybrid block copolymers through successive living radical and cationic polymerizations.
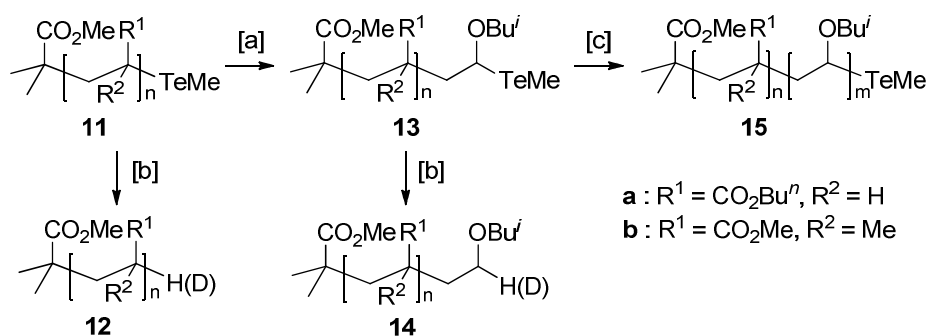
First, poly(*n*-butylacrylate) macroinitiator **11a**, which was prepared by reacting **10** and *n*-butyl acrylate (30 equiv) in the presence of 2,2'-azobis(2-methylpropionate) (V-601) at 60 ºC for 2 h, was purified by preparative GPC under nitrogen atmosphere in a glove box. The purified **11a** (M_n = 3000 and PDI = 1.13) was heated with 30 equiv of IBVE at 60 ºC for 4 h to give **13a** (M_n = 3100 and PDI = 1.20). The formation of **13a** was suggested by the similarity in the GPC data between **11a** and **13a** and by the ^{1}H NMR analysis by observing the characteristic signal at δ = 3.0-3.4 ppm of *iso*-butyloxy group. The end group structures of **11a** and **13a** were further examined after reduction of **11a** and **13a** with tributyltin hydride and deuteride to give **12a** and **14a** and **[D]12a** and **[D]14a**, respectively. In the ^{2}H NMR spectra of **[D]12a** and **[D]14a**, characteristic broad singlets were observed at 2.1 and 3.4 ppm, which are assigned to α-ester and α-alkoxy deuterium, respectively (Figure 3). The results indicate the selective and complete transformation from **11a** to **13a** by the treatment of **11a** with IBVE.

Figure 3. (a) ^{2}H NMR of **[D]12a** and (b) **[D]14a**.
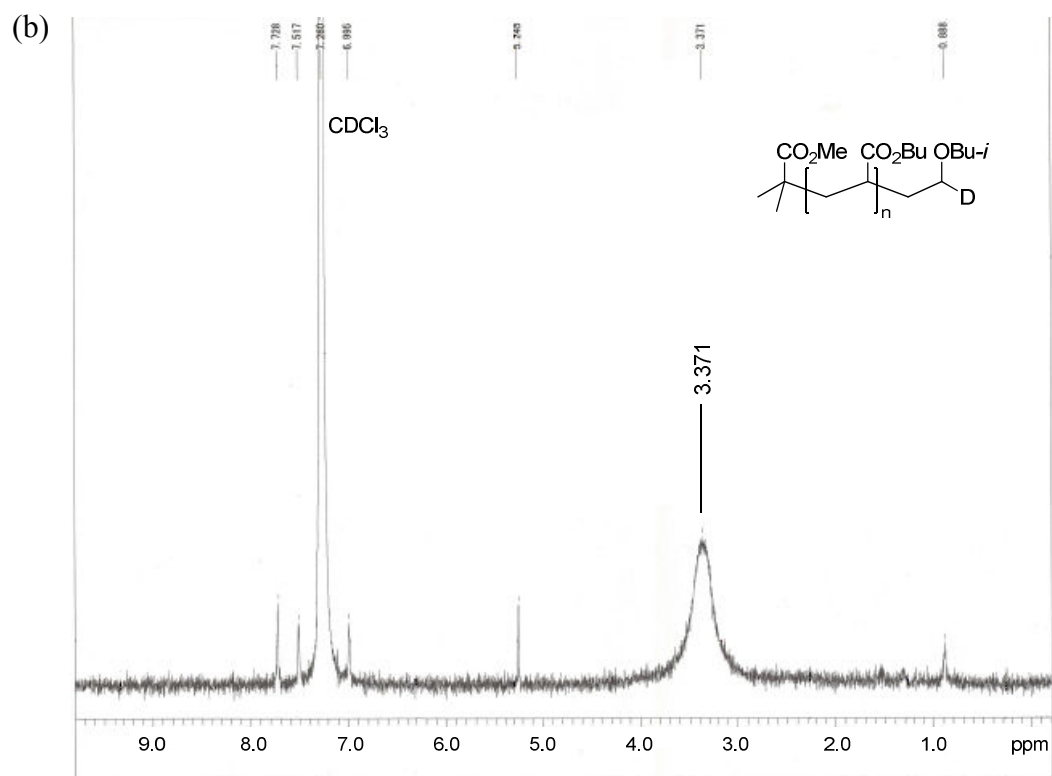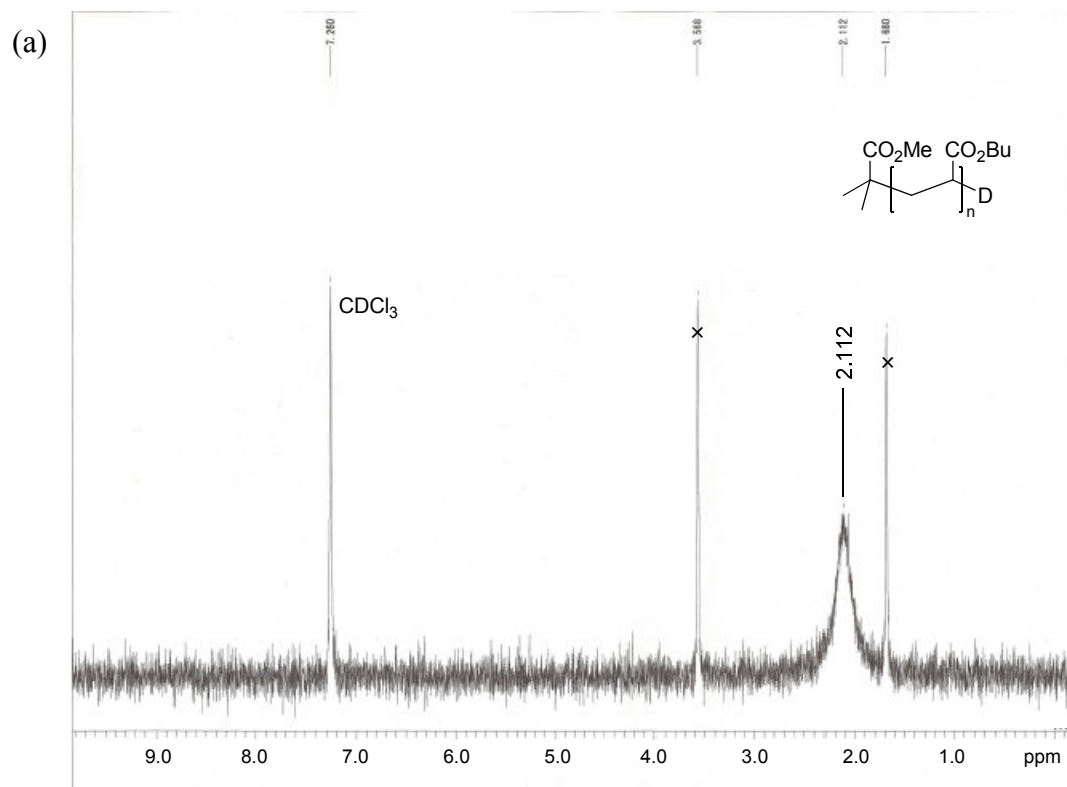
The matrix associated laser desorption ionization (MALDI) time of flight (TOF) mass spectrometry of **14a** indicated one to four IBVE molecules inserted into **11a** in the ratio of 75:21:2.8:0.3, respectively, together with a small amount (0.9%) of no insertion adduct **12a**. While the multi addition adducts that were formed arose from the high concentration of IBVE, these results clearly revealed that the polymer end group of **11a** was selectively substituted with IBVE(Figure 4).

Figure 4. (a) Full and (b) partical MALDI-TOF-MS spectra of **14a**.
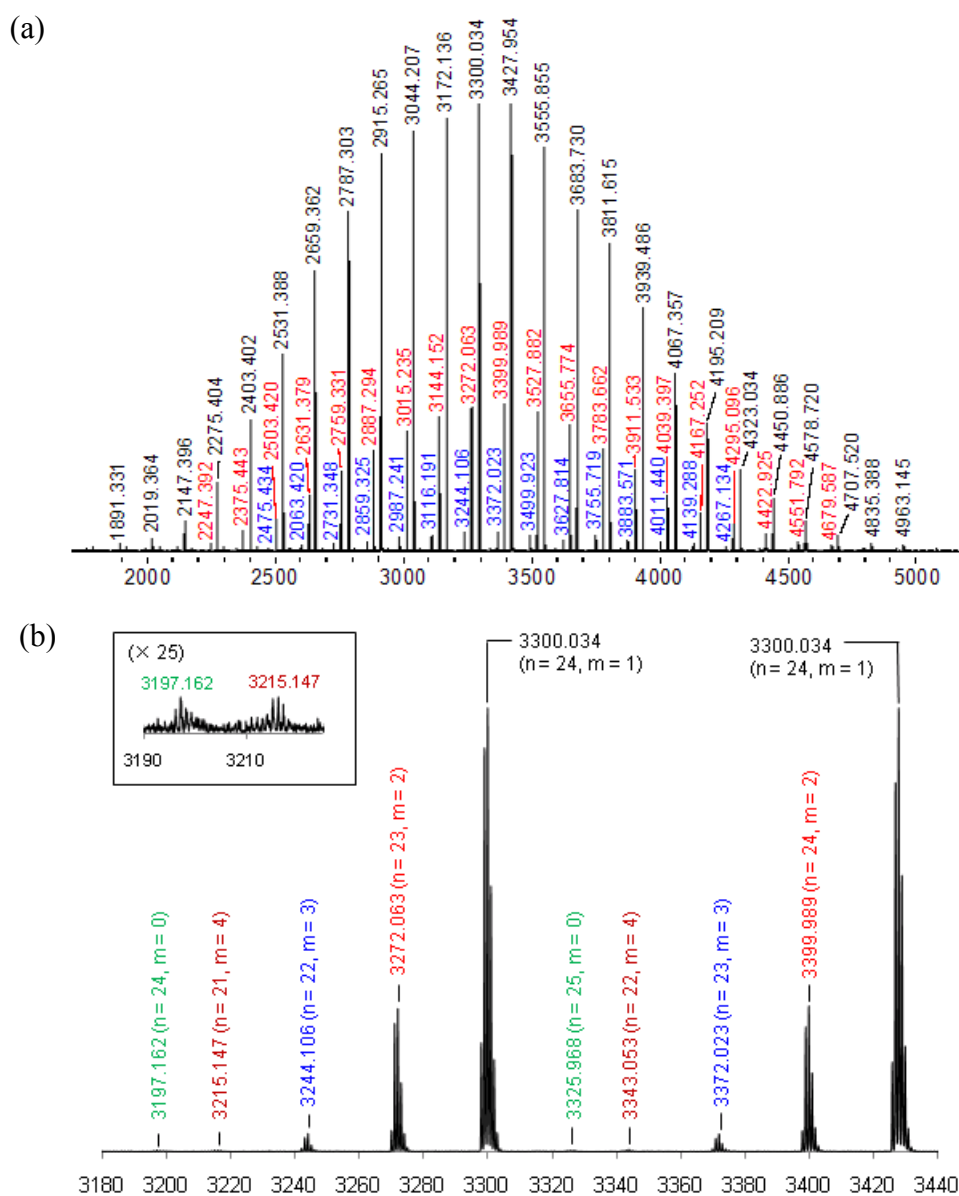
The same transformation was carried out with crude poly(n-butylacrylate) macroinitiator **11a** (M_n = 4500 and PDI = 1.09), prepared by reacting **10** and n-butyl acrylate (30 equiv) in the presence of V-601 at 60 ºC for 1.5 h with 96% monomer conversion. After the addition of IBVE (30 equiv), the solution was heated at 60 ºC for 4 h to give **13a** (M_n = 4800 and PDI = 1.13). GPC, ^{1}H NMR, and the deuterium labeling experiments supported the successful transformation from **11a** to **13a**. The MALDI TOF mass spectrometry of **14a**, however, indicated that one to eight IBVE molecules inserted into **11a** with the doubly and triply inserted products being the major products (Figure 5). As vinyl ethers do not homopolymerize but copolymerize with acrylates, remaining BA and IBVE were copolymerized in a living manner.[52] The results clearly suggest that all polymer ends were substituted with IBVE when an excess amount of IBVE was used.

End group transformation of poly(methyl methacrylate) has been next examined. Poly(methyl methacrylate) macroinitiator **11b** (M_n = 3300 and PDI = 1.20), which was prepared from **10** and methyl methacrylate (30 equiv) in the presence of dimethylditelluride (1.0 equiv)[25,53] and V-601 (0.2 equiv) at 60 ºC for 12 h with 100% monomer conversion, was heated with 100 equivalents of IBVE at 60 ºC for 4 h to give **13b** (M_n = 3500 and PDI = 1.19). Macro CTAs **11b** and **13b** were reduced with tributyltin hydride and deuteride to give protonated and deuterated polymers **12b** and **14b** and **[D]12b** and **[D]14b**, respectively. The formation of **13b** was initially suggested by the GPC and ^{1}H NMR spectrum of **13b**. It was further confirmed by the ^{2}H NMR spectra of **[D]12b** and **[D]14b**, which showed characteristic α-ester and α-alkoxy deuterium signals at 2.4 and 3.3 ppm, respectively, as broad singlets. These results clearly reveal the selective transformation from **11** to **13**.

Figure 5. (a) Full and (b) partical MALDI-TOF-MS spectra of **14a**.
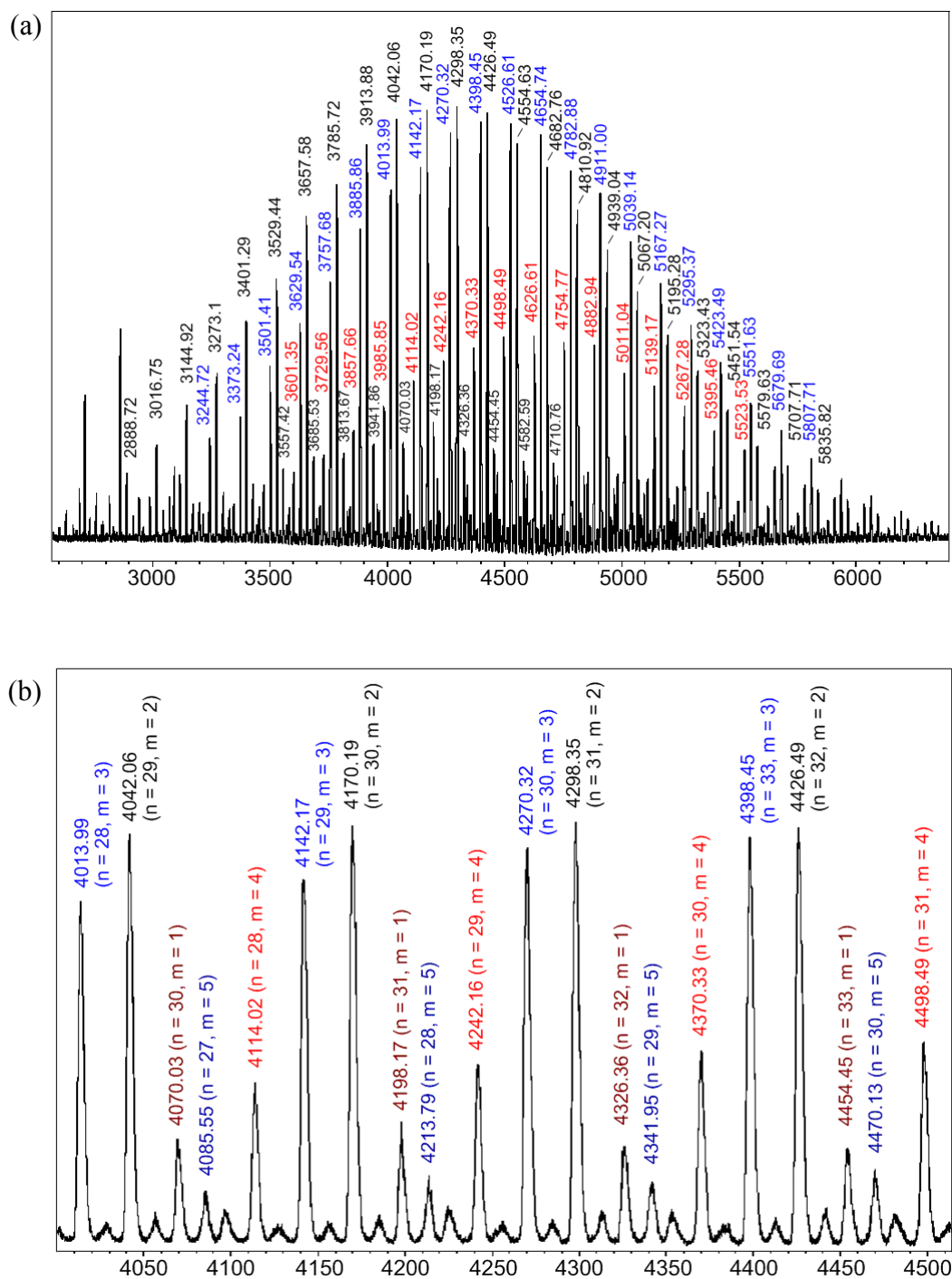
Synthesis of "hybrid" block copolymers. Living cationic polymerization was conducted on a mixture of **13a** (M_n = 4000, PDI = 1.12) and IBVE in the presence of a Lewis acid at –25 ºC. We found that the use of BF$_3$·OEt$_2$ (0.1 equiv) instead of In(OTf)$_3$ gave better results for the blocking

reaction, affording the desired block copolymer **15a** with a high monomer conversion (Table 3, run 1). In the GPC analysis, the peak corresponding to **13a** was disappeared, and a new unimodal peak corresponding to **15a** with M_n of 11200 and PDI of 1.30 was observed (Figure 6a). The same diblock copolymer with different block lengths was also prepared in a controlled manner by the reaction of **13a** (M_n = 14400, PDI = 1.13) and IBVE (100 equiv) to give **15a** (M_n = 20500, PDI = 1.23; Table 3, run 2).

Scheme 5. Chemical structures of CTA, Macro CTAs, and block copolymers.
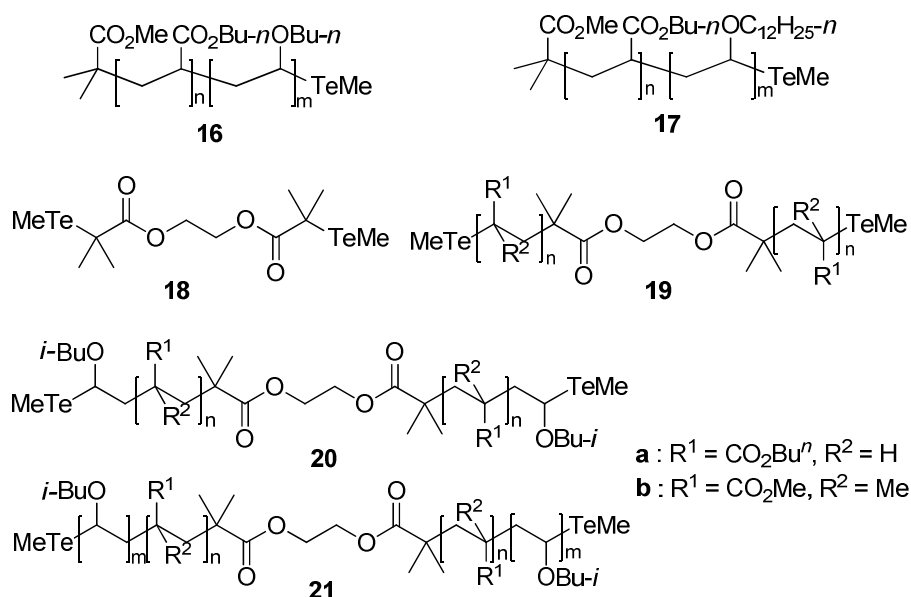
Synthetic scope of the block copolymers was further examined, and the results are summarized in Table 3, runs 3–7. The group-transfer addition reaction of **11a** with NBVE or DVE, followed by cationic polymerization of NBVE or DVE from **13a**, also took place efficiently in the presence of $BF_3 \cdot OEt_2$. Desired diblock copolymers **16** and **17** were obtained with sufficiently controlled macromolecular structures (PDI < 1.4; Table 3, runs 3 and 4), though shoulders were observed by GPC. The synthesis of block copolymer **15b** starting from poly(methyl methacrylate) macroinitiator **13b** (M_n = 9500 and PDI = 1.19) prepared from **11b** and 100 equivalents of IBVE in

the presence of $BF_3 \cdot OEt_2$ (0.1 equiv) proceeded smoothly and in a controlled manner (Table 3, run 5). As the polymer end structure of **13a** was identical to **13b**, the blocking reaction proceeded under the same conditions regardless to the structure of the first block.

Table 3. Synthesis of AB and ABA block copolymers by successive living radical and cationic polymerizations.[a]

Run	Macro CTA[a]	M_n/PDI[b]	IBVE (equiv)	Product	Conv.[c] (%)	M_n[d]	PDI[d]
1	**11a**	3200/1.12	100	**15a**	96	11200	1.30
2	**11a**	13400/1.12	100	**15a**	100	20500	1.23
3	**11a**	3800/1.16	100[e]	**16**	100	10400	1.37
4	**11a**	10900/1.16	100[f]	**17**	92	19700	1.46
5	**11b**	8900/1.20	94	**15b**	95	13800	1.21
6	**19a**	3100/1.14	90	**21a**	91	9500	1.29
7	**19b**	2600/1.34	100	**21b**	88	8000	1.41

[a]See experimental section and ref. 49 for the synthesis. [b]Number-average molecular weight (M_n) and polydispersity index (PDI) were obtained by using size exclusion chromatography calibrated with PMMA standards. [c]Monomer conversion determined by ^{1}H NMR analysis. [d]Number-average molecular weight (M_n) and polydispersity index (PDI) obtained by GPC calibrated with poly(methyl methacrylate) standards.

Figure 6. GPC traces before and after the blocking reaction (a) starting from poly(butyl acrylate) macro CTA **11a** to **15a** by way of **13a**, and (b) starting from poly(butyl acrylate) macro CTA **19a** to **21a** by way of **20a**.
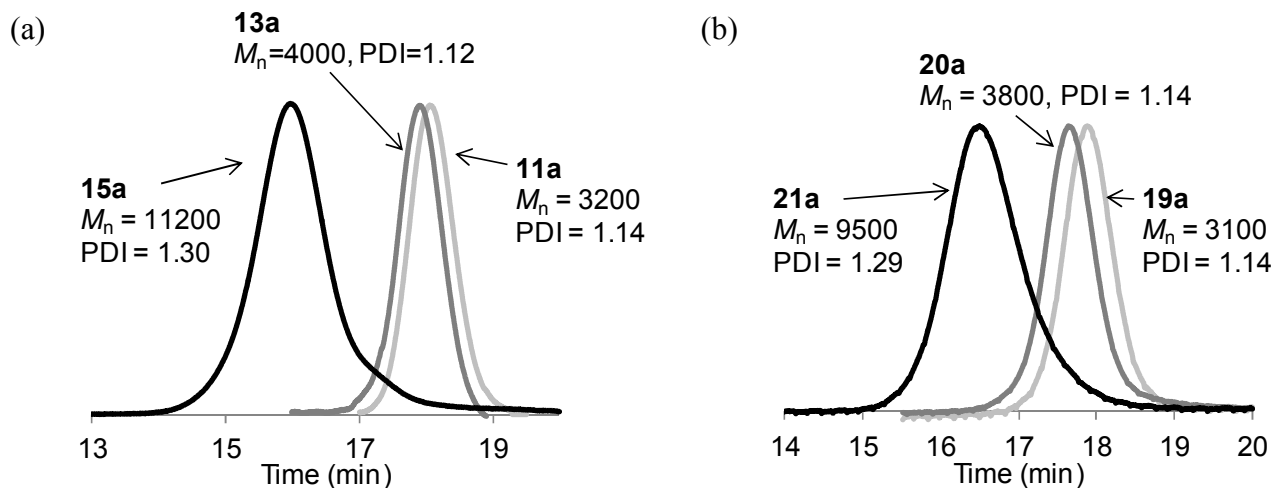
ABA triblock copolymers could be prepared starting from bifunctional initiator **18**. The reaction of **18** and *n*-butyl acrylates afforded **19a** (M_n = 3100 and PDI = 1.14), which was treated with IBVA (100 equiv) at 60 °C to give **20a** (M_n = 3800 and PDI = 1.14). It was further treated with BF$_3$·OEt$_2$ (0.1 equiv) to give structurally well controlled triblock copolymer **21a** (M_n = 9500, PDI = 1.29; Table 3, run 6, Figure 6b). Starting from bifunctional poly(methyl methacrylate) macro initiator **19b**, which was prepared from **18** and methyl methacrylate, triblock copolymer **21b** was prepared through **20b** (Table 3, run 7). These results clearly indicate the generality of this strategy (Scheme 5).

Conclusions

We demonstrated for the first time that organotellurium compounds are efficient initiators for living cationic polymerization. Poly(meth)acrylates prepared by using TERP are used as macroinitiators for living cationic polymerization through radical-mediated tellurium-group transfer addition reactions to vinyl ethers, and the corresponding block copolymers with controlled

macromolecular structures are obtained. As vinyl ethers are utilized for both end-group transformation and cationic polymerization, block copolymers are obtained through a one-pot procedure by successive addition of monomers without purification or isolation of the macroinitiators. This method gives access to new hybrid block copolymers, which are difficult to synthesize by other methods. Although we exclusively used organotellurium compounds in this study, organohalogen compounds would be also used as the common transfer agents because they are used as initiators for both living cationic polymerization and living radical polymerization.

Experimental Section

General. All reaction conditions dealing with air- and moisture sensitive compounds were carried out in a dry reaction vessel under nitrogen or argon atmosphere. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured for a CDCl$_3$ or C$_6$D$_6$ solution of a sample. ^{1}H NMR spectra are reported in parts per million (δ) from internal tetramethylsilane (0 ppm) or residual solvent peak, and ^{13}C NMR from solvent peak. IR spectra (absorption) are reported in cm^{-1}. High resolution mass spectra (HRMS) were obtained under electron impact ionization conditions. MALDI-TOF mass spectra were recorded on a spectrometer equipped with a 337 nm N$_2$ laser in the reflection mode and at 20 kV acceleration voltage. Samples were prepared from a tetrahydrofuran (THF) solution by mixing sample (1 mg/mL), dithranol (10 mg/mL), and sodium trifluoroacetate (1 mg/mL) in a ratio of 5:1:1. The GPC was performed on a liquid chromatography equipped with two linearly connected polystyrene (PSt) mixed gel columns (Shodex LF-604), which were calibrated with PSt standards for poly(vinyl ethers) or poly(methyl methacrylate) (PMMA) standards for block copolymers using CHCl$_3$ as an eluant. Preparative/recycling GPC was carried out under nitrogen atmosphere with two linearly connected PSt mixed gel columns in a glove box as previously described.[54]

Materials. Unless otherwise noted, materials were obtained from commercial suppliers. Isobutyl vinyl ether (IBVE; >99%), *n*-butyl vinyl ether (NBVE; 98 %), dodecyl vinyl ether (DVE; 98 %), *n*-butyl acrylate (BA; >99%,), methyl methacrylate (MMA; >99%), were washed with 5 % aqueous sodium hydroxide solution and were distilled over calcium hydride under reduced pressure. CH_2Cl_2 and AcOEt were distilled successively from P_2O_5 and K_2CO_3 and stored over molecular sieves 4A. Toluene and triethylamine were distilled from CaH_2 and stored over molecular sieves 4A. THF was distilled from sodium benzophenone ketyl before use. Methanol was distilled from Mg which was activated by I_2 and stored over molecular sieves 3A. Azobis(isobuthronitrile) (AIBN; 98 %) and dimethyl 2,2'-azobis(2-methylpropionate) (V-601) were recrystallized from methanol. Compound **8**,[55] **9**,[24] $Ga(OTf)_3$,[51] n-$Bu_2Sn(OTf)_2$,[56] 1, 2-bis(bromoisobutyryloxy)ethane[57] were prepared as reported.

Preparation of 1-methoxy-1-methyltellanylhexane (7).

n-Pent (OMe)(OMe) + (O)(Br) $\xrightarrow[\text{2. MeTeLi, THF, 0 °C - r. t., 2 h}]{\text{1. }CH_2Cl_2\text{, 0 °C - r. t., 1 h}}$ n-Pent (OMe)(TeMe)
7
66 % (2 step)
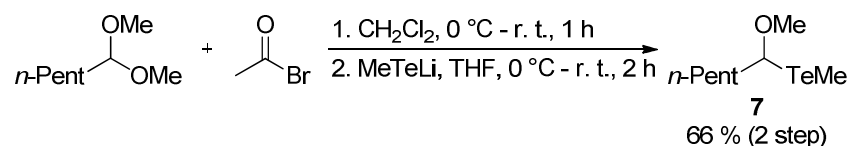
Acetyl bromide (8.81 g, 71.7 mmol) was added to a solution of 1,1-dimethoxyhexane (8.47 g, 57.9 mmol) in CH_2Cl_2 (20 mL) at 0 °C, and the resulting solution was stirred for 1 h at room temperature. The solvent and methyl acetate generated was removed under reduced pressure to give 1-bromo-1-methoxyhexane, which was used in the next step without purification. To this mixture was slowly added a solution of lithium methyltellurolate, which was prepared by mixing tellurium metal powder (7.39 g, 58.0 mmol) and methyllithium (58 mL, 1.05 M, 60.9 mmol) in THF (30 mL). After stirring for 2 h at room temperature, the reaction was quenched by addition of unaerated water, and the aqueous layer was separated. The organic phase was washed successively with saturated and unaerated aqueous ammonium chloride and sodium chloride solutions, dried over $MgSO_4$ and

filtered. All work-up procedures were carried out under a nitrogen atmosphere. The organic extracts were concentrated under reduced pressure to give a crude oil. Distillation under reduced pressure (b.p. 41 °C/1.7 mmHg) afforded the title compound as a pale yellow oil in 66% yield (9.46 g). IR (KBr) v = 2955, 1458, 1126, 901, 629, 521 cm^{-1}; ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C) δ = 0.85 (t, J = 7.0 Hz, 3 H), 1.15–1.24 (m, 4 H), 1.43–1.47 (m, 2 H), 1.65 (s, 3 H), 1.98–2.05 (m, 2 H), 3.05 (s, 3 H), 4.67 ppm (t, J = 6.4 Hz, 1 H); ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C) δ = –23.77, 13.62, 23.33, 28.28, 31.93, 40.89, 58.63, 74.83 ppm; HRMS (EI) m/z: calcd for C$_8$H$_{18}$OTe (M)$^+$: 260.0420; found: 260.0410.

Preparation of methyl 2-methyl-2-methyltellanylpropionate (10).
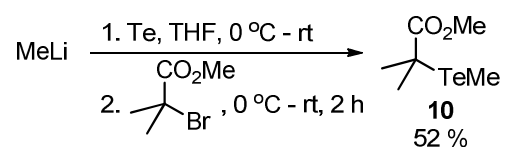
Methyl 2-bromo- 2-emthylpropionate (19.59 g, 108.2 mmol) was added to a solution of lithium methyltellurolate, which was prepared by mixing tellurium metal powder (13.15 g, 103.1 mmol) and methyllithium (104 mL, 1.04 M, 108.2 mmol) in THF (50 mL), at 0 °C, and the resulting solution was stirred for 2 h at room temperature. The reaction was quenched by addition of unaerated water, and then the water layer was separated. The resulting organic phase was washed successively with saturated and unaerated aqueous ammonium chloride and sodium chloride solutions. The resulting organic phase was dried over MgSO$_4$, filtered under a nitrogen atmosphere, and concentrated under reduced pressure to give a crude oil. All work-up procedures were carried out under a nitrogen atmosphere. Distillation under reduced pressure (b.p. 40 °C/0.8 mmHg) gave the title compound as a pale yellow oil in 52% yield (12.96 g). IR (KBr) v = 2951, 1713, 1466, 1273, 1146, 1013, 824, 766 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 1.75 (s, 6 H), 2.15 (s, 3 H),

3.71 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = −16.76, 23.39, 28.00, 52.51, 177.54

ppm; HRMS (EI) m/z: calcd for C$_6$H$_{12}$O$_2$Te (M)$^+$: 245.9900; found: 245.9913.

Preparation of 18.
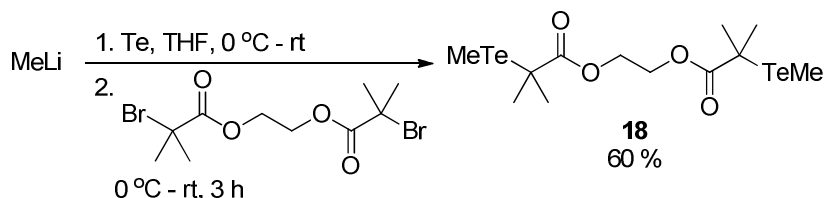
1,2-Bis(2-bromoisobutyryloxy)ethane (18.00 g, 50.0 mmol)[57] in THF (30 mL) was added to a

solution of lithium methyltellurolate, which was prepared by mixing tellurium metal powder (14.04

g, 110.3 mmol) and methyllithium (112 mL, 0.98 M, 110.0 mmol) in THF (30 mL), at 0 °C, and the

resulting solution was stirred for 3 h at room temperature. The reaction was quenched by addition of

unaerated water, and the water layer was removed by a syringe. The resulting organic phase was

washed with saturated and unaerated aqueous ammonium chloride and sodium chloride solutions,

dried over MgSO$_4$, filtered, and concentrated under reduced pressure to give a crude oil. All

work-up procedures were carried out under a nitrogen atmosphere. Purification by preparative GPC

under nitrogen atmosphere afforded the pure title compound as a pale yellow oil in 60% yield (14.7

g). IR (KBr) ν=2918, 2253, 1719, 1458, 1389, 1142, 912, 743, 650 cm^{-1}; ^{1}H NMR (400 MHz,

CDCl$_3$, 25 °C): δ=1.75 (s, 12 H), 2.16 (s, 6 H), 4.32 ppm (s, 4 H); ^{13}C NMR (100 MHz, CDCl$_3$,

25 °C): δ=−16.76, 23.39, 28.00, 52.51, 177.54 ppm; HRMS (FAB): m/z: calcd for C$_{12}$H$_{22}$O$_4$Te$_2$

(M)$^+$: 489.9643; found: 489.9643.

Typical procedure for living cationic polymerization: Synthesis of PIBVE. A solution of

7 (51.4 mg, 0.199 mmol), IBVE (1.0 g, 10.0 mmol), and 2,6-di-*tert*-butyl-4-methylpyridine

(DTBMP; 4.6 mg, 0.022 mmol) in CH$_2$Cl$_2$ (3.0 mL) was added to a solution of In(OTf)$_3$ (13.0 mg,

0.023 mmol) in CH$_2$Cl$_2$ (5.0 mL) at −72 °C. The resulting solution was stirred at −25 °C for 1 h, and

the reaction was quenched by adding triethylamine (0.3 mL) followed by methanol (0.1 mL). The monomer conversion (100%) was determined by ^{1}H NMR. After removing the solvent, aqueous $NaHCO_3$ solution and ethyl acetate were introduced. Water phase was separated and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with a saturated aqueous NaCl solution, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the product (1.0 g). The number averaged molecular weight (M_n=6600) and the polydispersity index (PDI=1.10) were determined by using GPC calibrated with PSt standards.

Polymerization results by using other Lewis acids are summarized in Table 4

Table 4. Effects of Lewis acid in the cationic polymerization of IBVE in the presence of **7**.

Entry	Lewis acid	Conv. (%)[a]	M_n(calc)	M_n(exp)[b]	PDI[b]
1	In(OTf)$_3$	100	5300	6100	1.24
2	Bi(OTf)$_3$	100	5300	4900	1.31
3	Ga(OTf)$_3$	100	5300	4100	1.31
4	AgOTf	100	5300	3900	1.35
5	Cu(OTf)$_2$	100	5300	4100	1.43
6	BF$_3$·OEt$_2$	100	5300	4800	1.46
7	Hf(OTf)$_4$	100	5300	5100	1.50
8	Y(OTf)$_3$	100	5300	1300	1.50
9	PhTeOTf	100	5300	3000	1.57
10	Sn(OTf)$_2$	100	5300	2800	1.59
11	Bu$_2$Sn(OTf)$_2$	100	5300	5400	1.65
12	Sc(OTf)$_3$	100	5300	3500	1.65
13	Zn(OTf)$_2$	100	5300	2500	1.65
14	TMSOTf	100	5300	6300	2.24

Table 4, continued.

15	Au(OTf)$_3$	91	4800	1600	1.86
16	AuCl$_3$	60	3300	1200	1.27
17	Yb(OTf)$_3$	59	3200	2500	1.46

[a]Monomer conversion determined by ^{1}H NMR spectroscopy. [b]Number-average molecular weight (M_n) and polydispersity index (PDI) obtained by GPC calibrated with PSt standards.

Polymerization of NBVE. To a solution of In(OTf)$_3$ (14.9 mg, 0.027 mmol) in CH$_2$Cl$_2$ (5.0 ml) was added a solution of **7** (51.4 mg, 0.199 mmol), NBVE (1.0 g, 10.1 mmol), and DTBMP (5.4 mg, 0.026 mmol) in CH$_2$Cl$_2$ (3.0 ml) at -72 °C. The resulting solution was stirred at -25 °C for 30 min. The reaction was quenched by addition of triethylamine (0.3 ml) and methanol (0.1 ml). The conversion of monomer (100%) was determined by ^{1}H NMR. After routine workup, crude product was obtained (1.0 g). The M_n of 4500 and the PDI of 1.18 were determined by GPC calibrated with PSt standards.

Polymerization of dodecyl vinyl ether. To a solution of In(OTf)$_3$ (16.0 mg, 0.028 mmol) in CH$_2$Cl$_2$ (5.0 ml) was added a solution of **7** (51.4 mg, 0.199 mmol), DVE (2.1 g, 10.0 mmol), and DTBMP (5.6 mg, 0.027 mmol) in CH$_2$Cl$_2$ (3.0 ml) at -72 °C. The resulting solution was stirred at -25 °C for 1 h. The reaction was quenched by addition of triethylamine (0.3 ml) and methanol (0.1 ml). The conversion of monomer (100%) was determined by ^{1}H NMR. After routine workup, crude product was obtained (2.2 g). The Mn of 11100 and the PDI of 1.24 were determined by GPC calibrated with PSt standards.

Chain extension test. To a solution of In(OTf)$_3$ (12.8 mg, 0.023 mmol) in CH$_2$Cl$_2$ (5.0 ml) was added a solution of **7** (51.4 mg, 0.199 mmol) and IBVE (1.0 g, 10.0 mmol) in CH$_2$Cl$_2$ (3.0 ml) at -72 °C. The resulting solution was stirred at -25 °C for 15 min. The GPC analysis of the polymer prepared by a different batch indicated the formation of PIBVE with Mn of 6100 and PDI of 1.09.

The reaction mixture was cooled at -72 °C. Isobutyl vinyl ether (4.0 g, 40.0 mmol) was added, and the resulting solution was stirred at -40 °C for 2 h. The reaction was quenched by addition of triethylamine (0.3 ml) and methanol (0.1 ml). The conversion of monomer (100%) was determined by ^{1}H NMR. After routine workup, crude product was obtained (5.1 g). GPC analysis revealed that PIBVE formed with M_n of 22200 and PDI of 1.36 (Figure 2).

Insertion of IBVE to PBA polymer end. A solution of **10** (25.3 mg, 0.10 mmol), BA (0.39 g, 3.1 mmol), and V-601 (5.6 mg, 0.02 mmol) was stirred at 60 °C for 1.5 h under a nitrogen atmosphere to give **11a** (Mn = 4500, PDI = 1.09). Conversion of the monomer (96 %) was determined by ^{1}H NMR. IBVE (0.31 g, 3.1 mmol) was added to the resulting mixture and the solution was heated at 60 °C for 4 h to give the end modified polymer **13a** (Mn = 4800, PDI = 1.13). Then, tributyltin hydride (35.7 mg, 0.12 mmol) and V-601 (0.2 equiv) was added to the solution and stirred at 60 °C for 2 h. Volatile materials were removed under reduced pressure and purification by preparative/recyclig GPC gave **14a** (0.39 g). The M_n of 5000 and the PDI of 1.13 were determined by GPC calibrated with PMMA standards.

Synthesis of poly(BA-*block*-IBVE) (Table 3, run 1)**.** A solution of **10** (25.3 mg, 0.10 mmol), butyl acrylate (0.4 g, 3.1 mmol), and V-601 (5.6 mg, 0.02 mmol) was stirred at 60 °C for 1.5 h under a nitrogen atmosphere. Monomer conversion (92%) was determined from ^{1}H NMR spectra. GPC analysis indicated polymer **11a** with M_n of 3200 and PDI of 1.14 formed. IBVE (1.0 g, 10.4 mmol) was added, and the mixture was heated at 60 °C for 4 h to give **13a** (M_n=4000 and PDI = 1.12). To this solution was added CH_2Cl_2 (4.0 mL) and $BF_3 \cdot Et_2O$ (1.6 mg, 0.01 mmol) at -72 °C, and the resulting solution was stirred at -25 °C for 1.5 h. The reaction was quenched by addition of triethylamine (0.3 mL) followed by methanol (0.1 mL). Monomer conversion (100%) was determined by ^{1}H NMR spectroscopy. After standard work-up, block copolymer **15a** was obtained

(1.5 g) with M_n of 11200 and PDI of 1.30 determined by GPC calibrated with PMMA standards (Figure 6a).

Synthesis of poly(BA-*block*-IBVE) (Table 3, run 2)**.** A solution of **10** (25.3 mg, 0.10 mmol), butyl acrylate (1.3 g, 10.5 mmol), and V-601 (5.6 mg, 0.02 mmol) was stirred at 60 °C for 2 h under a nitrogen atmosphere. Monomer conversion (96%) was determined from ^{1}H NMR spectra. GPC analysis indicated polymer **11a** with M_n of 13400 and PDI of 1.12 formed. Isobutyl vinyl ether (1.0 g, 10.4 mmol) was added, and the mixture was heated at 60 °C for 4 h to give **13a** (M_n=14400 and PDI = 1.13). To this solution was added CH_2Cl_2 (4.0 mL) and $BF_3 \cdot Et_2O$ (1.6 mg, 0.01 mmol) at −72 °C, and the resulting solution was stirred at −25 °C for 1.5 h. The reaction was quenched by addition of triethylamine (0.3 mL) followed by methanol (0.1 mL). Monomer conversion (100%) was determined by ^{1}H NMR spectroscopy. After standard work-up, block copolymer **15a** was obtained (2.4 g) with M_n of 20500 and PDI of 1.23 determined by GPC calibrated with PMMA standards (Figure 7).
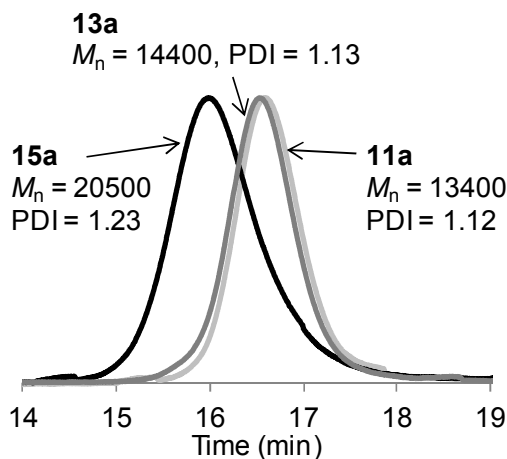
Figure 7. GPC traces of **11a**, **13a**, and **15a**.

Synthesis of poly(*n*BA-block-NBVE). A solution of **10** (25.3 mg, 0.10 mmol), *n*BA (0.4 g, 3.1 mmol), and V-601 (4.6 mg, 0.02 mmol) was stirred at 60 °C for 1.5 h under a nitrogen

atmosphere to give **11a** (M_n = 3800, PDI = 1.16). Conversion of the monomer (90 %) was determined by ^{1}H-NMR. NBVE (1.0 g, 10.4 mmol) was added to the resulting mixture and the solution was heated at 60 °C for 4 h to give the end modified polymer **13a** (M_n = 4800, PDI = 1.14). CH_2Cl_2 (4.0 ml) was added and the resulting mixture was cooled to -72 °C. $BF_3 \cdot Et_2O$ (1.6 mg, 0.01 mmol) was added at this temperature, and the resulting solution was stirred at -25 °C for 1.5 h. The reaction was quenched by addition of triethylamine (0.3 ml) and methanol (0.1 ml). The conversion of monomer (100%) was determined by ^{1}H NMR. After routine work-up, block copolymer **16** was obtained (1.3 g) with M_n of 10400 and PDI of 1.37 determined by GPC calibrated with PMMA standards (Figure 8).
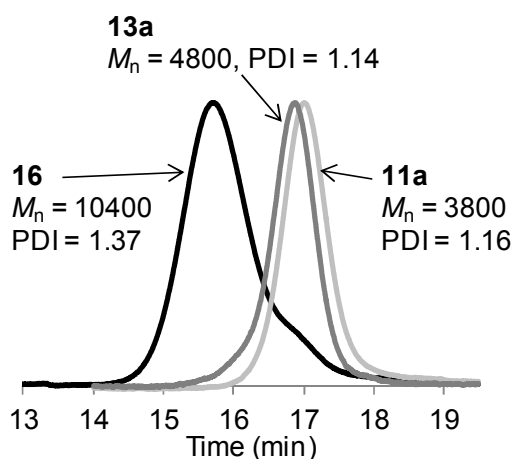
Figure 8. GPC trace of **11a**, **13a**, and **16**.

Synthesis of poly(*n*BA-block-DVE). A solution of **10** (25.3 mg, 0.10 mmol), *n*BA (1.3 g, 10.5 mmol), and V-601 (4.6 mg, 0.02 mmol) was stirred at 60 °C for 2 h under a nitrogen atmosphere to give **11a** (M_n = 10900, PDI = 1.16). Conversion of the monomer (86 %) was determined by ^{1}H-NMR DVE (2.2 g, 10.4 mmol) was added, and the resulting mixture was heated at 60 °C for 4 h to give **13a** (M_n = 14600, PDI = 1.13). CH_2Cl_2 (4.0 ml) was added, and the resulting solution was cooled to -72 °C. $BF_3 \cdot Et_2O$ (1.6 mg, 0.01 mmol) was added at this temperature, and the resulting solution was stirred at -25 °C for 1.5 h. The reaction was quenched

by addition of triethylamine (0.3 ml) and methanol (0.1 ml). The conversion of monomer (100%) was determined by ^{1}H NMR. After routine work-up, block copolymer **17** was obtained (3.4 g) with M_n of 19700 and PDI of 1.46 determined by GPC calibrated with PMMA standards (Figure 9).
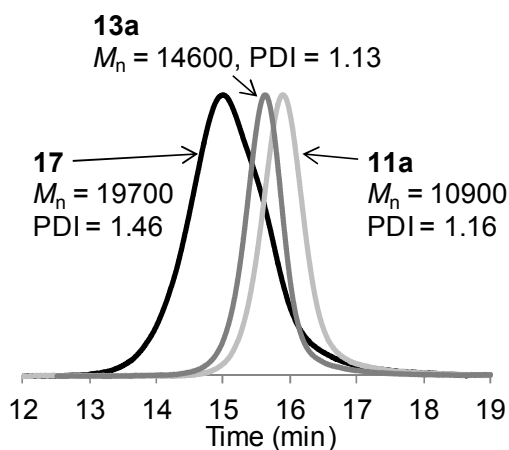
Figure 9. GPC trace of **11a**, **13a**, and **17**.

Synthesis of poly(MMA-*block*-IBVE). A solution of **10** (25.3 mg, 0.10 mmol), MMA (1.0 g, 10.3 mmol), dimethyl ditelluride (29.6 mg, 0.10 mmol), and V-601 (5.2 mg, 0.02 mmol) was stirred at 60 °C for 13 h under a nitrogen atmosphere to give **11b** (M_n = 8900, PDI = 1.20). Conversion of the monomer (94 %) was determined by ^{1}H NMR. IBVE (1.0 g, 10.4 mmol) was added, and the resulting solution was stirred at 60 °C for 4 h to give **13b** (M_n = 9500, PDI = 1.19). CH_2Cl_2 (4.0 ml) was added, and the resulting solution was cooled to -72 °C. $BF_3 \cdot Et_2O$ (1.6 mg, 0.01 mmol) was added at this temperature, and the resulting solution was stirred at -25 °C for 1.5 h. The reaction was quenched by addition of triethylamine (0.3 ml) and methanol (0.1 ml). The conversion of monomer (95%) was determined by ^{1}H NMR. After routine work-up, block copolymer **15b** was obtained (2.4 g) with M_n of 13800 and PDI of 1.21 determined by GPC calibrated with PMMA standards (Figure 10).
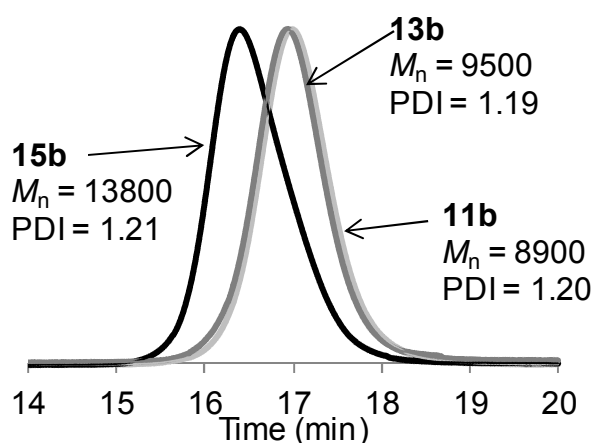
Figure 10. GPC trace of **11b**, **13b**, and **15b**.

Synthesis of poly(IBVE-*block*-*n*BA-*block*-IBVE). A solution of **18** (24.2 mg, 0.05 mmol), *n*BA_(0.2 g, 1.6 mmol), and V-601 (2.5 mg, 0.01 mmol) was stirred at 60 °C for 5 h under a nitrogen atmosphere to give **19a** (M_n = 3100, PDI = 1.14). Conversion of the monomer (90 %) was determined by ^{1}H NMR. IBVE (0.5 g, 5.0 mmol) was added, and the resulting mixture was stirred at 60 °C for 4 h to give **20a** (M_n = 3800, PDI = 1.14). CH_2Cl_2 (4.0 ml) was added, and the resulting solution was cooled to -72 °C. $BF_3 \cdot Et_2O$ (1.6 mg, 0.01 mmol) was added at this temperature, and the resulting solution was stirred at -25 °C for 1.5 h. The reaction was quenched by addition of triethylamine (0.3 ml) and methanol (0.1 ml). The conversion of monomer (91%) was determined by ^{1}H NMR. After routine work-up, block copolymer **21a** was obtained (0.65 g) with M_n of 9500 and PDI of 1.29 determined by GPC calibrated with PMMA standards (Figure 6b).

Synthesis of poly(IBVE-*block*-MMA-*block*-IBVE). A solution of **18** (24.2 mg, 0.05 mmol), MMA (0.15 g, 1.5 mmol), (MeTe)$_2$ (14.3 mg, 0.05 mmol), and V-601 (2.5 mg, 0.01 mmol) was stirred at 60 °C for 5 h under a nitrogen atmosphere to give **19b** (M_n = 2600, PDI = 1.34). Conversion of the monomer (100 %) was determined by ^{1}H NMR. IBVE (0.5 g, 5.0 mmol) was added, and the resulting solution was stirred at 60 °C for 4 h to give **20b** (M_n = 2800, PDI = 1.32). $CHCl_2$ (4.0 ml) was added, and the resulting solution was cooled to -72 °C. $BF_3 \cdot Et_2O$ (1.6 mg, 0.01

mmol) was added at this temperature, and the resulting solution was stirred at -25 °C for 1.5 h. The reaction was quenched by addition of triethylamine (0.3 ml) and methanol (0.1 ml). The conversion of monomer (88%) was determined by ^{1}H NMR. After routine work-up, block copolymer **21b** was obtained (2.4 g) with M_n of 8000 and PDI of 1.41 determined by GPC calibrated with PMMA standards (Figure 11).
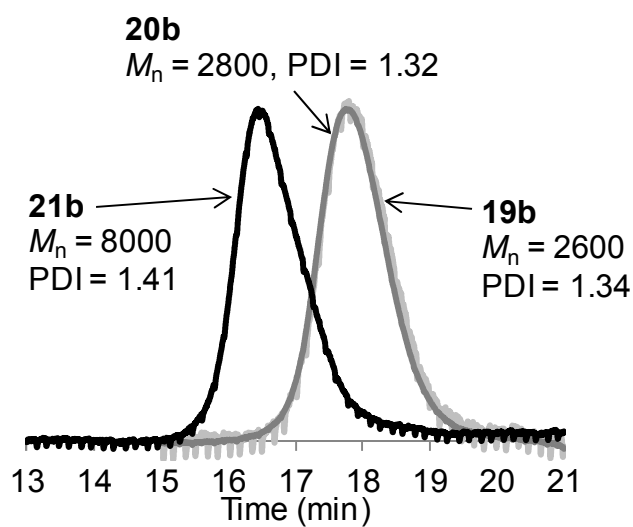

Figure 11. GPC trace of **19b**, **20b**, and **21b**.

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Chapter 3

Highly Controlled Random and Alternating Copolymerization of (Meth)acrylates, Acrylonitrile, and (Meth)acrylamides with Vinyl Ethers by Organotellurium, Organostibine, and Organobismuthine Mediated Living Radical Polymerization Reactions.

Abstract

Random and alternating copolymerizations of acrylates, methacrylates, acrylonitorile, and acrylamides with vinyl ethers under organotellurium-, organostibine-, and organobismuthine-mediated living radical polymerization (TERP, SBRP, and BIRP, respectively) have been studied. Structurally well-controlled random and alternating copolymers with controlled molecular weights and polydispersities were synthesized. The highly alternating copolymeriztion occurred in a combination of acrylates and vinyl ethers and acrylonitorile and vinyl ethers by employing excess amount of vinyl ethers over acrylates and acrylonitorile. On the contrary, alternating copolymerization did not occur in a combination of acrylamides and vinyl ethers even excess amount of vinyl ethers were used. The reactivity of polymer-end radicals to a vinyl ether was estimated by the theoretical calculations, and it was suggested that the energy level of singly occupied molecular orbital (SOMO) of polymer-end radical species determined the reactivity. By combining living random and alternating copolymerization with living radical or living cationic

polymerization, new block copolymers, such as (PBA-*alt*-PIBVE)-*block*-(P*t*BA-*co*-PIBVE), PBA-*block*-(PBA-*alt*-PIBVE), and (PTFEA-*alt*-PIBVE)-*block*-PIBVE, with controlled macromolecular structures were successfully synthesized.

Introduction

Living radical polymerization (LRP) has become an indispensable method for the synthesis of structurally well-controlled polymeric materials with novel and improved properties.[1-3] Despite of the developments of various methods for LRPs, there is no universal method which can be applicable to different monomer families.[4-10] Therefore, more versatile method which can control both conjugated and nonconjugated monomers under similar conditions has been awaited to increase the ability of macromolecular engineering. All LRP methods so far reported rely on the reversible generation of a radical species from a dormant species (Scheme 1), and efficient activation/deactivation cycles within the polymerization period leads to the control of polydispersity.[11] Conjugated monomers generating stabilized polymer-end radicals are usually experience sufficient activation/deactivation cycle and are easy monomer families to be controlled by LRP. On the other hands, controlled polymerization of nonconjugated monomers, which generate unstabilized radicals, has been less successful so far. While reversible addition-fragmentation chain transfer polymerization (RAFT) can polymerize both conjugated and nonconjugated monomers,[8] the RAFT agent has to be carefully selected depending on the monomer species.[12-14] A certain initiator for cobalt-mediated radical polymerization (CMRP) is recently proved to be effective for the controlled polymerization of nonconjugated monomers especially vinyl acetate and *N*-vinylamides,[15-19] but its application to conjugated monomers has been so far limited.[20-23]

Scheme 1. Reversible activation process in living radical polymerization.
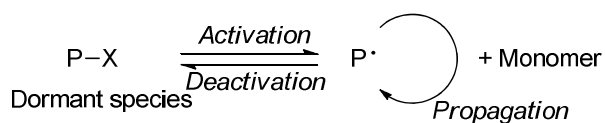
Controlled synthesis of random copolymers by LRP has been a significant challenge, as polymer properties can be finely tuned depending on the type of monomers and their compositions. While monomers having similar reactivities have been successfully copolymerized in a controlled manner, those having different reactivities, such as conjugated and nonconjugated monomers, have been limited success.[24-31]

We have recently developed new LRP methods using organotellurium, organostibine, and organobismuthine compounds, which are abbreviated to TERP, SBRP, and BIRP (organotellurium-, organostibine-, and organobismuthine-mediated living radical polymerization), respectively.[32-38] One of the most characteristic features of these methods is their versatility in polymerizing both conjugated and nonconjugated monomers by using the same chain transfer agent.[32,33,39-41] This feature has been exemplified in the first controlled synthesis of a block copolymer of conjugated and nonconjugated monomers.[32,33,39,40,42] These results prompted us to investigate random copolymerization of conjugated and nonconjugated monomers by TERP, SBRP, and BIRP. We report here the controlled random and alternating copolymerization of (meth)acrylates, acrylonitrile, and (meth)acrylamides with vinyl ethers under TERP, SBRP, and BIRP conditions (Scheme 2).

We also report the synthesis of new block copolymers by combining the alternative copolymerization with already reported living radical and cationic polymerizations.

Scheme 2. Controlled copolymerization of (meth)acrylates and vinyl ethers by using TERP, SBRP, and BIRP.

a: R = Me, **X** = TeMe
b: R = Et, **X** = SbMe$_2$
c: R = Me, **X** = BiMe$_2$
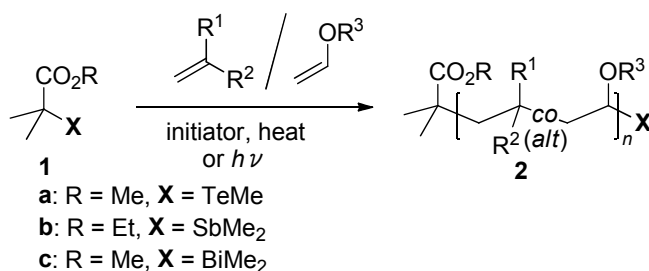
Vinyl ethers are nonconjugated and electron rich monomers, which only homopolymerize under cationic conditions. However, they undergo copolymerization with electron deficient monomers, such as (meth)acrylates, under radical condition. Since the stabilities of polymer end radicals generated from vinyl ethers and (meth)acrylates are different considerably, the control of the copolymerization by LRP has been a significant challenge. Recently, Kamigaito and coworkers reported random copolymerization of (meth)acrylates and vinyl ether under RAFT conditions.[43] However, the incorporation of vinyl ethers in the copolymer was low and PDIs of the resulting copolymers were high.

Results and Discussion

Random and alternating copolymerization of 2,2,2-trifluoroethyl acrylates (TFEA) and *iso*-butyl vinyl ether (IBVE). Copolymerization of TFEA; (R^1 = CO$_2$CH$_2$CF$_3$, R^2 = H, 20 equiv) and IBVE (R^3 = *i*-Bu, 20 equiv) in the presence of organotellurium chain transfer agent (CTA) **1a** and dimethyl 2,2'-azobis(2-methylpropionate) (V-601, 0.2 equiv) was examined at 60 °C for 1 h.[44,45] The conversion of TFEA and IBVE followed first-order kinetics (Figure 1) and reached 100% and 79%, respectively, after 1 h (Table 1, run 1). The polymerization did not proceed further after all TFEA was consumed, and IBVE remained under the polymerization conditions. This is because a polymer-end radical formed from TFEA reacts with TFEA and IBVE, while that formed

from IBVE only reacts with TFEA. Gel permeation chromatography (GPC) analysis indicated the formation of a structurally well-controlled copolymer with a number average molecular weight (M_n) of 4900 and a polydispersity index (PDI) of 1.12. The mole fraction of IBVE (MF_{IBVE}) in the copolymer was 0.43 as judged by ^{1}H NMR spectroscopy after isolation, and the value is identical to the one estimated from the monomer conversion.

Figure 1. Monomer conversion in the copolymerization
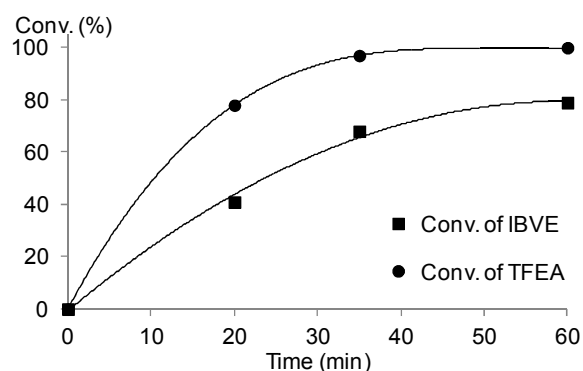
The MF_{IBVE} increased with an increase in the amount of IBVE, and a nearly completely alternating copolymer formed in a controlled manner when IBVE/TFEA > 10 (Table 1, runs 2, 3, and 4). Copolymeriztion also proceeded under photoirradiation by 60 W black lamp and 500 W Hg lamp with a combination of a cut-off filter without an azo-initiator,[41] and the nearly alternating copolymers (MF_{IBVE} = 0.48~0.49) with low polydispersities (PDI < 1.13) were formed with complete conversion of TFEA (Table 1, runs 6 and 7). Copolymers with high M_n were obtained by increasing the amount of TFEA and IBVE over **1a** (Table 1, runs 5 and 7–9), and the results are consistent with the living character. The M_ns of the resulting copolymers determined by GPC using poly(methyl methacrylate) standards were considerably lower than the theoretical values when the target M_n was greater than 20000. The M_ns determined by MALLS were slightly higher than those obtained by GPC but still lower than the theoretical values. While further studies are needed to

clarify this deviation, structurally well-controlled copolymers with considerably high M_ns (~75000), low PDIs, and nearly alternating monomer sequence formed in all cases.

Table 1. Alternating copolymerization of TFEA and IBVE using **1a**[a]

run	TFEA/IBVE (equiv)	M_n (theo)[b]	M_n (exp)[c]	PDI[c]	MF$_{IBVE}$[e]
1	20/20	4600	4900	1.12	0.43
2	20/40	4600	5700	1.13	0.44
3	20/100	5000	5700	1.18	0.49
4	20/200	5200	6400	1.16	0.50
5	100/500	25000	17500 (19200)[d]	1.15	0.49
6[f]	20/100	4800	4500	1.13	0.48
7[g]	100/500	24500	18800	1.06	0.49
8	250/1250	61300	36100 (46700)[d]	1.17	0.48
9	500/2500	123700	54000 (75200)[d]	1.20	0.48
10[h]	20/100	5000	6000	1.16	0.49

[a]**1a** (1.0 equiv), TFEA, IBVE, and V-601(0.2 equiv.) were stirred at 60 °C for 0.5–8 h. Conversion of TFEA reached 100% in all cases. [b]M_n(theo) was caluculated from monomer conversion determined by ^{1}H NMR spectroscopy. [c]Number-average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) were obtained by using size exclusion chromatography calibrated with poly(methyl methacrylate) standards. M_w refers to weight-average molecular weight. [d]M_n calculated from M_w obtained by using multi-angle laser light scattering and PDI by GPC. [e]Ratio of TFEA and IBVE units in polymer determined by ^{1}H NMR. [f]Polymerization was carried out under photoirradiation (60W black light) without V-601 at 60 °C. [g]Polymerization was carried out under photoirradiation (500 W Hg lamp with a >470 nm cut-off filter) without V-601 at 0 °C. [h]**5** was used instead of **1a** as a CTA.

Confirmation of alternating structure. Alternating and end-group structures of the copolymer were analyzed by ^{1}H, ^{13}C, 2-dimentional, and ^{2}H NMR spectra after polymer-end tellanyl group was reduced to hydrogen or deuteride by PhSH or Bu$_3$SnD, respectively (Scheme 3).[46] In the ^{13}C spectra, the signals corresponding to methylene carbons in the main chain appeared different position from those of the homo polymers, namely poly(TFEA) and poly(IBVE) (Figure 2a). In hetero-nuclear multiple-bond connectivity (HMBC) spectra, a cross peak between **C**ii and **H**iv, which are the α-carbon to the ester and α-proton to the *i*-butyloxy group, respectively, was observed as shown an arrow (Figure 2b). Furthermore, in hetero-nuclear single quantum coherence-totally correlated spectroscopy (HSQC-TOCSY) spectra, a series of cross peaks was observed between **H**ii and **H**iii and **H**ii and **H**iv, as shown arrows (Figure 2c). In ^{2}H NMR spectra of **4-d**, a single resonance was observed at 3.4 ppm (>99 % purity), indicating that the polymer-end monomer unit derived from IBVE due to the use of excess amount of IBVE over TFFA (Figure 2d).

Scheme 3. Reduction of polymer end group.

3 (R = CH$_2$CF$_3$)   **4 [4-d]** (R = CH$_2$CF$_3$)
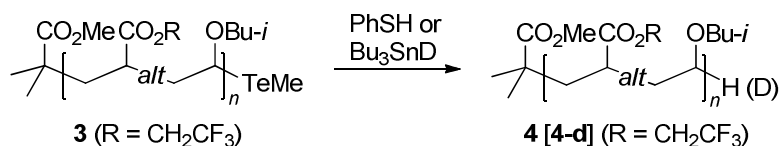
An alternating structure was further supported by the matrix assisted laser desorption ionization time of flight (MALDI TOF) mass spectrometry (Figure 3). Two major and three minor sets of peaks in a ratio of 39:34:18:5:4 were observed, and they are corresponded to copolymers with the following numbers of TFFA (*l*) and IBVE units (*m*): $l = m + 1$, $l = m$, $l = m + 2$, $l = m - 1$, and $l = m + 3$, respectively. A negligible amount of copolymers with $l = m + 4$ and $l = m - 2$ was also detected (< 0.6%). The MF$_{IBVE}$ was calculated to be 0.49 from the intensity of each peak, which is consistent with the data obtained from ^{1}H NMR spectroscopy.

Figure 2. (a) ^{13}C NMR spectra of poly(TFEA), and poly(IBVE), and alternating copolymer **4**,   (b) HMBC, and (c) HSQC-TOCSY spectra of **4**.
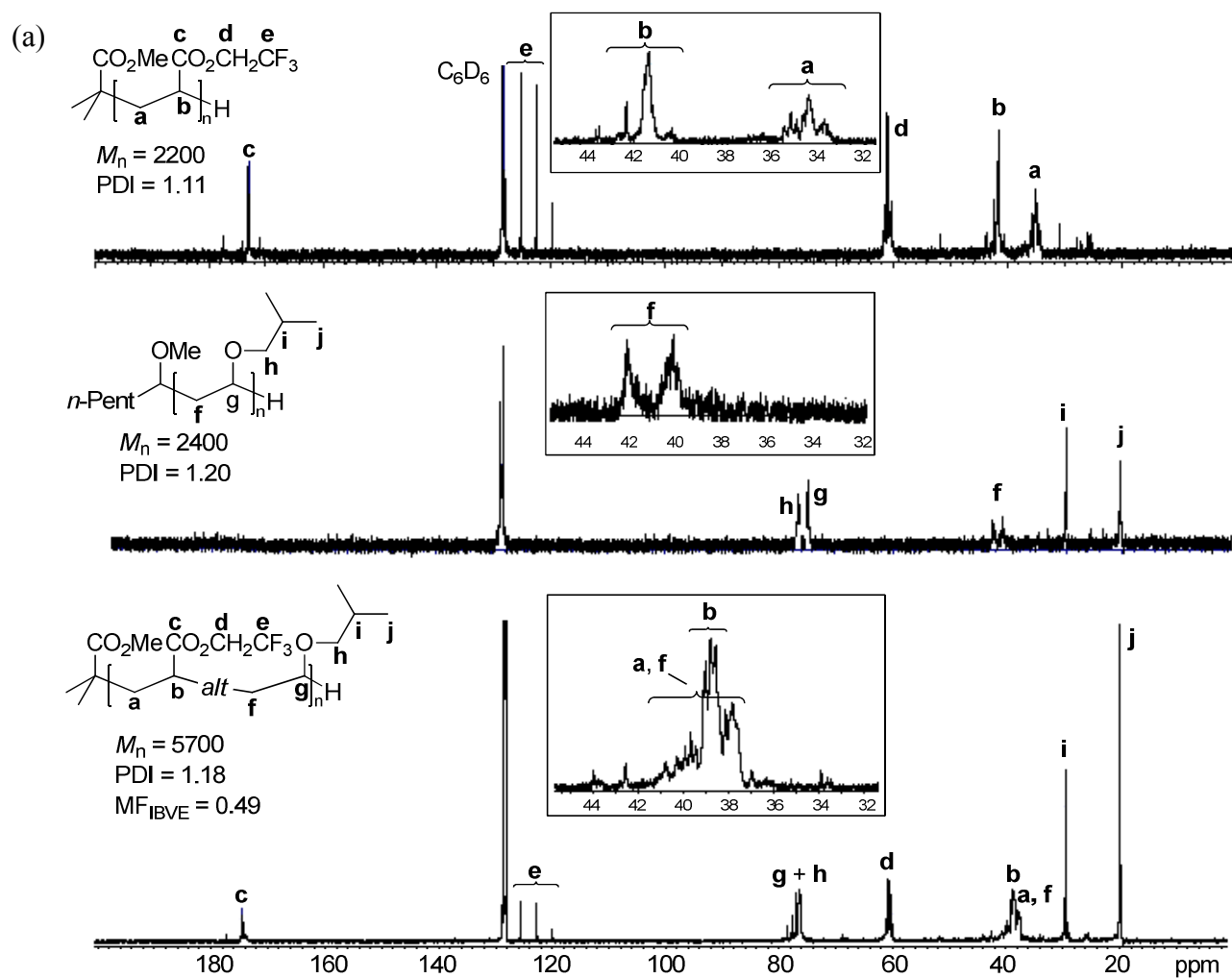
Figure 2 continued.

(b)

(c)

(d)

Figure 3. (a) Full and (b) partial MALDI TOF mass spectra of **4**; *l* and *m* refer to the number of

TFEA and IBVE units, respectively.

(a)

(b)
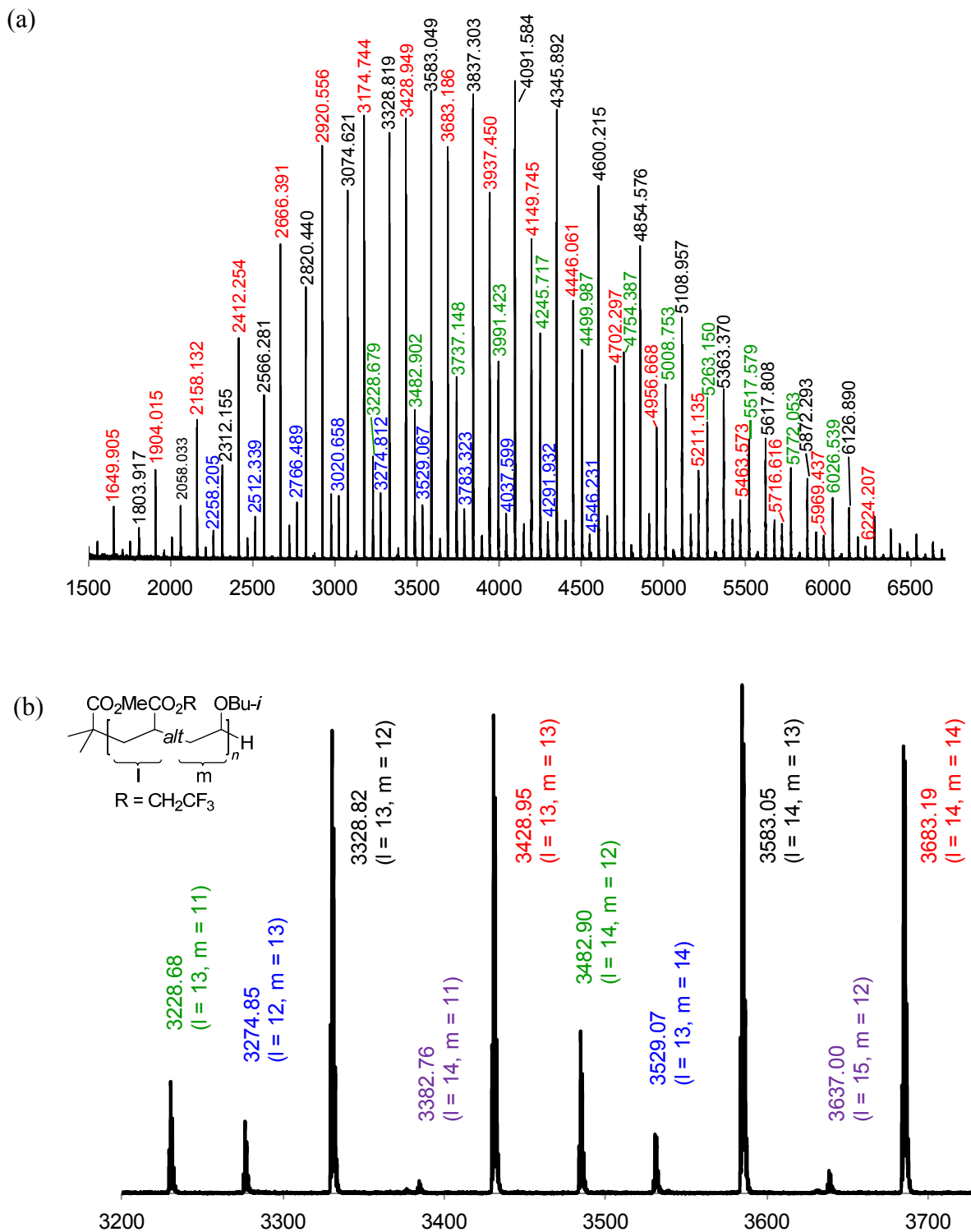
Since vinyl ethers do not homopolymerize, copolymers having $m > l$ formed ca. 5% may be primarily attributed to the addition of the radical generated from **1a** to IBVE instead of TFFA. However, we recently clarified that multiple addition of vinyl ethers occurs in a small extents under radical conditions when large excess amount of vinyl ether was present.[47] To clarify the contribution of multi-addition, we next examined the copolymerization by using CTA **5** which generates α-alkoxy radical which should selectively react with TFEA.

CTA **5** was heated with TFEA (20 equiv), IBVE (100 equiv), and V-601 (0.2 equiv) at 60 °C for 0.5 h, and the resulting copolymer **6a** was treated with PhSH to give end-hydrogenated copolymer **6b** (Scheme 4). GPC analysis indicated the formation of well controlled copolymer with M_n of 6000 and a PDI of 1.16 (Table 1, run 10). High alternating character ($MF_{IBVE} = 0.49$) was also confirmed by ^{1}H NMR analysis. The MALDI TOF mass analysis revealed the existence of three major and two minor sets of peaks in a ratio of 41:26:20:10:2, which correspond to copolymers with the following numbers of TFFA (l) and IBVE units (m) as $l = m + 1, l = m + 2, l = m, l = m + 3$, and $l = m + 4$, respectively. The MF_{IBVE} obtained from the mass was determined to be 0.49. Formation of the copolymer having $l < m$ was below 0.9%, and the results suggest that the existence of IBVE-IBVE linkage is negligible.
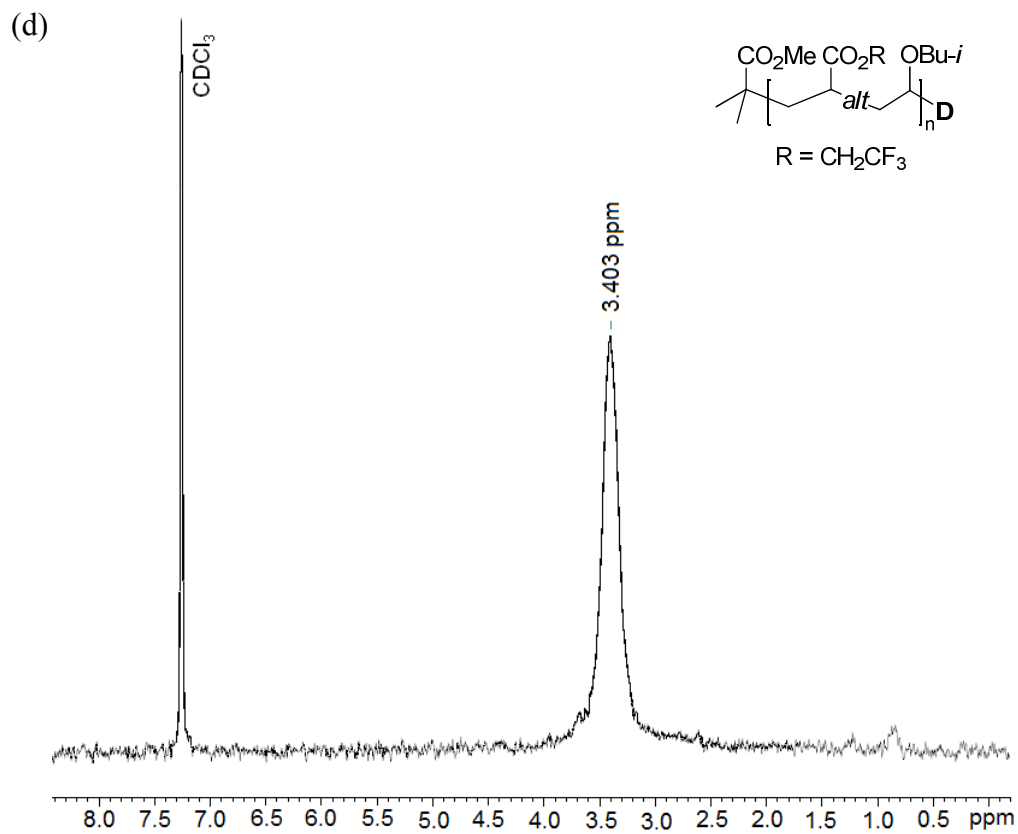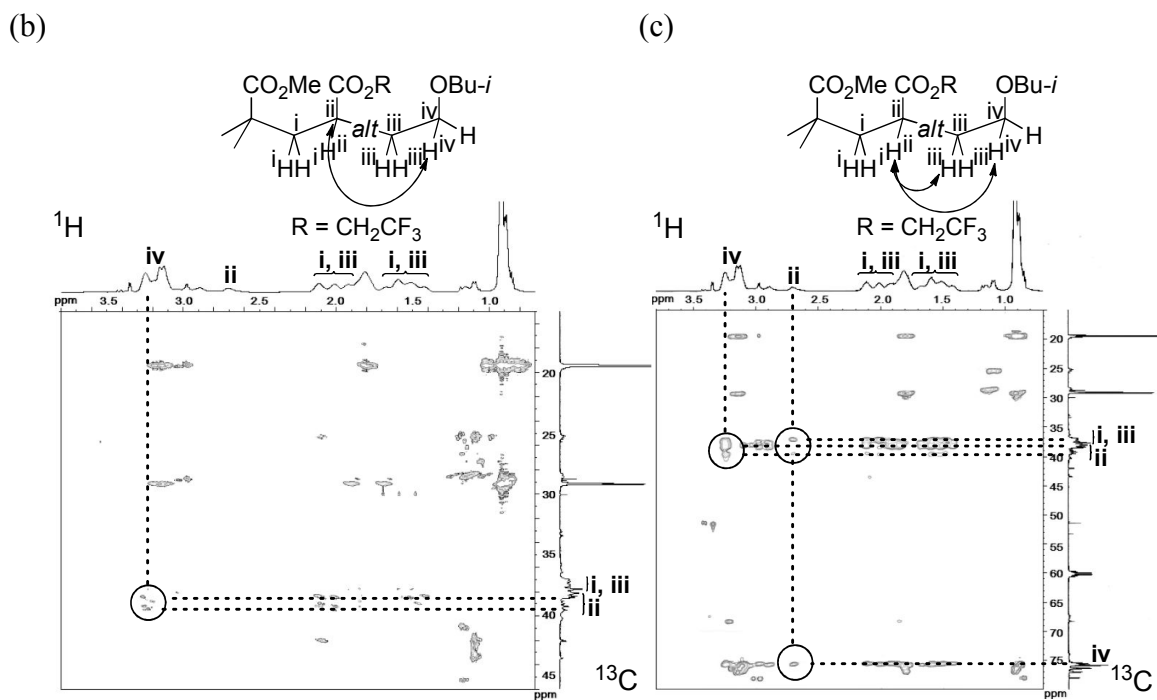
Scheme 4. Alternating copolymerization by using CAT **5**.
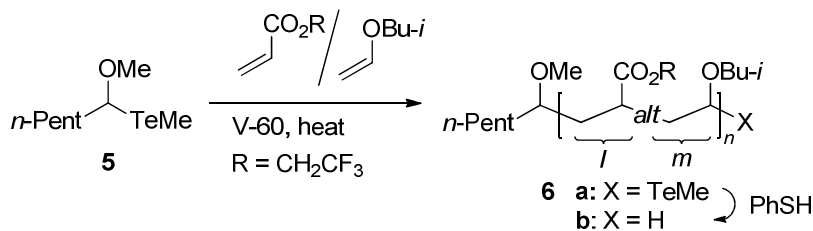
Figure 4. (a) Full and (b) partial MALDI TOF mass spectra of **6**; *l* and *m* refer to the number of TFEA and IBVE units, respectively.

(a)

(b)
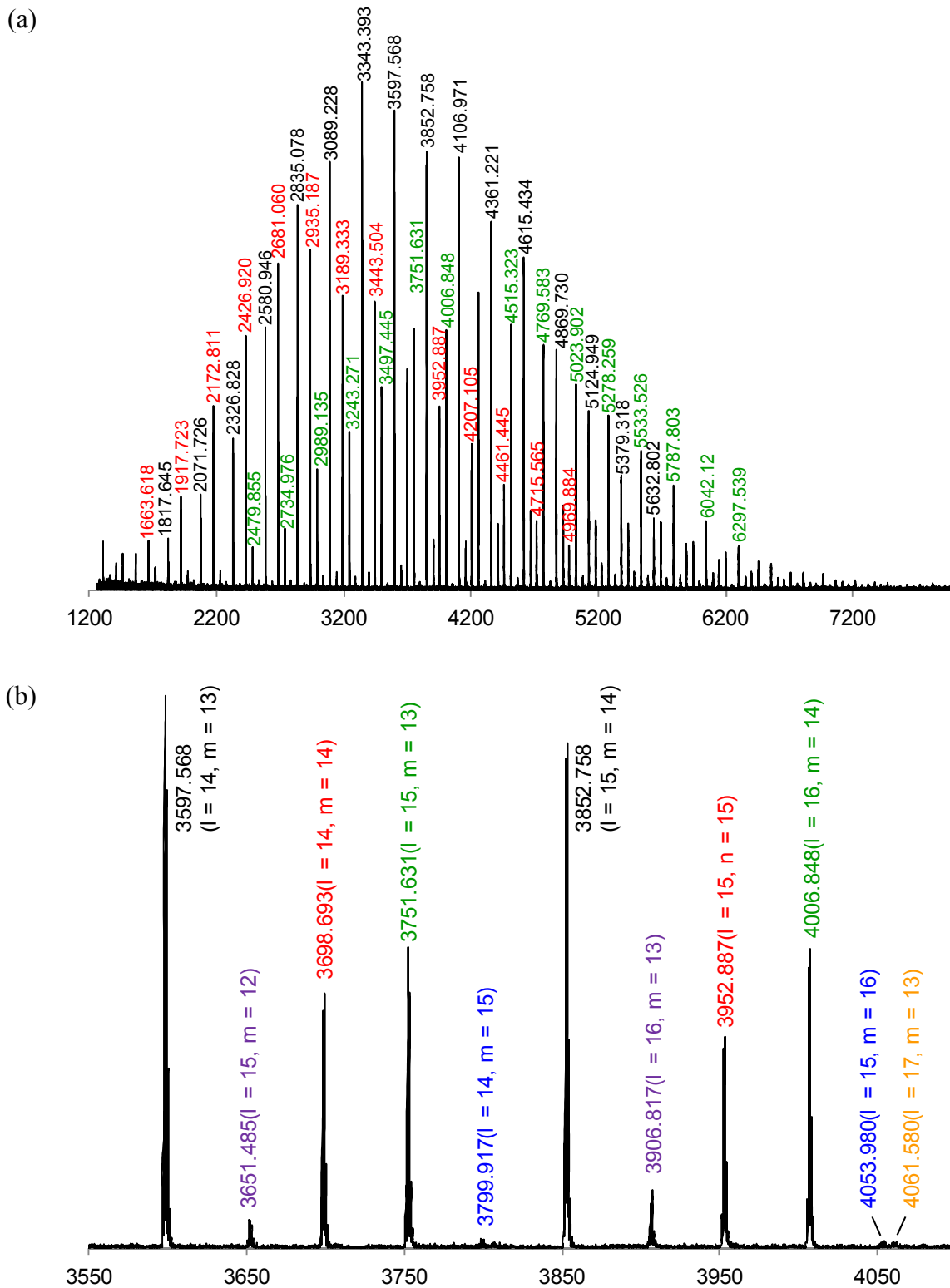
Synthetic scope. Syntheses of random and alternating copolymers were examined for various combination of electron deficient monomers, such as (meth)acrylates, acrylonitrile, and (meth)acryloamides, and vinyl ethers under TERP, SBRP, and BIRP conditions, and the results are summarized in Table 2.

Nearly alternating copolymerization of TFEA and *tert*-butyl vinyl ether (*t*BVE) and TFEA and trimethylsilyl vinyl ether (TMVS) occurred when an excess amount of vinyl ethers (vinyl ether/TFEA = 2~5) were used in the presence of **1a**. Conversion of TFEA completed within 1 h at 60 °C, and the corresponding alternating copolymers (MF$_{(vinyl\ ether)}$ = 0.50) with M_n of 5600~25000 and low PDIs of 1.09~1.18 were obtained (Table 2, runs 1-4).

Copolymerization of acrylates, such as *n*-butyl acrylate (BA) and *t*-butyl acrylates (*t*BA) and vinyl ethers, such as IBVE, *t*BVE, and TMVS, also proceeded in a controlled manner by employing **1a** under thermal and photochemical conditions (Table 2, runs 5, 7-15, and 18-24). When a same amount of an acrylate and a vinyl ether was used, the MF$_{(vinyl\ ether)}$ was 0.32~0.41, the value of which was slightly smaller than that obtained in the copolymerization of TFEA and vinyl ethers (Table 2, runs 5, 18, and 22). The results are attributed to the reactivity of polymer-end radicals as discussed below.

Addition of Lewis acid in the copolymerization of (meth)acrylates and α-olefin leads to the increase of MF$_{(α-olefin)}$ by the coordination of Lewis acid to (meth)acrylates as well as polymer-end radicals derived from (meth)acrylates.[25,48] Therefore, the effect of Lewis acid on the copolymerization was examined. Various Lewis acids, such as Mg(OTf)$_2$ and methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD)[49] were compatible with organotellurium CTA, and the copolymerization gave the controlled copolymer with low PDI (Table 2, run 6). However, the MF$_{IBVE}$ decreased by the addition of Lewis acids. NMR experiments by mixing Mg(OTf)$_2$ to a mixture of MA and IBVE in CDCl$_3$ revealed that no significant change of chemical shifts were

observed in ^{13}C NMR for both MA and IBVE. Therefore, the similar Lewis basicity of acrylates and vinyl ethers must be the origin of the insensitivity of MF_{IBVE} by the addition of Lewis acid.

The $MF_{(vinyl\ ether)}$ increased to near 0.50 by employing an excess amount of vinyl ether in all cases (Table 2, runs 7-15, 19-21, 23 and 24). Nearly alternating copolymers with M_n ranging from 4000 to 57000 with low PDIs (1.11~1.34) were successfully synthesized by changing the acrylate/CTA ratio with keeping the same acrylate/vinyl ether ratio. The $MF_{(vinyl\ ether)}$s slightly decreased as the target M_n increased (Table 2, runs 11-15), but they still keep high level of alternating character (MF > 0.45) and were identical to the values under the conventional radical polymerization conditions without **1a** (Table 2, runs 16 and 17).

Table 2. Random/alternating copolymerization of (meth)acrylates and vinyl ethers in the presence of CTAs **1a–c**.[a]

run	CTA	Monomer (equiv)	M_n (theo)[b]	M_n(exp)[c]	PDI[c]	$MF_{(vinyl\ ether)}$[d]
1	**1a**	TFEA/*t*BVE (20/20)	4800	4900	1.16	0.46
2	**1a**	TFEA/*t*BVE (20/40)	5200	5600	1.17	0.50
3	**1a**	TFEA/*t*BVE (100/200)	25500	16300	1.18	0.50
4	**1a**	TFEA/TMVS(100/500)	25300	24700	1.09	0.50
5	**1a**	BA/IBVE (20/20)	3500	3800	1.14	0.32
6[e]	**1a**	BA/IBVE (20/20)	3500	3300	1.13	0.30
7	**1a**	BA/IBVE (20/200)	4500	4500	1.17	0.49
8[f]	**1a**	BA/IBVE (20/200)	4400	4400	1.11	0.48
9	**1b**	BA/IBVE (20/200)	4600	4800	1.15	0.50
10	**1c**	BA/IBVE (20/200)	4500	5100	1.18	0.50
11	**1a**	BA/IBVE (50/500)	10600	8900	1.15	0.46

Table 2, continued.

12	**1a**	BA/IBVE (100/1000)	21600	18300	1.21	0.47
13[f]	**1a**	BA/IBVE (100/1000)	21100	19200	1.12	0.46
14	**1a**	BA/IBVE (250/2500)	52300	36400 (40100)[g]	1.20	0.45
15	**1a**	BA/IBVE (500/5000)	104800	57000 (59000)[g]	1.24	0.45
16[h]	**none**	TFEA/IBVE (20/20)	4500	15800	15.59	0.41
17[h]	**none**	TFEA/IBVE (20/200)	5100	36900	8.10	0.50
18	**1a**	BA/ *t*BVE (20/20)	4200	3500	1.17	0.41
19	**1a**	BA/ *t*BVE (20/100)	4600	4200	1.25	0.50
20	**1a**	BA/ *t*BVE (100/500)	22100	18600	1.30	0.47
21	**1a**	BA/TMVS (100/1000)	24700	18000	1.24	0.50
22	**1a**	*t*BA/*t*BVE (20/20)	3500	3300	1.15	0.32
23	**1a**	*t*BA/*t*BVE (20/100)	4600	3100	1.45	0.50
24	**1a**	*t*BA/*t*BVE (100/500)	22300	14400	1.34	0.50
25	**1a**	AN/ *t*BVE (20/20)	2900	4000	1.20	0.44
26	**1a**	AN/ *t*BVE (20/40)	3000	2500	1.22	0.50
27	**1a**	AN/ *t*BVE (500/1000)	73700	60500	1.19	0.50
28[i]	**1a**	NIPAM/IBVE (50/50)	6400	7100	1.09	0.14
29[i]	**1a**	NIPAM/IBVE (50/500)	7400	9000	1.08	0.32
30	**1a**	DMAA/IBVE (50/50)	5700	6400	1.09	0.13
31	**1a**	DMAA/IBVE (50/500)	8900	5800	1.13	0.35
32[j]	**1a**	DMAA/IBVE (50/500)	7200	7200	1.07	0.31

Table 2, continued.

33	**1a**	MMA/IBVE (20/20)	2800	2400	1.57	0.23
34[k]	**1a**	MMA/IBVE (20/100)	3800	3900	1.31	0.47
35[k]	**1a**	MMA/IBVE (100/1000)	16500	17500	1.15	0.39
36[f]	**1a**	MMA/IBVE (100/1000)	15400	17000	1.22	0.38
37[k]	**1a**	TFEMA/IBVE (20/200)	5300	5000	1.23	0.49
38[l]	**1a**	EMA/IBVE(20/200)	3700	3900	1.24	0.45

[a]**1**, monomers, and V-601 (0.2 equiv) were stirred at 60 °C for 5–36 h. [b]M_n(theo) was caluculated from conversion which was determined by ^{1}H NMR spectroscopy. [c]M_n and PDI were obtained by using size exclusion chromatography calibrated with poly(methy methacrylate) standards. [d]Ratio of (meth)acrylate and vinyl ether units in polymer determined by ^{1}H NMR. [e]1.0 equiv. of Mg(OTf)$_2$ was added. [f]Polymerization was carried out under photoirradiation (500 W Hg lamp with a >470 nm cut-off filter) at 50 °C for 4-24 h. [g]M_n calculated from M_w obtained by using multi-angle laser light scattering and PDI by GPC. [h]Polymerization was carried out in the absence of **1a**. [i]0.5 ml of DMF was added. [j]Polymerization was carried out under photoirradiation (500 W Hg lamp with >550 nm cut-off filter) at 50 °C for 48 h. [k]Polymerization was carried out at 80 °C in the absence of V-601. [l]Polymerization was carried out at 100 °C in the absence of V-601.

Organostibine and organobismuthine CTAs **1b** and **1c**, respectively, were also effective for the controlled alternating copolymerization (Table 2, runs 9 and 10). The MF$_{(vinyl\ ethers)}$ was insensitive to the heteroatom species in the CTAs, and the results are consistent with the involvement of free radicals in the propagation step.

Acrylonitrile (AN) also underwent controlled copolymerization with vinyl ethers. In the copolymerization of AN and tBVE, the high MF$_{tBVE}$ of 0.44 was observed when an equal amount of AN and tBVE was employed (Table 2, run 25). Alternating copolymerization (MF$_{tBVE}$ = 0.50) occurred even when tBVE/AN = 2 (Table 2, run 26) and gave the resulting highly controlled and high-molecular weight alternating copolymer with M_n = 60500 and PDI = 1.19 (Table 2, run 27). The higher alternating character of AN than acrylates can be attributed to the lower energy level of the singly occupied molecular orbital (SOMO) generated from AN than that from acrylates as discussed below.

Copolymerizations of acrylamides, such as *N*-isopropylacrylamide (NIPAM) and *N,N*-dimethylacrylamide (DMAA), and IBVE were next examined by using **1a**. When the copolymerization was employed by mixing an equal amount of an acrylamide and IBVE, the resulting copolymers with controlled M_ns and low PDIs (1.09) were obtained (Table 2, run 28 and 30). However, the $MF_{(vinyl\ ether)}$s was much smaller than those observed in the copolymerization by using acrylates and acrylonitrile as an electron deficient monomer. The $MF_{(vinyl\ ether)}$s increased to 0.32 and 0.35 when IBVE/acrylamide = 10 (Table 2, run 29 and 31), but they did not increase by the addition of further IBVE. The results can be also explained by the SOMO energies of acrylamide-derived polymer-end radical species as discussed below. Despite of the low $MF_{(vinyl\ ether)}$s, highly controlled random copolymer with low PDIs (1.07~1.13) were obtained in all cases under thermal and photochemical conditions.

Methacrylates, such as methyl methacrylate (MMA), ethyl methacrylate (EMA), and trifluoroethyl methacrylate (TFEMA), also underwent highly controlled alternating copolymerization when an excess amount of vinyl ether over methacrylate was used. Polymerization proceeded under thermal conditions without azo-initiators,[37,50] or photochemical condition and poly(MMA-*alt*-IBVE), poly(EMA-*alt*-IBVE), and poly(TFEMA-*alt*-IBVE) with M_n close to the theoretical values and low PDIs were obtained under TERP conditions (Table 2, runs 33-38).

Origin of the alternating character. The above experiments revealed that the incorporation of vinyl ethers into polymer chains depends on the type of electron deficient monomers; AN showed highest followed by acrylates and, then, methacrylates and acrylamides when a same ratio of monomers was employed.

Polymer-end radicals generated from (meth)acrylate, (meth)acrylonitrile, and (meth)acrylamides are classified into an ambiphilic-electrophilic radical,[51] and the rate of addition

to alkene increased when the alkene becomes both more electron deficient and electron rich. Since vinyl ethers are electron rich alkenes, the rate of the addition reaction should be accelerated when the polymer-end radical becomes more electrophilic. To clarify this point, we calculated the SOMO energy of the model radicals for polymer-end species.

Structures of radicals **7**~**12**, which mimic polyacrylate, polymethacrylate, polyacrylonitrile, polymethacrylonitrile, polyacrylamide, and polymethacrylamide-polymer end radicals, respectively, were optimized by using the density functional theory (DFT) calculation at the UB3LYP/6-31G* level of theory. Radicals **13** and **14**, which mimic PTFEA and PTFEMA, respectively, were also calculated to understand the effect of the pendant ester moiety. Radicals **15** and **16** mimicking poly(vinyl ether) and poly(α-methylvinyl ether) polymer-end radicals were also calculated. The SOMO energies are summarized in Figure 5.

Figure 5. SOMO energy (eV) of model compounds for polymer-end radicals.

	7	**8**	**9**	**10**	**11**	**12**
SOMO energy (eV)	-0.22803	-0.20947	-0.25242	-0.21995	-0.21333	-0.19915

	13	**14**	**15**	**16**
SOMO energy (eV)	-0.24176	-0.22368	-0.15563	-0.14735
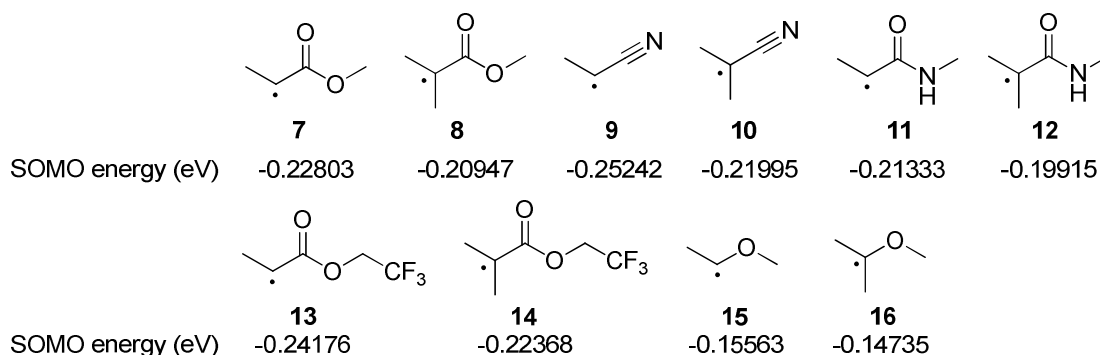
Among polyacrylate radical models **7**, **9**, and **11**, polyacrylonitrile model **9** possesses lowest SOMO level followed by polyacrylate model **7** and then polyacrylamide model **11**. This order is consistent with the electron withdrawing ability of nitrile, ester, and amide groups. The results suggest that the reactivity of **9** to vinyl ethers is highest followed by **7** and then **11**, and the order is consistent with the experimental results. The same trend was also observed among polymethacrylate models, and the SOMO level increases in the order of polymethacrylonitrile

model **10**, polymethacrylate model **8**, and polymethacrylamide model **12**. Due to the electron donating character of alkyl group, all polymethacrylate models possess higher SOMO energies than the corresponding acrylate models, and the energy levels are in good agreement with the experimental results on the ease of cross propagation to vinyl ethers. TFE group serves as an electron withdrawing group, and the radicals **13** and **14** bearing TFE group possess lower SOMO energies than methyl derivatives **7** and **8**, respectively. The calculated energies are also consistent with the experimental trend on the vinyl ether insertion. These results clearly indicate that the SOMO (radicals)-highest occupied molecular orbital (HOMO; vinyl ethers) interaction is the primary factor to determine the MF of vinyl ethers. Of course, other factors, such as charge-transfer, dipole-dipole, and steric interactions between the polymer-end radical and monomer, would also contribute to determine the reactivity.

Synthesis of block copolymers. New block copolymers were synthesized by using controlled alternating copolymerization reactions. For example, poly(butyl acrylate) macro CTA **17** (M_n = 10200 and PDI = 1.12) with a methyltellanyl group at the polymer end, which was prepared by reacting **1a** with BA, was treated with a mixture of BA (100 equiv) and IBVE (1000 equiv). Conversion of BA reached 92% after 8 h at 60 ºC, and block copolymer poly[BA-*block*-(BA-*alt*-IBVE)] **18** with M_n = 27700 and PDI = 1.22 was obtained (Scheme 5i). The GPC trace of **17** and **18** clearly revealed the successful chain extension reaction (Figure 6a). The MF_{IBVE} in the second block was determined to be 0.44 by ^{1}H NMR spectroscopy, suggesting that highly alternating copolymerization occurred.

Scheme 5. Synthesis of novel block copolymers. Reaction conditions: [a] **1a**, BA (100 equiv), V-601 (0.2 equiv), 60 °C, 2 h, 92% conv. [b] BA (100 equiv), IBVE (1000 equiv), 60 °C, 8 h, 100% conv. of BA.   [c] **1a**, BA (20 equiv), IBVE (100 equiv), V-601 (0.2 equiv), 60 °C, 3 h, 100% conv. of BA. [d] tBA (50 equiv), 60 °C, 2h, 100% conv. of tBA. [e] **1a,** TFEA (20 equiv), IBVE (200 equiv), 500 W high-pressure Hg lamp thorough a filter (>470 nm), 50 °C, 12 h, 100% conv. of TFEA.   [f] $BF_3 \cdot OEt_2$ (0.2 equiv), CH_2Cl_2, -72~-25 °C, 4 h.
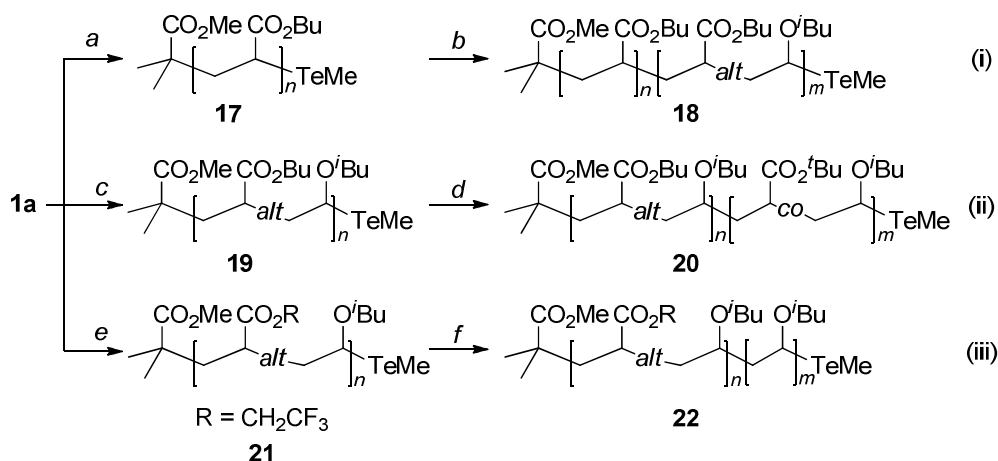
An alternating copolymer could be used as a macro CTA. Poly(BA-*alt*-IBVE)-TeMe **19** (M_n = 3900, PDI = 1.20, and MF_{IBVE} = 0.49) was prepared by copolymerizing BA (20 equiv) and IBVE (100 equiv) in the presence of **1a** at 60 °C. Since ca. 80 equiv of unreacted IBVE remained in the reaction mixture, addition of *t*BA (50 equiv) triggered to reinitiate the polymerization, affording poly[(BA-*alt*-IBVE)-*block*-(*t*BA-*co*-IBVE)] **20** with M_n = 11700 and low PDI = 1.20 (Scheme 5ii). The MF_{IBVE} in the second block was determined to be 0.30. The GPC traces also indicate the clean conversion from the macro CTA to the block copolymer (Figure 6b).

Moreover, alternating copolymers could be used as initiators for living cationic polymerization.[47] Poly(TFEA-*alt*-IBVE)-TeMe **21** (M_n = 4100, PDI = 1.12, and TFEA/IBVE = 50/50) was prepared by reacting TFEA (20 equiv) and IBVE (200 equiv) in the presence of **1a** under photoirradiation. After the reaction mixture was diluted with CH_2Cl_2, the addition of $BF_3 \cdot OEt_2$ (0.1 equiv) triggered cationic polymerization of the remaining IBVE from **21** to give

poly[(TFEA-*alt*-IBVE]-*block*-IBVE] **22** with M_n = 17700 and narrow PDI = 1.19 (Scheme 5iii and

Figure 6c).

Figure 6. GPC traces of macro CTAs and block copolymers

(a) **18** M_n = 27700 PDI = 1.25   **17** M_n = 10200 PDI = 1.12

(b) **20** M_n = 11700 PDI = 1.20   **19** M_n = 3900 PDI = 1.20

(c) **22** M_n = 17700 PDI = 1.19   **21** M_n = 4100 PDI = 1.12
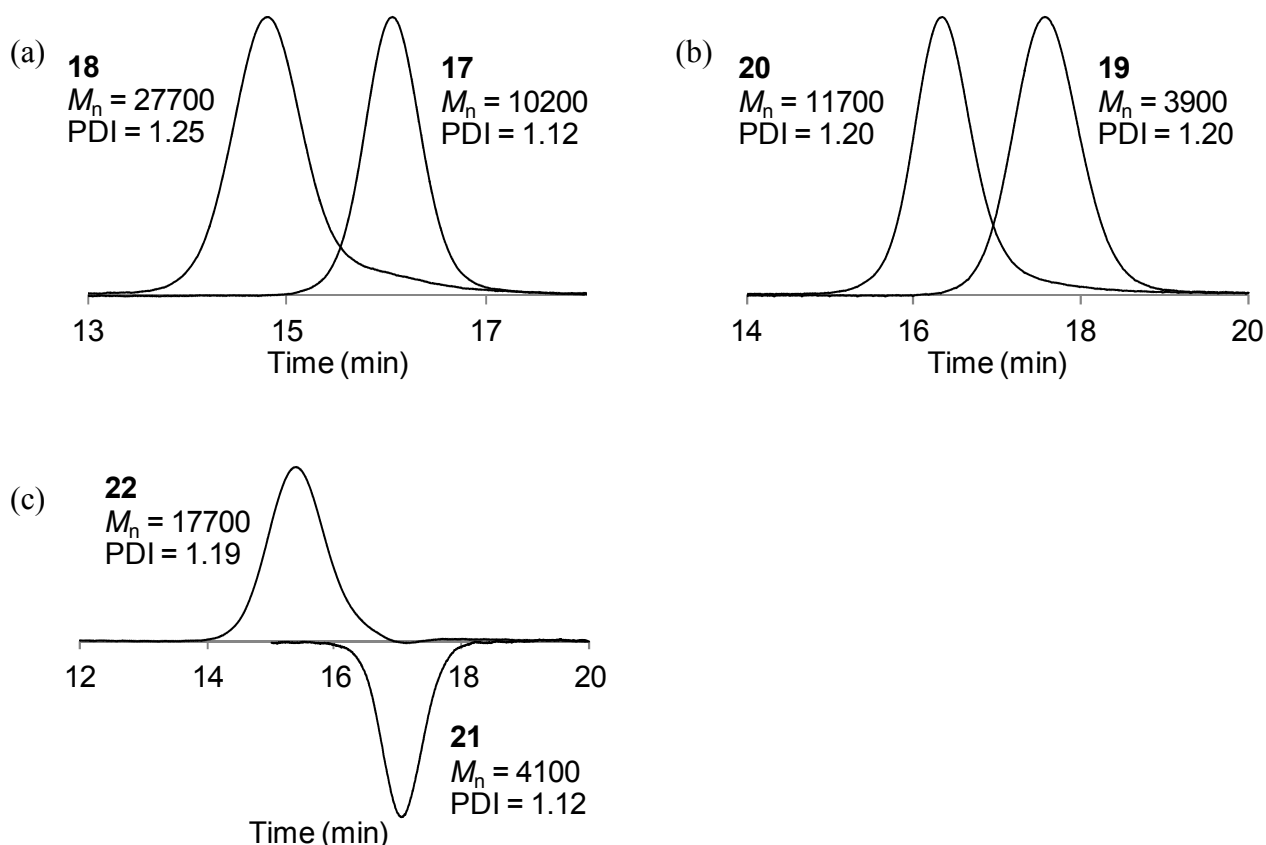
Transformation of polymer main chain. The unique sequence of functionality in the

alternating copolymer backbones was used in the selective transformation of the polymer main

chain structure. Copolymer **23**, prepared using the conditions for run 4 in Table 2, was treated with

tetrabutylammonium fluoride (TBAF) in ethanol/THF at room temperature for 12 h. Desilylation

followed by the lactonization gave polymer **24** with lactone units in the polymer chain with M_n =

18400 and PDI = 1.18 (Scheme 6). The same transformation was achieved by acid treatment of **23**

in aqueous 3N HCl/EtOH/THF solution at room temperature to give **24** with M_n = 19700 and PDI =

1.18. A characteristic carbonyl absorption of polymer **23** at 1759 cm^{-1} in the IR was shifted to 1769

cm^{-1} corresponding to γ-lactone of **24** upon the transformation (Figure 7a and 7b). In the ^{1}H NMR spectrum, the proton derived from α−CH to the trimethylsiloxy group in **23** at 3.6 ppm was shifted to 4.2–5.0 ppm in **24** (Figure 7c). These data clearly reveals the formation of lactone ring. The existence of free alcohol and unreacted trifluoroethyl ester were suggested by the IR (3050–3700 cm^{-1} for OH) and ^{13}C NMR (178 ppm for the ester) spectra, respectively. From ^{13}C NMR spectroscopy with inverse gated proton decoupling and a long pulse delay period (10 s), the ratio of the lactone, ester, and hydroxyl groups in **24** was determined to be 81:9:10 (Figure 7d). Grass transition temperature of **24** was determined to be 113~116 °C.

Scheme 6. Transformation of main polymer chain. Reaction conditions: [a] TBAF·3H₂O, EtOH/THF, rt, 12 h. [b] 3N HCl/EtOH/THF, THF, 0 °C, 4 h.
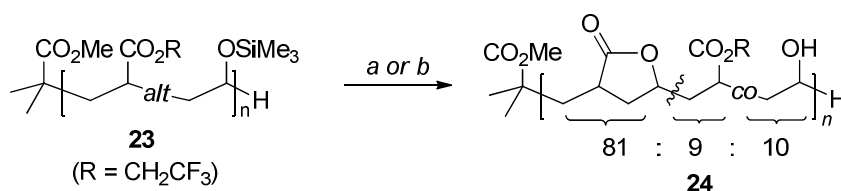
Figure 7. (a) IR spectra of the carbonyl region of **23** and (b) **24**, and (c) ^{1}H NMR and (d) ^{13}C NMR spectra of **24**.

(a)

(b)
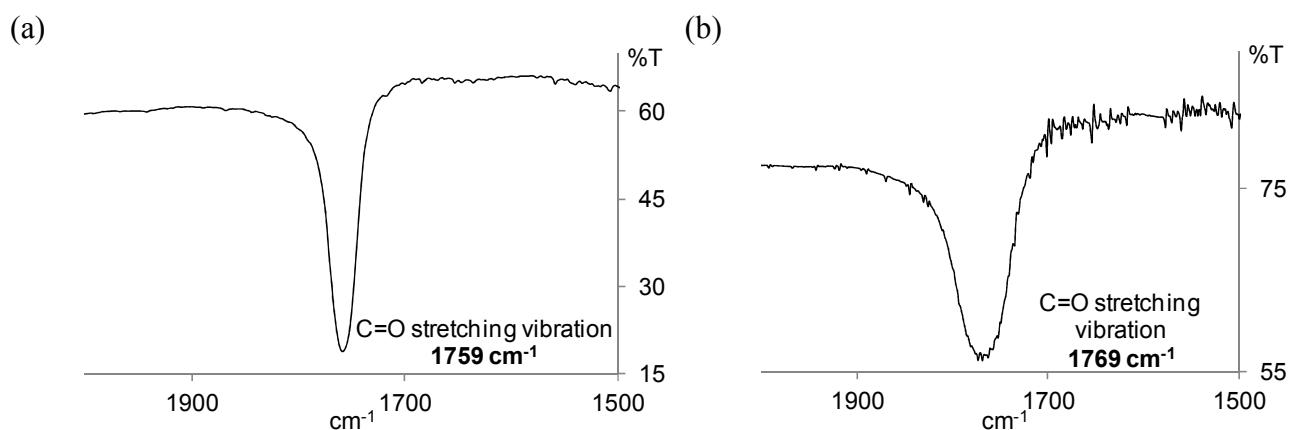
Figure 7, continued.

(c)
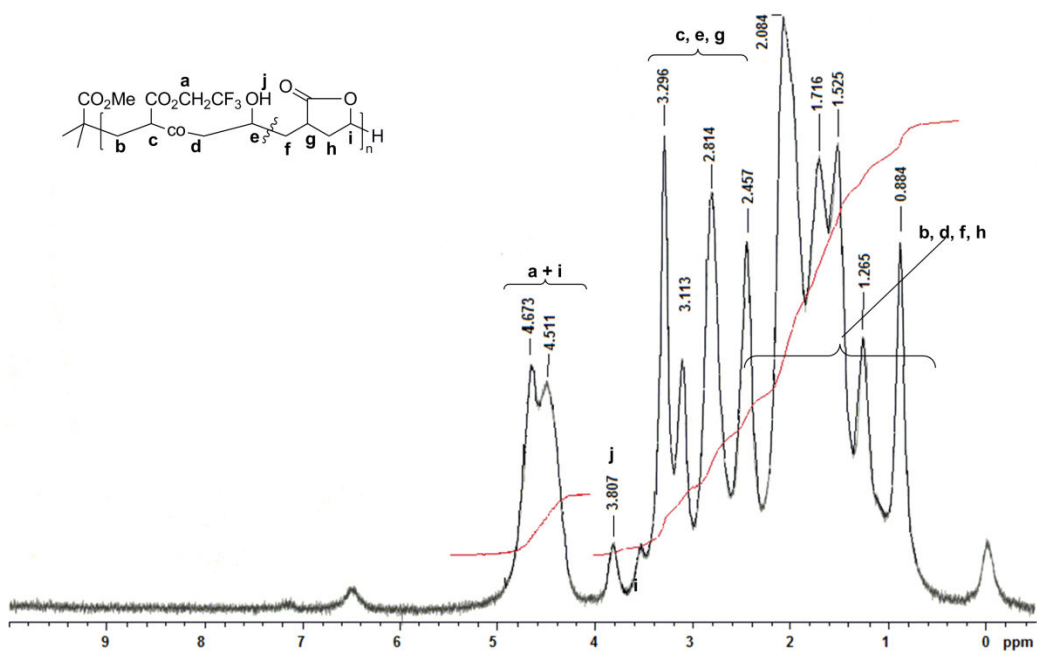
(d)
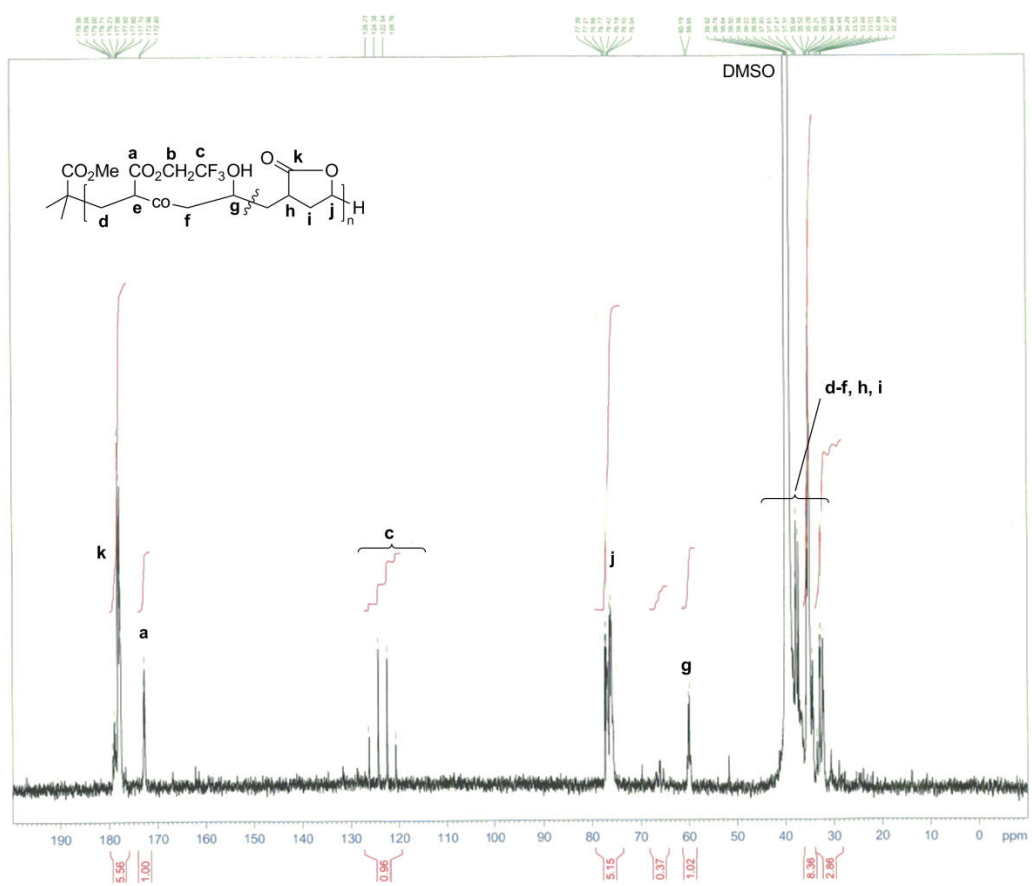
A similar transformation forming lactone unit in the polymer main chain in a random copolymer prepared from of methyl acrylate and vinyl acetate has been reported.[29] However, the number of lactone unit was low due to the low incorporation of vinyl acetate in the copolymer. Since the number of lactone unit is high and can be tuned by changing the MF of vinyl ethers in our case, the current method provides flexible synthetic route to this type of intriguing main-chain functionalized polymers.

Conclusions

Controlled copolymerization of (meth)acrylates and vinyl ethers was achieved under TERP, SBRP, and BIRP conditions, giving the corresponding structurally well-defined random and alternating copolymers with low PDIs. Nearly complete control of the monomer sequence was achieved by adding excess amounts of vinyl ethers. Several new block copolymers were synthesized by combining the alternating copolymerization and living radical or living cationic polymerization. These methods will be useful for the synthesis of new polymer materials with controlled macromolecular structures and monomer sequences.

Experimental Section

Measurements. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured for a CDCl$_3$ or CD$_2$Cl$_2$ solution of a sample. ^{1}H NMR spectra are reported in parts per million (δ) from internal tetramethylsilane or residual solvent peak, and ^{13}C NMR from solvent peak. Matrix assisted laser desorption ionization (MALDI) time of flight (TOF) mass spectra were recorded on a spectrometer equipped with a 337 nm N$_2$ laser in the reflection mode and at 20 kV acceleration voltage. Samples were prepared from a tetrahydrofuran (THF) solution by mixing sample (1 mg/mL), dithranol (10 mg/mL), and sodium trifluoroacetate (1 mg/mL) in a ratio of 5:1:1. GPC was

performed on a liquid chromatography equipped with two linearly connected polystyrene (PSt) mixed gel columns (Shodex LF-604), which were calibrated with poly(methyl methacrylate) (PMMA) standards using $CHCl_3$ or DMF containing LiBr (0.1 mol/L) as an eluant. Multiangle laser light scattering (MALLS) was carried out in THF at 40 °C on a Dawn E instrument (Wyatt Technology) which is connected to GPC. Preparative/recycling GPC was carried out with two linearly connected polystyrene mixed gel columns. The refractive index increment (dn/dc) was measured in THF at 40 °C. Differential scanning calorimetry (DSC) was performed with Shimazu DSC-60. The temperature range was -50 to 200 °C and the heating and cooling rates were 5 °C/min. During the measurement, the sample was purged by nitrogen gas. Glass transition temperature (Tg) was defined as the temperature of the midpoint of the change in heat capacity on second heating scan.

Materials. Unless otherwise noted, materials obtained from commercial suppliers were used without purification. Isobutyl vinyl ether (IBVE; >99%), *t*-butyl vinyl ether (*t*BVE; >98 %), and trimethyl(vinyloxy)silane (TMVS; >97 %) were distilled over calcium hydride. *n*-Butyl acrylate (BA; >99%), *t*-butyl acrylate (*t*BA; >99%), 2,2,2-trifluoroethyl acrylate (TFEA; >98 %), acrylonitrile (AN; >99%), *N,N*-dimethylacrylamide (DMAA; >99%), methyl methacrylate (MMA; >99%), ethyl methacrylate (EMA; >99%), and 2,2,2-trifluoroethyl methacrylate (TFEMA; ＞98 %) were washed with 5 % aqueous sodium hydroxide solution and were distilled over calcium hydride under reduced pressure. *N*-Isopropylacrylamide (NIPAM; >98 %) was recrystalized from hexane. CH_2Cl_2 was distilled successively from P_2O_5 and K_2CO_3 and stored over molecular sieves 3A. Triethylamine was distilled from CaH_2 and stored over molecular sieves 4A. Methanol was distilled from Mg which was activated by I_2 and stored over molecular sieves 3A. Dimethyl 2,2'-azobis(2-methylpropionate) (V-601) was recrystallized from methanol. Methyl 2-methyl-2-methyltellanylpropionate (**1a**),[47] ethyl 2-methyl-2-dimethylstibanylpropionate (**1b**),[33]

methyl 2-methyl-2-dimethylbismuthanyl-propionate (**1c**), and 1-methoxy-1-methyltellanylhexane (**5**)[47] were prepared as reported.

Typical procedure for copolymerization under thermal conditions. Synthesis of poly(TFEA-*alt*-IBVE). A solution of TFEA (0.316 g, 2.1 mmol), IBVE (1.04 g, 10 mmol), V-601 (4.50 mg, 0.020 mmol) and **1a** (16.0 μl, 0.10 mmol) was heated at 60 °C for 1 h with stirring under a nitrogen atmosphere in a glove box. A small portion of the reaction mixture was withdrawn and dissolved in CDCl$_3$. The conversion of the monomer (TFEA: 100%, IBVE: 20%) was determined by using ^{1}H NMR spectroscopy. PhSH (12.0 μl, 0.13 mmol) was added to the reaction mixture, and the resulting solution was stirred at 80 °C for 2 h. The mixture was concentrated under reduced pressure to give the crude product (0.50 g). The MF_{IBVE} = 0.49 was determined by using ^{1}H NMR spectrometry, and the M_n = 5500 and the PDI = 1.17 were determined by GPC calibrated against PMMA standards. Treatment of Bu$_3$SnD instead of PhSH gave the end-deuterated copolymer.

Typical procedure for copolymerization under photo irradiation conditions. Synthesis of poly(TFEA-*alt*-IBVE). A solution of TFEA (0.316 g, 2.1 mmol), IBVE (1.04 g, 10 mmol), and **1a** (16.0 μl, 0.10 mmol) was irradiated by 60 W black lamp at 60 °C for 0.5 h with stirring under a nitrogen atmosphere. A small portion of the reaction mixture was withdrawn and dissolved in CDCl$_3$. The conversion of the monomer (TFEA: 99%, IBVE: 20%) was determined by using ^{1}H NMR spectroscopy. PhSH (12.0 μl, 0.13 mmol) was added to the reaction mixture, and the resulting solution was stirred at 80 °C for 2 h. The mixture was concentrated under reduced pressure to give the crude product (0.60 g). The MF_{IBVE} = 0.48 was determined by using ^{1}H NMR spectrometry, and the M_n = 4500 and the PDI = 1.13 were determined by GPC calibrated against PMMA standards.

Synthesis of poly[BA-*block*-poly(BA-*alt*-IBVE)]. A solution of **1a** (8.0 μl,, 0.052 mmol), BA (0.662 g, 5.2 mmol), and V-601 (2.60 mg, 0.011 mmol) was stirred at 60 °C for 2 h under a

nitrogen atmosphere to give PBA with M_n = 10200 and PDI = 1.12. Conversion of the monomer (92 %) was determined by ^{1}H-NMR. BA (0.662 g, 5.2 mmol) and IBVE (5.18 g, 52 mmol) were added, and the resulting solution was heated at 60 °C for 8 h. The excess IBVE was removed under reduced pressure to give the block copolymer (1.8 g, 100 % yield) with M_n = 27700 and PDI = 1.25. The MF_{IBVE} = 0.44 in the second block was determined by ^{1}H NMR spectroscopy.

Synthesis of poly[(BA-*alt*-IBVE)-block-poly(*t*BA-*co*-IBVE)]. A solution of **1a** (16.0 μl,, 0.10 mmol), BA (0.268 g, 2.1 mmol), IBVE (1.04 g, 10 mmol), and V-601 (5.0 mg, 0.022 mmol) was stirred at 60 °C for 3 h under a nitrogen atmosphere to give poly(BA-*alt*-IBVE) with M_n = 3900, PDI = 1.20, and MF_{IBVE} = 0.49. Consumption of BA was ascertained by ^{1}H-NMR. *t*BA (0.665 g, 5.2 mmol) was added to the reaction mixture, and the resulting solution was heated at 60 °C for 2 h to give the block copolymer (1.4 g, 84 % yield) with M_n = 11700 and PDI = 1.20. The MF_{IBVE} = 0.30 in the second block was determined by ^{1}H NMR spectroscopy.

Synthesis of poly[(TFEA-*alt*-IBVE)-*block*-poly(IBVE)]. A solution of **1a** (8.00 μl,,0.052 mmol), TFEA (0.158 g, 1.0 mmol), IBVE (1.04 g, 10 mmol), and V-601 (1.80 mg, 0.0078 mmol) was stirred at 60 °C for 1.5 h under a nitrogen atmosphere to give poly(TFEA-*alt*-IBVE) with M_n = 3900, PDI = 1.19, MF_{IBVE} = 0.50). Consumption of TFEA was ascertained by ^{1}H-NMR. CH_2Cl_2 (2.0 ml) was added, and the resulting solution was cooled to -72 °C. $BF_3 \cdot Et_2O$ (0.70 μl, 0.0056 mmol) was added at this temperature, and the resulting solution was stirred at -40 °C for 3 h and then -25 °C for 1 h. The reaction was quenched by addition of triethylamine (40.0 μl) followed by methanol (10.0 μl). The conversion of IBVE (100%) was determined by ^{1}H NMR. After routine work-up, the block copolymer was obtained (1.2 g, 100 % yield) with M_n = 23300 and PDI = 1.32.

Desilylation of 23 by TBAF. Tetrabutylammonium fluoride trihydrate (2.34 g, 7.4 mmol) was added to a mixture of copolymer **23** (201 mg; M_n = 24700, PDI = 1.09, MF_{TMVS} = 0.50) in a 2/1 EtOH/THF (= 1/2 v/v, 15 mL), and the mixture was stirred at room temperature for 12 h. The

precipitate was collected, washed with water, and dried under reduced pressure to give **24** (83 mg,

100 % yield) with M_n = 18400 and PDI = 1.18. Treatment of **23** with 3N HCl (in EtOH, 10   mL) in

THF (30 mL) at 0 °C for 4 h also gave **24** (79 mg, 100 % yield) with M_n = 19700 and PDI = 1.18.

The IR spectra of **23** and **24** are shown in Figure 7.

Figure 8. ^{13}C-NMR spectra of alternating copolymers.
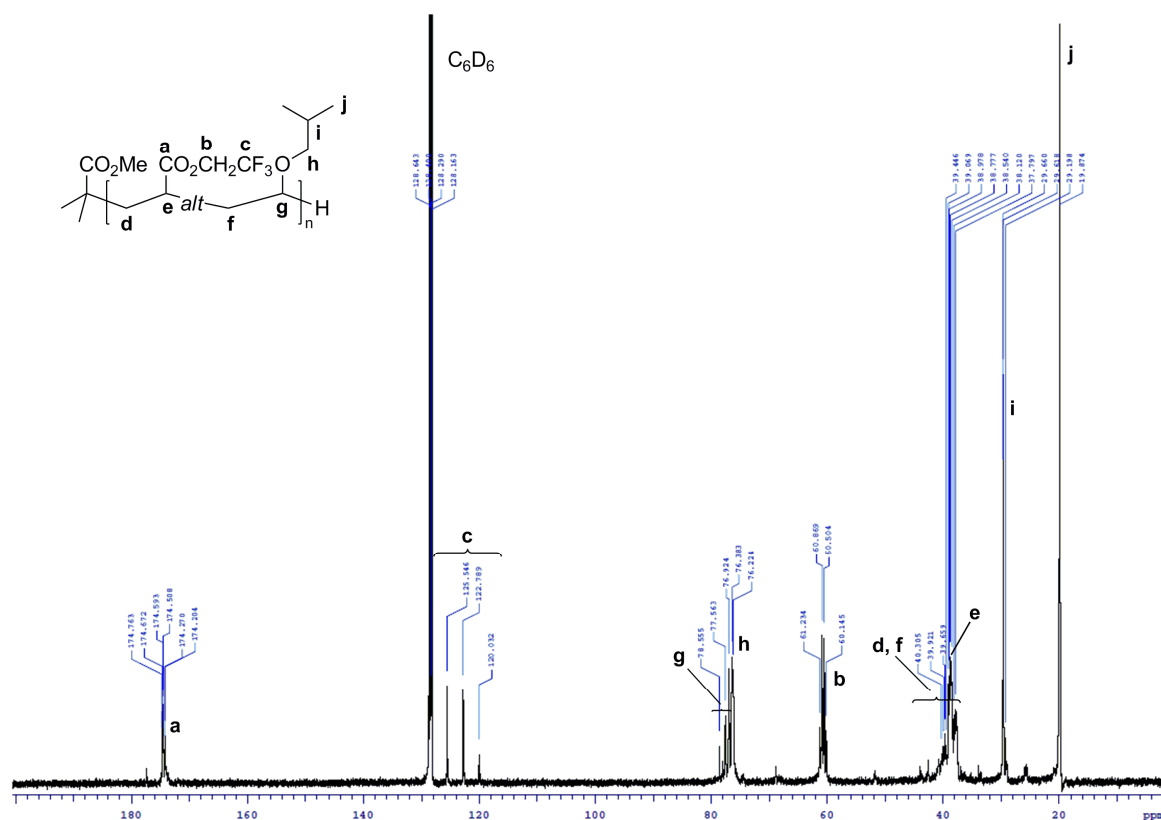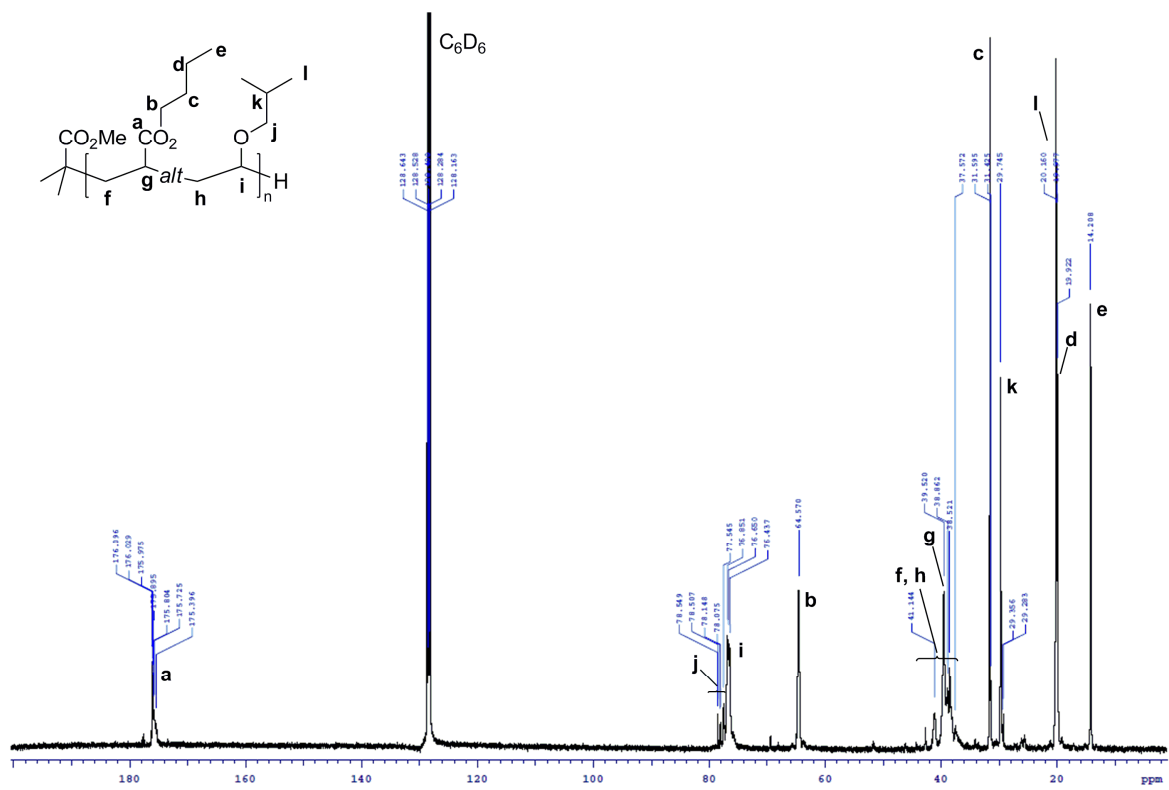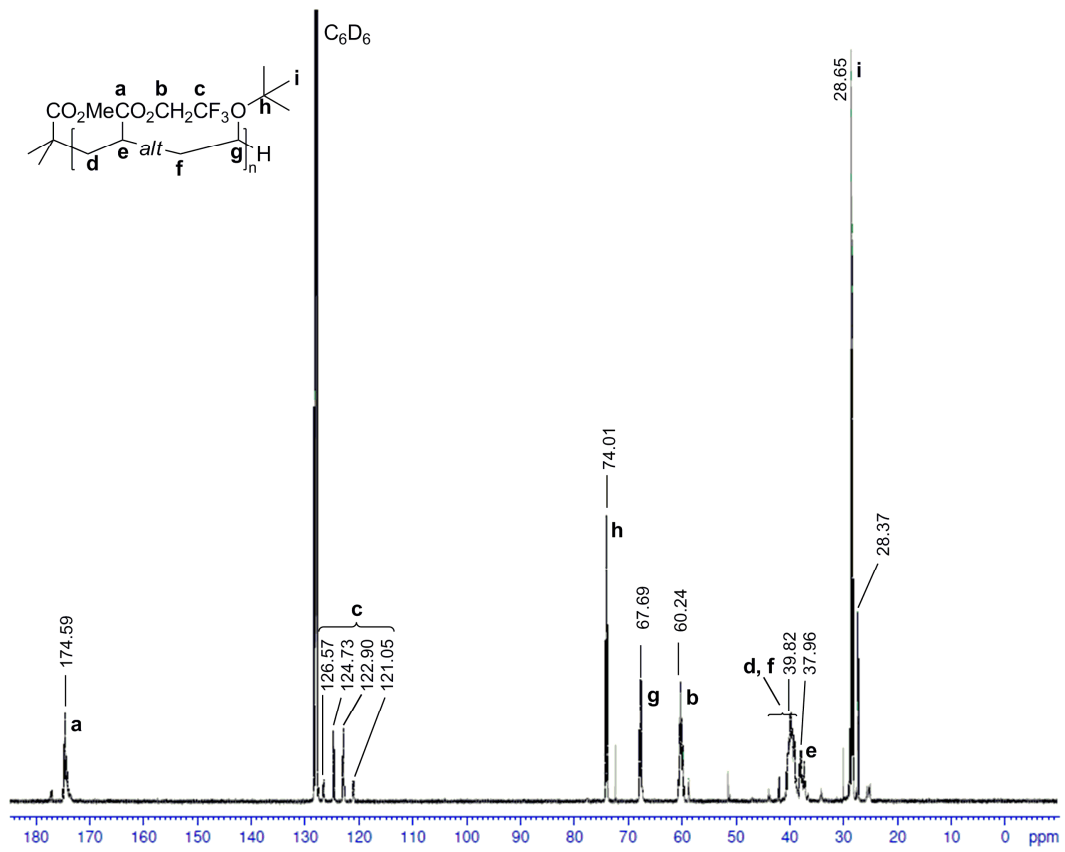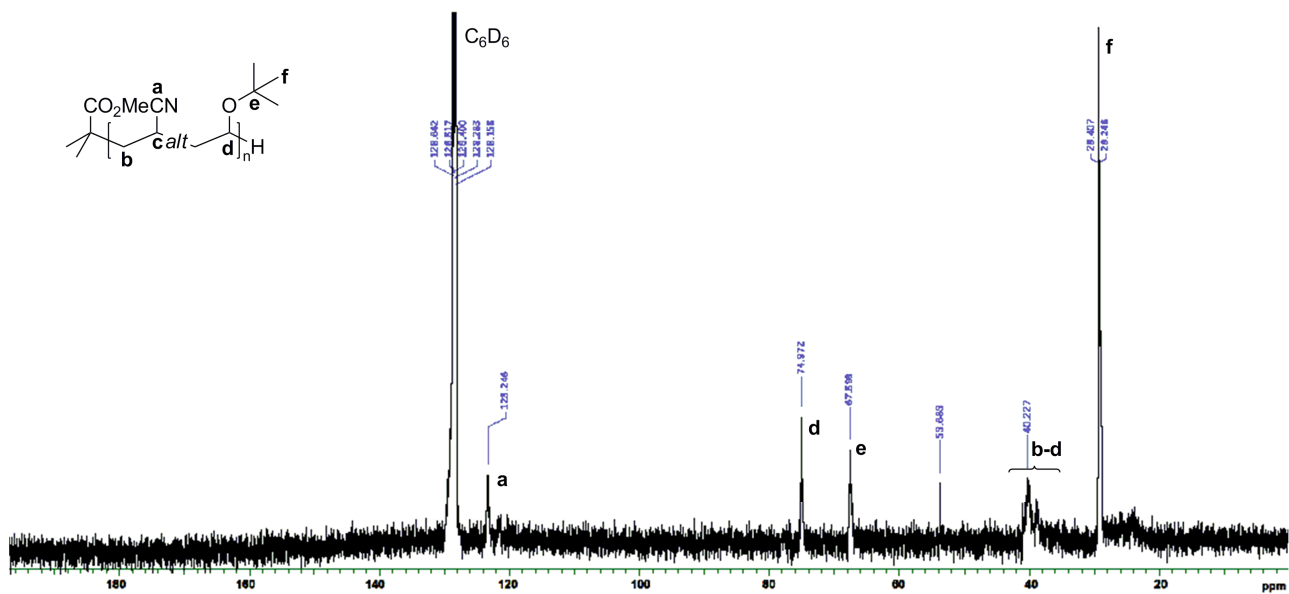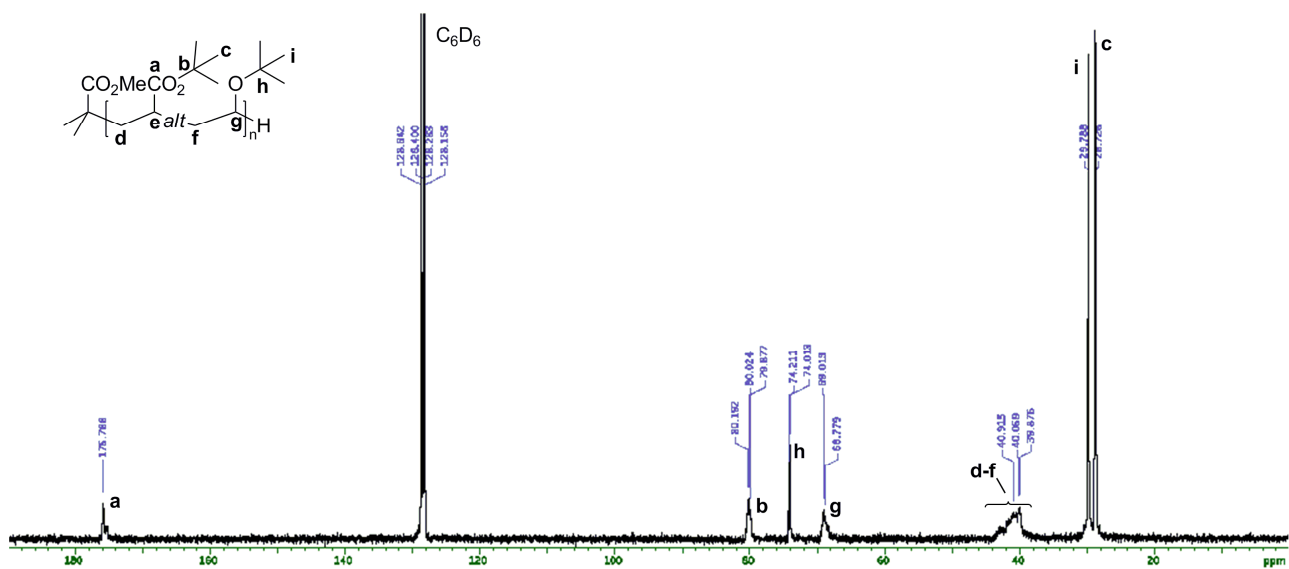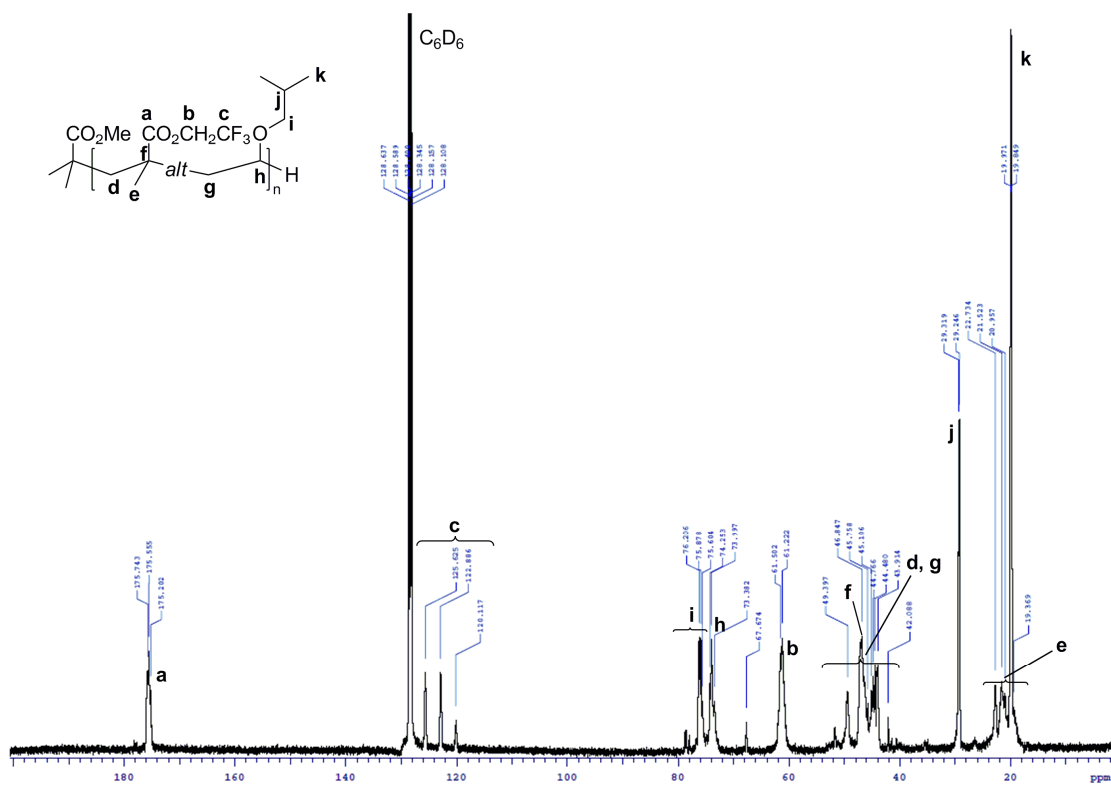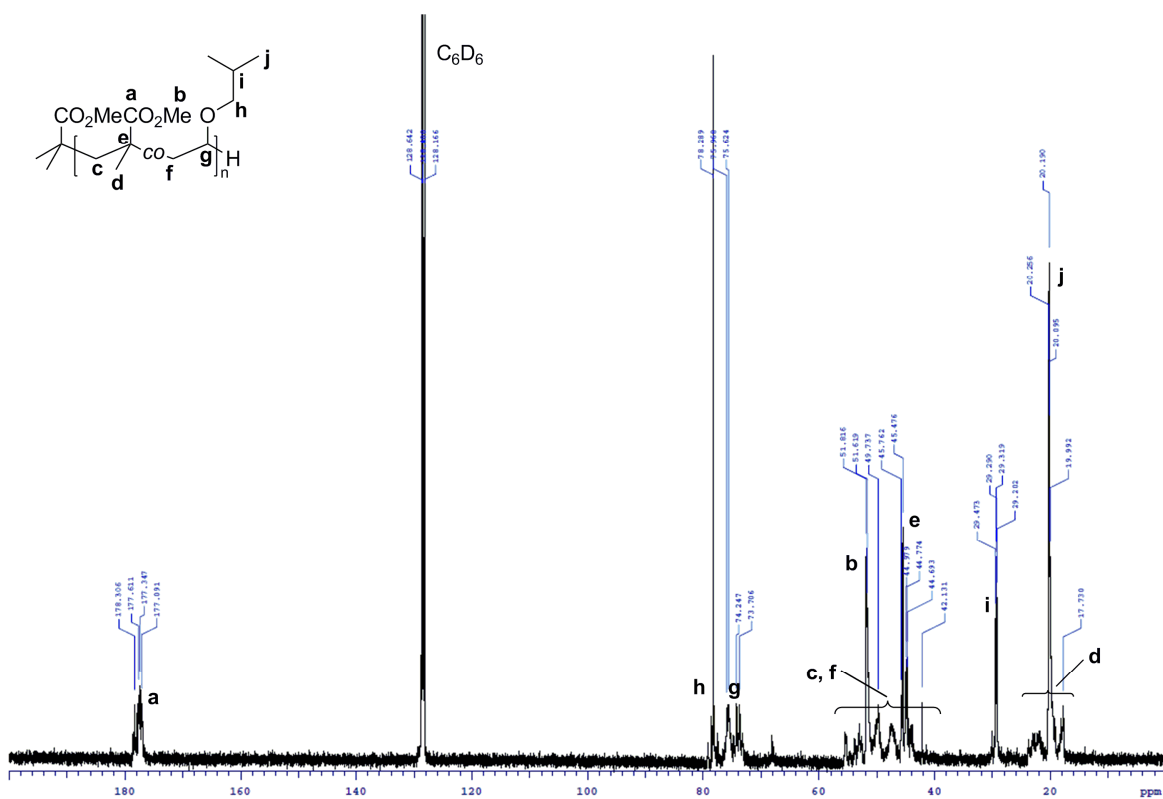
Table 3. Grass transition temperature of copolymer

Copolymer	M_n	PDI	MF$_{(vinyl\ ether)}$	Tg (°C)[a]
PTFEA-*alt*-PIBVE	5700	1.18	0.49	-17.9
PTFEA-*alt*-PIBVE	17500 (19200)	1.15	0.49	-11.4
PTFEA-*alt*-PIBVE	36100 (49600)	1.17	0.48	-10.5
PTFEA-*alt*-PIBVE	54000 (75200)	1.20	0.48	-9.4
PTFEA-*alt*-P*t*BVE	5600	1.17	0.50	10.5
PTFEA-*alt*-P*t*BVE	16300	1.18	0.50	18.2
PBA-*co*-PIBVE	3800	1.14	0.32	-63.4
PBA-*alt*-PIBVE	4500	1.17	0.49	-44.5
PBA-*co*-PIBVE	18300 (18800)	1.21	0.47	-37.8
PBA-*co*-PIBVE	36400 (38900)	1.20	0.45	-38.1
PBA-*co*-PIBVE	57000 (63400)	1.24	0.45	-38.5
P*t*BA- *alt* -P*t*BVE	14400	1.34	0.50	48.8
PAN- *alt* -P*t*BVE	60500	1.19	0.50	74.4
PMMA-*co*-PIBVE	3900	1.31	0.47	12.8
PTFEMA- *alt*-PIBVE	5000	1.23	0.49	13.4

[a]Measurement was made from -80 to 200 °C by a heating rate of 5 °C/min. The glass transition temperature was determined as the inflection point of the second scan.

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Chapter 4

Controlled Copolymerization of (Meth)acrylate and α-Olefines by Organotellurium-Mediated Living Radical Polymerization (TERP).

Abstract

Copolymerization of (meth)acrylates, such as methyl acrylates (MA) and 2,2,2-trifluoroethyl acrylate (TFEA), and α-olefines such as 6-methyleneundecane (MU) and 1-octene under organotellurium-mediated living radical polymerization (TERP) by using organotellurium chain transfer agent (CTA) **1** have been investigated. Structurally well controlled copolymers having predetermined number-average molecular weights (M_n =3000-14200) from monomer/**1** ratio and low polydispersity indexes (PDI = 1.14-1.45) were obtained under thermal condition in the presence of an azo-initiator or photochemical conditions. Addition of Brønsted acids such as 1,3-C_6H_4[$C(CF_3)_2OH$]$_2$ and $(CF_3)_2CHOH$ efficiently increased the insertion of α-olefines into the copolymer. Structure of the ω-polymer-end group was analyzed by labeling experiments, which reveal that the majority of the end group derived from α-olefin. Despite of the difficulty in regenerating radical species from α-olefin polmer-end species, the copolymers were successfully reactivated and served as macro CTA for the synthesis of block copolymers. Poly(MA-*co*-MU)-*block*-styrene and poly(MA-*co*-MU)-*block*-(*N*-vinylpyrrolidone) with controlled structures were successfully synthesized for the first time.

Introduction

Living radical polymerization (LRP) has become one of the most powerful polymerization method for the synthesis of structurally well controlled macromolecules with rich functionalities, because LRP does not require stringent conditions those required for living anionic, cationic, and coordination polymerization.[1] Extension of LRP from homopolymerization to copolymerization significantly increases the availability of polymers for macromolecular engineering, because copolymerization can finely tailor the properties of polymer materials by the composition of monomers. However, while the controlled synthesis of copolymers by LRP by using monomers having similar reactivities has been well documented, and controlled copolymerization of monomers having different reactivities, such as conjugated and nonconjugated monomers as exemplified in acrylates and α-olefins, has been limited.[2-12] For example, while random copolymerization of methyl acrylate and α-olefins was already examined by reversible addition-fragmentation chain transfer polymerization (RAFT),[13-15] atom-transfer radical polymerization (ATRP),[2,15-19] nitroxide-mediated radical polymerization (NMP),[20] and iodine-mediated LRP,[4] structurally well controlled copolymers with low polydispersity indexes (PDIs) were obtained only low molecular weight copolymers. In addition, mole fraction of α-olefins (MF_{alkene}) in the copolymers was low (< 0.26). When copolymers of high molecular weights were targeted ($M_n > 10000$, where M_n refers to number average molecular weight), PDI exceeded to 1.5 which is a theoretical criterion for LRP. This is due to the accumulation of the dormant species terminated by α-alkene monomer unit which is less efficient in regenerating polymer end radical than those terminated by acrylate monomer.[17,21] Furthermore, while addition of Lewis and Brønsted acids, such as $AlCl_3$,[15] $Sc(OTf)_3$,[22] $(CF_3)_2CHOH$, and $(CF_3)_3COH$[4] under RAFT and iodine-mediated LRP conditions significantly increased the MF_{alkene} =0.27-0.50, the control of PDIs was decreased (> 1.9). Moreover, there is no report on use of the copolymers as macro chain transfer agents (CTAs) for the controlled synthesis of block copolymers.

We have already developed organotellurium-, organostibine-, and organobismuthine-mediated LRPs (TERP,[23-29] SBRP,[30-32] and BIRP,[33,34] respectively).[35-37] One of the most characteristic features of these methods is their high versatility in polymerizing both conjugated and nonconjugated monomers by using a same CTA. This feature has been exemplified in the first controlled synthesis of a block copolymer of conjugated and nonconjugated monomers[30,31,33,38] and controlled random and alternating copolymerization of (meth)acrylates and vinyl ethers.[39] These results prompted us to investigate controlled random copolymerization of acrylate and simple alkene by taking 6-methyleneundecane (MU) and 1-octene as a model monomer under TERP by using methyl 2-methyl-2-methyltellanylpropionate (**1**) as a CTA (Scheme 1). We have recently reported that photo irradiation can effectively activate organotellurium dormant species possessing stable carbon-tellurium bonds.[40-43] Therefore, the effect of photo irradiation on the copolymerization was also examined.[44] We also report the synthesis of block copolymers starting from the copolymer as a macro CTA.

Scheme 1. Controlled copolymerization of (meth)acrylates and α-olefins under TERP.

a: R^1 = CH_3 (MA)
b: R^1 = CH_2CF_3 (TFEA)
c: R^2 = R^3 = C_5H_{11} (MU)
d: R^2 = H, R^3 = C_6H_{13} (1-octene)
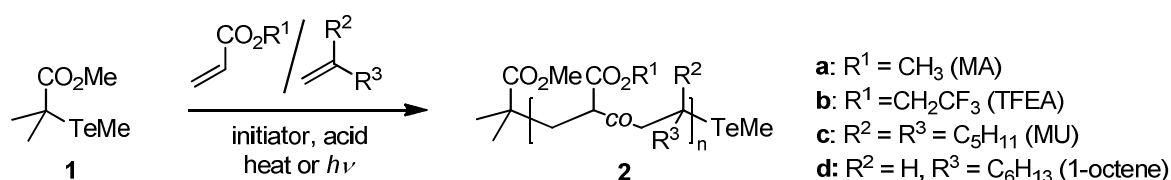
Results and Discussion

Copolymerization of MA and MU. Methyl acrylate (MA, 30 equiv) and MU (30 equiv) were

polymerized in the presence of **1** and dimethyl 2,2'-azobis(2- methylpropionate) (V-601, 0.2 equiv)

at 60 °C for 12 h. The conversion of MA and MU followed first-order kinetics (Figure 1) and

reached 89% and 22%, respectively, after 12 h. GPC analysis indicated the formation of a

structurally well-controlled copolymer **2ac** (R^1 = CH_3, R^2 = R^3 = C_5H_{11}) with the M_n of 3400 and

the PDI of 1.26. The mole fraction of MU (MF_{MU}) in the copolymer was determined to be 0.22 by

using ^1H NMR analysis after isolation, and the ratio is identical to the one estimated from the

monomer conversion.

Figure 1. Kinetic prot of copolymerization of MA and MU.
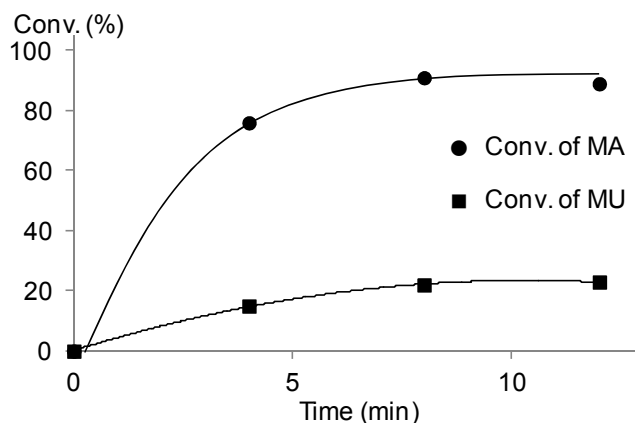
We next examined the effects of acids because they increase the MF of α-alkene in the

copolymerization of acrylates and α-alkenes.[45-47] While TERP was compatible with various

inorganic Lewis acids, such as $Mg(OTf)_2$, $Sm(OTf)_3$, $Yb(OTf)_3$, $Lu(OTf)_3$, and $Ti(OiPr)_4$, and

copolymerization afforded structurally well controlled copolymers with M_ns close to the theoretical

values (M_n = 2800~4100) and low PDIs (PDI = 1.18~1.31), no significant effects on the MF_{MU} were

observed (MF_{MU} = 0.17~0.24). This is partly because these Lewis acids coordinated strongly with

MA and copolymers and the resulting complexes phaseseparated from the reaction mixture. Then, organic and liquid Brønsted acids **3**, **4**, and **5** (Chart 1), which were recently used by Kamigaito and coworkers to increase the MF_{alkene} in the iodine-mediated copolymerization of acrylate and α-olefin, were examined next. [4]

Chart 1. Structure of Brønsted acids used in this study.
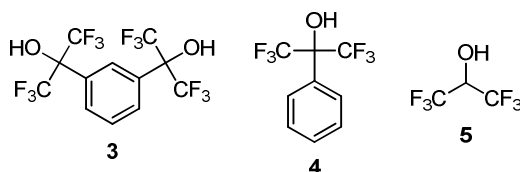
Table 1. Random copolymerization of MA and MU in the presence of **1** in the presence of acid.[a]

run	MA/MU (equiv)	Additive (equiv)	Condition[b]	Conv. of MA (%)[c]	M_n(theo)	M_n(exp)[d]	PDI[d]	MF_{MU}[e]
1	30/30	none	A	89	3700	3400	1.26	0.22
2	30/30	**3** (1)	A	90	4100	4400	1.17	0.28
3	30/30	**3** (30)	A	93	4600	5700	1.14	0.32
4	30/150	**3** (30)	A	100	6200	5500	1.32	0.42
5	30/30	**4** (30)	A	89	4500	5600	1.17	0.33
6	30/30	**5** (30)	A	92	4600	4800	1.18	0.32
7	30/30	**3** (30)	B	93	5000	5100	1.24	0.32
8	30/150	**3** (30)	B	95	5400	3900	1.38	0.38
9[f]	30/30	**5** (30)	B	92	4800	4700	1.20	0.34
10[e]	100/100	**5** (100)	B	83	11700	13100	1.19	0.28
11	30/30	**5** (30)	C	93	4400	2800	1.32	0.30

[a] **1** (1.0 equiv), MA, and MU in the absence of presence of acids **3-5** were stirred at 60 °C for 6-83 h. [b] A: V-601 (0.2 equiv), B: $h\nu$ (500 W high pressure Hg lamp through a >470 nm cut-off filter, C: $h\nu$ (60 W black lamp). [c] Determined by ^{1}H NMR. [d] Number-average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) determined by size exclusion chromatography calibrated with poly(methyl methacrylate) standards. [e] Mole fraction of MU in a copolymer determined by ^{1}H NMR. [f] Polymerization was carried out at 20 °C.

Copolymerization in the presence of **3** under otherwise identical conditions proceeded in a controlled manner giving the copolymer with the M_n close to the theoretical value (M_n = 4400) and low PDI (1.17) (run 2). The MF_{MU} was slightly increased to 0.28. The MF_{MU} was further increased to 0.32 and 0.42 by increase the amount of **3** (30 equiv to **1**) and the use of excess amount of MU over MA with keeping low PDIs of the resulting copolymers (PDI = 1.14-1.32), respectively (runs 3 and 4). Fluoroalcohols **4** and **5** were also effective to increase the MF_{MU}, and the copolymerization gave corresponding copolymers in a controlled manner (M_ns = 4800-5600, PDIs = 1.17-1.18) with high MF_{MU} = 0.32~0.34 (runs 5 and 6). The effect of other Brønsted acid, such as phenol and phosphoric acid, were also examined. However, no positive effects on the MF_{MU} were observed, while the copolymerization proceeded in a controlled manner.

We next examined the copolymerization under photoirradiation, which is effective for the activation of organotellurium dormant species having stable carbon-tellurium bond.[40-43] The copolymerization under photo irradiation with a 500 W high-pressure mercury lamp through a > 480 nm cut-off filter or 60 W black lamp proceeded smoothly at 60 °C, and controlled copolymers with M_n close to the theoretical values and narrow PDIs were obtained with high MF_{MU} (0.30-0.32) in the presence of acid **3** (run 7 and 11). The copolymerization in the presence of excess amount of MU over MA further increased MF_{MU} (0.38) (run 8). Polymerization also proceeded under low temperature, such as 20 °C, because radicals are effectively generated from the dormant species under low temperature by photoirradiation (run 9). A structurally well controlled copolymer with high MF_{MU} was obtained in the presence of **5.** A copolymer with high M_n = 13100 and low PDI = 1.19 was obtained by increasing the amount of MA and MU over that of **1** (run 10), and the result is consistent with the living character of TERP.

Copolymerization of TFEA and MU. 2,2,2-Trifluoroethyl acrylate (TFEA) was next employed as an acrylate monomer, because high electrophilic character of TFEA-polymer end radical would increase the insertion of MU.[48] When an equimolar of TFEA and MU (30 equiv each)

was polymerized in the presence of **1** without acid under photo irradiation at 60 °C, the polymerization followed the first order kinetics for both TFEA and MU and reached 92% and 46% conversion, respectively, after 20 h. A structurally well-controlled copolymer **2bc** ($R^1 = CH_2CF_3$, $R^2 = R^3 = C_5H_{11}$) with $M_n = 4600$ and low PDI of 1.18 was obtained (Table 2, run 1). The MF_{MU} in **2bc** was 0.34, the value considerably higher than that in **2ac**.

Table 2. Photoinduced TERP of TFEA and MU using **1**.[a]

run	Monomer (equiv)	Additive (equiv)	Time (h)	Conv. (%)[b]	M_n(theo)	M_n(exp)[c]	PDI[c]	MF_{MU}[d]
1	TFEA/MU (30/30)	none	20	92	6300	4600	1.18	0.31
2	TFEA/MU (30/30)	**5** (30)	24	98	7800	6400	1.15	0.40
3	TFEA/MU (30/150)	**5** (30)	24	94	7900	5300	1.19	0.49
4[e]	TFEA/MU (30/30)	**5** (30)	66	75	5300	2300	1.15	0.35
5[e]	TFEA/MU (100/100)	**5** (100)	220	80	19800	10100	1.07	0.35
6[e]	TFEA/MU (200/200)	**5** (200)	384	81	35300	14200	1.14	0.33

[a] **1** (1.0 equiv), TFEA, and MU with or without **5** were stirred under irradiation of 60 W black lamp at 60 °C. [b] Conversion of acrylate determined by ^{1}H NMR. [c] Number-average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n, in which M_w refers to weight-average molecular weight) were obtained by using size exclusion chromatography calibrated with poly(methyl methacrylate) standards. [d] The ratio of TFEA and MU units in polymer determined by ^{1}H NMR. [e] Polymerization was carried out at 20 °C.

Addition of acid **5** was also effective to increase the MF_{MU} giving the corresponding controlled copolymer with MF_{MU} of 0.40 (run 2). The MF_{MU} further increased to 0.49 when when 5

times amount of MU was employed over TFEA in the presence of **5**, suggesting that nearly alternative copolymerization occurred (run 3). High molecular weight copolymers (M_n > 10000) with low PDIs (< 1.14) and considerably high MF_{MU} (0.33-0.35) were successfully synthesized by increasing the amount of TFEA and MU over that of **1** (runs 5 and 6).

Copolymerization of acrylate and 1-octene. We next investigated the use of 1-octene as an α-olefin. Copolymerization involving 1-octene is considered to be more difficult than that of MU, because the polymer-end species derived from 1-octene has more stable carbon-tellurium bond and more difficult to be activated than that from MU does.

MA (30 equiv) and 1-octene (30 equiv) were polymerized in the presence of **1** and V-601 (0.2 equiv) at 60 °C for 20 h. The conversion of MA and 1-octene followed first-order kinetics and reached 91% and 18%, respectively, after 20 h (Figure 2).

Figure 2. Kinetic prot of copolymerization of MA and 1-octene.
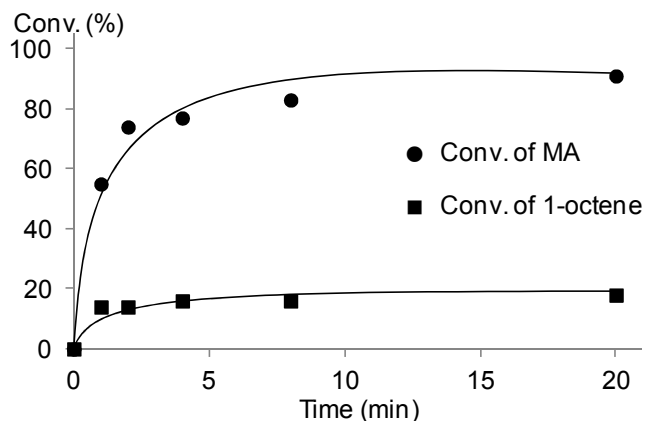
However, while the M_n of the corresponding copolymer **2ad** (R^1 = Me, R^2 = H, R^3 = C_6H_{13}) was close to the theoretical value, the PDI was considerably high (1.47), suggesting that the polymerization was not well controlled. In addition, the MF of 1-octene (MF_{oct}) was low (0.19). When the copolymerization was carried out by the addition of acids **3** and **5** or excess amount of 1-octene over MA, the MF_{oct} increased to 0.26-0.41 as expected (Table 3, runs 2-4). However, the

polymerizations were less controlled than that the control, and copolymers with high PDIs (< 1.5) were obtained.

Table 3. Living radical copolymerization of various acrylates and 1-octene using **1**.[a]

run	Monomer	**Additive** (equiv)	Condition (°C/h)	Conv. of acrylate (%)[b]	M_n (theo)	M_n (exp)[c]	PDI[c]	MF_{Oct}[d]
1	MA	**none**	A (60/20)	91	3200	3700	1.47	0.19
2	MA	**3** (30)	A (60/69)	100	3900	3000	2.06	0.28
3[e]	MA	**3** (30)	A (60/69)	100	4900	3000	2.22	0.41
4	MA	**5** (30)	A (60/9)	94	3500	4900	1.62	0.26
5	MA	**3** (30)	B (60/20)	88	3900	3200	1.45	0.27
6[e]	MA	**3** (30)	B (60/33)	58	4900	3500	1.39	0.35
7	MA	**5** (30)	B (60/22)	75	2500	2900	1.34	0.24
8	MA	**5** (30)	B (20/24)	79	2500	2800	1.39	0.16
9	MA	**5** (30)	C (60/36)	78	3200	3100	1.45	0.24
10[f]	MA	**5** (100)	B (20/83)	73	8200	9000	1.31	0.19
11	TFEA	**none**	C (60/24)	81	4600	2700	1.21	0.24
12	TFEA	**5** (30)	C (60/40)	70	4300	3900	1.22	0.32
13[e]	TFEA	**5** (30)	C (60/60)	97	5000	3500	1.37	0.43
14[g]	TFEA	**5** (30)	C (60/36)	73	5500	2200	1.28	0.47

[a] **1** (1.0 equiv), acrylate, and 1-octene with or without fluoroalcohol were stirred under various conditions. Conditions were (A) V-601 (0.2 equiv), (B) Pyrex tube by irradiation with a 500 W high-pressure mercury lamp through a filter (> 470 nm), or (C) 60 W black lamp. [b] Conversion of acrylate determined by ^{1}H NMR. [c] Number-average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) were obtained by using size exclusion chromatography calibrated with poly(methyl methacrylate) standards. M_w refers to weight-average molecular weight. [d] MF of 1-octene determined by ^{1}H NMR. [e] 150 equivalents of 1-octene was used. [f] 100 equivalents of monomer were used. [g] 300 equivalents of 1-octene was used.

The copolymerization under photoirradiation was next carried out in the presence of **3** or **5** under irradiation of 500 W high-pressure Hg lamp through a >470 nm cutoff filter or 60 W black

lamp (Table 3, runs 5-9). The copolymers with lower PDIs than that prepared under thermal conditions were obtained (M_ns = 2800-3500, PDIs = 1.34-1.45) while keeping same level of MF_{oct}. The copolymer with high M_n was obtained by increasing the amount of MA and 1-octene over that of CTA **1** (Table 3, run 10).

Copolymerization of TFEA (30 equiv) and 1-octene (30 equiv) was next examined in the presence of **1** under irradiation of 60 W black lamp at 60 °C (Table 3, run 11). The conversion of TFEA and 1-octene reached 81% and 45%, respectively, after 24 h. GPC analysis indicated the formation of a structurally well-controlled copolymer **2bd** ($R^1 = CH_2CF_3$, $R^2 = H$, $R^3 = C_6H_{13}$)with M_n = 2700 and PDI = 1.21. The MF_{oct} was 0.24, which was increased to 0.32 by the addition of acid **5** (Table 3, run 12). Nearly alternating copolymers with MF_{oct} = 0.43 and 0.47 with low PDIs (< 1.4) were obtained by increasing the amount of 1-octene over TFEA (1-octene/TFEA = 5 and 10) (Table 3, runs 13 and 14).

Confirmation of ω-end structure. ω-Polymer-end structure of the copolymer **2bc** was analyzed by deuterium labeling experiments. Thus, after nearly alternative copolymer **2bc** was prepared under the condition in Table 2, run 3, it was reduced by Bu_3SnD giving ω-end deuterated **2bc**-D and **2bc'**-D having MU and TFEA unit at the polymer end, respectively. In ^{2}H NMR spectra, two signals corresponding to **2bc**-D and **2bc'**-D were observed at 1.2 ppm and 2.3 ppm in a ratio of 85:15 (Figure 3a). The same experiments starting from copolymer **2bd** prepared under the same condition of Table 3, run 14 also revealed that **2bd**-D having 1-octene unit at the ω-end formed predominantly over **2bd'**-D having TFEA unit did (**2bd**-D:**2bd'**-D = 92:8, Figure 3b). These results are consistent with the previous observation.[17,21] Since the polymer-end derived from 1-octene possesses higher carbon-tellurium bond and less reactive in regenerating polymer-end radicals than that from MU, the lower control in the copolymerization of 1-octene than MU must be due to the difficulty to regenerate polymer-end radicals from the dormant species.

Figure 3. ^{2}H NMR spectra of (a) **2bc**-D and **2bc'**-D and (b) **2bd**-D and **2bd'**-D.

(a)

(b)
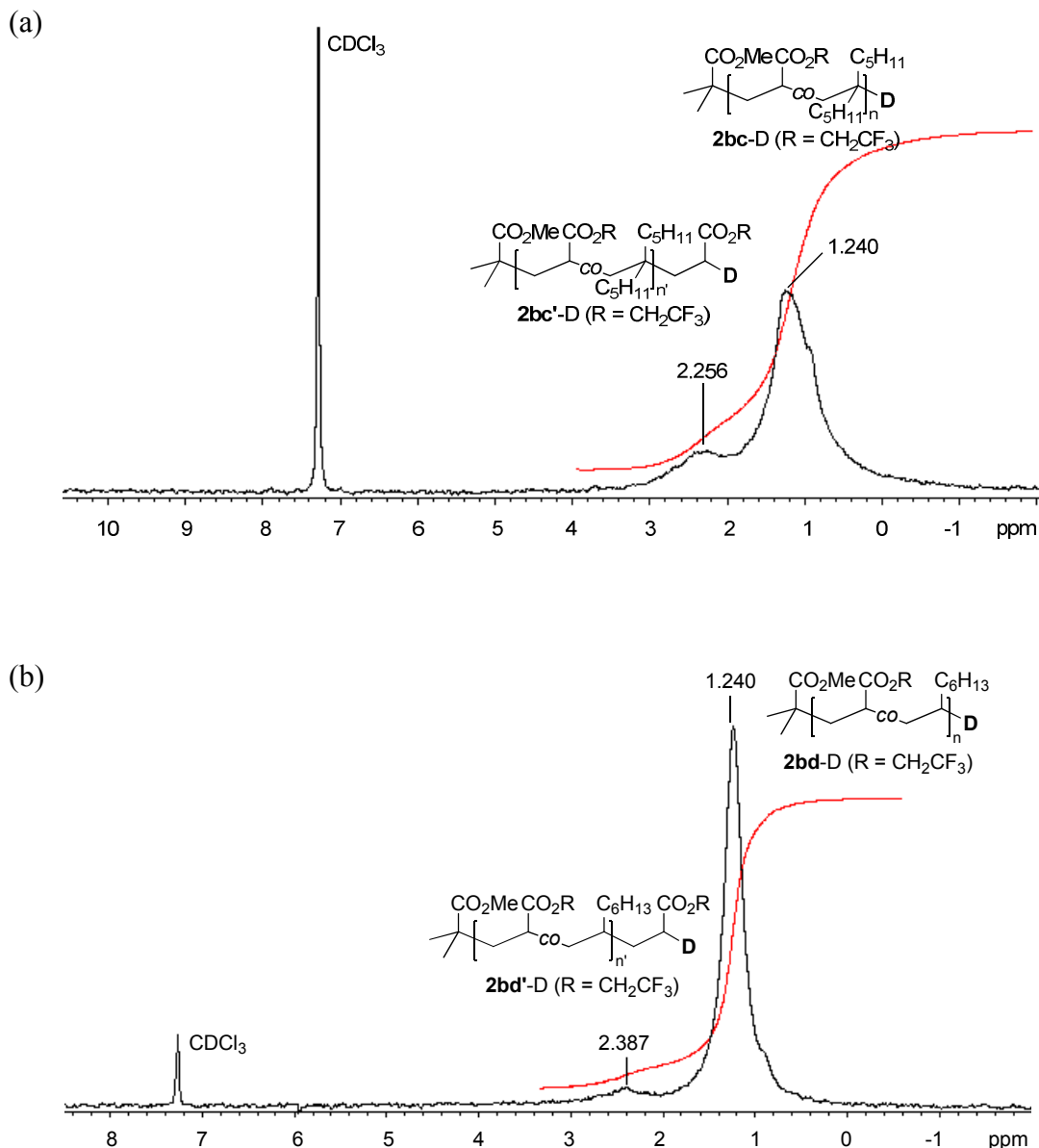
Synthesis of block copolymer. We next examined the synthesis of block copolymers starting from **2** (Scheme 2). Thus, **2bc** (M_n = 3800, PDI = 1.24, MF_{MU} = 0.44), which was prepared from **1**, TFEA (15 equiv), and MU (150 equiv) in the presence of **5** (15 equiv), was heated with TFEA (85 equiv) and V-601 (0.2 equiv) at 60 °C for 10 h (Scheme 3i). Copolymer **2bc** completely disappeared and the desired structurally well defined block copolymer,

poly[(TFEA-*co*-MU)-*block*-TFEA] (**6**), with M_n = 16700 and PDI = 1.13 was formed as judged from GPC traces (Figure 4a).

Scheme 2. Synthesis of novel block copolymers.
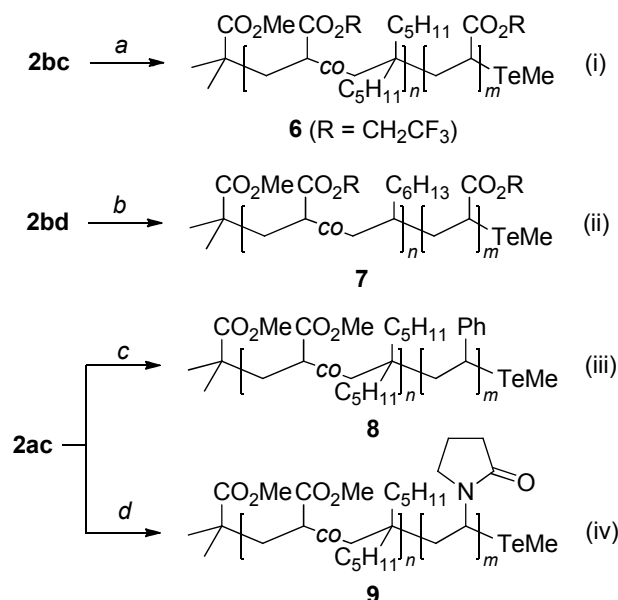
Reaction conditions: [a] **2bc** (M_n = 3800, PDI = 1.24, MF$_{MU}$ = 0.44), TFEA (85 equiv), V-601 (0.2 equiv), 60 °C, 10 h, 98% conv. of TFEA. [b] **2bd** (M_n = 2600, PDI = 1.20, MF$_{Oct}$ = 0.43), TFEA (85 equiv), V-601 (0.2 equiv), 60 °C, 10 h, 96% conv. of TFEA. [d] **2ac** (M_n = 5000, PDI = 1.18, MF$_{MU}$ = 0.31), St (300 equiv), V-601 (0.2 equiv), 60 °C, 40 h, 72 % conv. of St. [d] **2ac** (M_n = 4000, PDI = 1.22, MF$_{MU}$ = 0.31), NVP (200 equiv), 500 W high-pressure Hg lamp/> 580 nm cutoff filter, 60 °C, 110 h, 82% conv. of NVP.

The block copolymers poly[(TFEA-*co*-octene)-*block*-TFEA] (**7**), poly[(MA-*co*-MU)-*block*-St] (**8**), and poly[(MA-*co*-MU)-*block*-NVP] (**9**) were also obtained from **2bd** (M_n = 2600, PDI = 1.20, MF$_{MU}$ = 0.43), **2ac** (M_n = 5000, PDI = 1.18, MF$_{MU}$ = 0.31), **2ac** (M_n = 4000, PDI = 1.22, MF$_{MU}$ = 0.31) and TFEA, styrene, and *N*-vinyl pyrrolidone (NVP), respectively (Scheme 3ii-iv and Figure 4b-d). The macro CTAs were completely consumed and the corresponding copolymers with low PDIs (1.22-1.41) were formed in all cases. These results clearly

indicate that polymer-end species having not only acrylates units but also α-olefine units were efficiently activated and generated the corresponding polymer-end radical species.

Figure 4. GPC traces before and after the block copolymerization.

(a)

2bc
M_n = 3800
PDI = 1.24
MF_{MU} = 0.44

6
M_n = 16700
PDI = 1.13

Time (min)

(b)

7
M_n = 12100
PDI = 1.19

2bd
M_n = 2600
PDI = 1.20
MF_{Oct} = 0.43

Time (min)

(c)

8
M_n = 21900
PDI = 1.41

2ac
M_n = 5000
PDI = 1.18
MF_{MU} = 0.31

log M

(d)

9
M_n = 31000
PDI = 1.22

2ac
M_n = 4000
PDI = 1.22
MF_{MU} = 0.31

log M
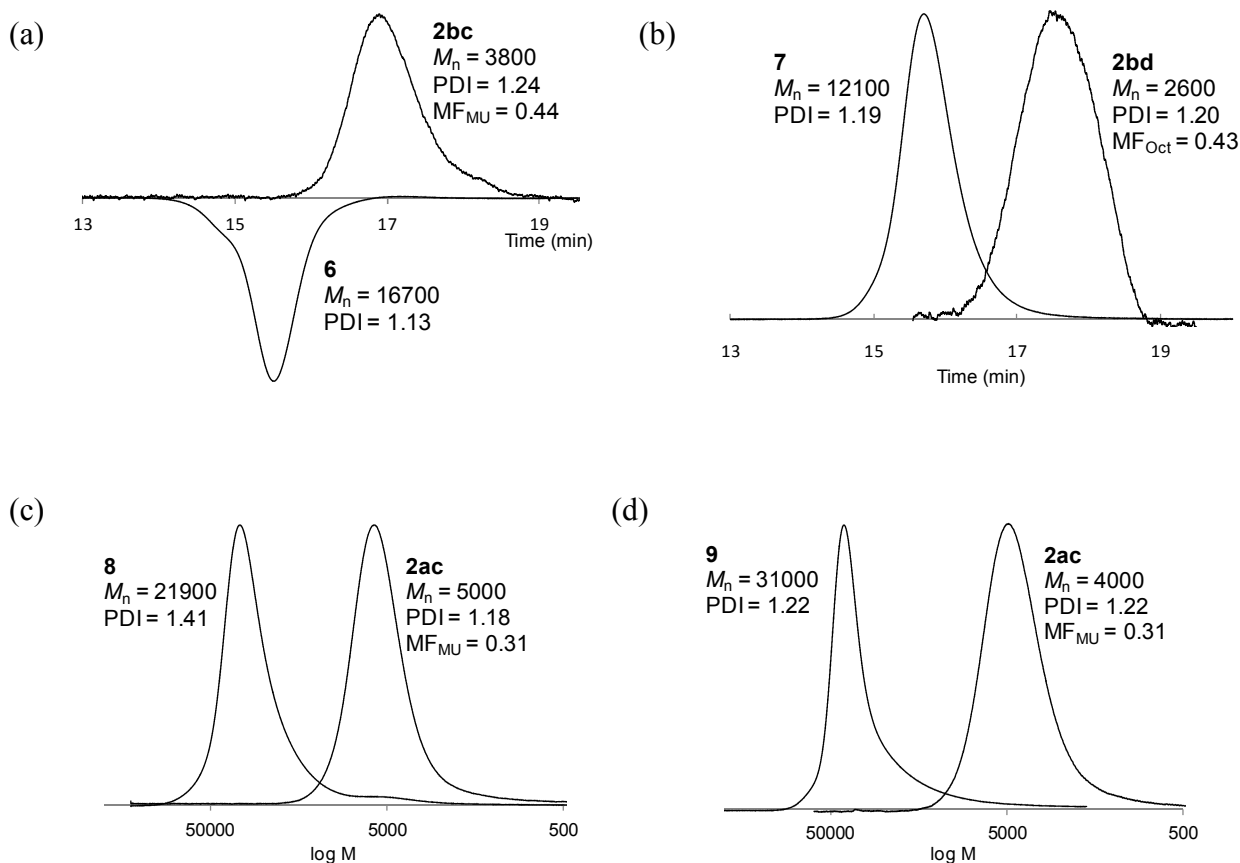
Conclusions

Controlled copolymerizations of acrylates and α-olefins was examined by using MA and TFEA as the former and MU and 1-octene as the latter were achieved under TERP condition. Highly controlled copolymers with low to high molecular weights (M_n = 3000-14000) with low PDIs (< 1.4) were successfully synthesized. Photoirradiation was effective to increase PDI control when 1-octene was used due to the effeicient activation of polymer-end group derived from 1-octene unit. Insertion of α-olefins to the copolymer was increased by the addition of several

Brønsted acids while keeping the control of PDI. While the majority of the ω-polymer end group was derived from α-olefins, all polymer-ends were successfully activated in the presence of various monomers giving the corresponding structurally well-defined block copolymers. This is the first example for the use of copolymers consisting of acrylates and α-olefins as macro CTA. These results clearly indicate that the current method would considerably increase the availability of polymer materials with controlled macromolecular structures and monomer sequences.

Experimental Section

General. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured for a CDCl$_3$ solution of a sample. ^{1}H NMR spectra are reported in parts per million (δ) from internal tetramethylsilane or residual solvent peak, and ^{13}C NMR from solvent peak. GPC was performed on a liquid chromatography equipped with two linearly connected polystyrene (PSt) mixed gel columns (Shodex LF-604), which were calibrated with poly(methyl methacrylate) (PMMA) standards using CHCl$_3$ or DMF containing LiBr (0.1 mol/L) as an eluant. Preparative/recycling GPC was carried out with two linearly connected PSt mixed gel columns.

Materials. Unless otherwise noted, materials obtained from commercial suppliers were used without purification. Methy acrylate (MA; >99%), 2,2,2-trifluoroethyl acrylate (TFEA; >98 %), stylene (St; >99%), and *N*-vinylpyrrolidone (NVP; >99%) were washed with 5 % aqueous sodium hydroxide solution and were distilled over calcium hydride under reduced pressure. 1-Octene was distilled over calcium hydride under reduced pressure. Dimethyl 2,2'-azobis(2-methylpropionate) (V-601) was recrystallized from methanol. 1, 3-C$_6$H$_4$[C(CF$_3$)$_2$OH]$_2$ (**3**; >97%), C$_6$H$_5$[C(CF$_3$)$_2$OH] (**4**; >97%), and (CF$_3$)$_2$CHOH (**5**; >99%) were distilled from CaH$_2$ and deoxygenated by bubbling with dry nitrogen. Toluene and hexane were distilled from CaH$_2$ and stored over molecular sieves. Methyl 2-methyl-2-methyltellanylpropionate (**1**) was prepared as reported.[49]

Syntesis of MU. To a 500 ml, 3 necked, round bottom flask, which was placed under a

nitrogen atmosphere was added 14.5 g (in 60 % dispersion in mineral oil; 0.36 mol) of sodium hydride. The mineral oil was washed with hexane (20 ml) three times and residual hexane was removed under vacuum. Methyl triphenylphosphonium bromide (81.5 g, 0.23 mol) and 300 ml dry toluene was added. After the resulting suspension was stirred at 60 °C for 1.5 h, 6-undecanone (37.5 ml, 18 mol) was added. After being stirred for 15 h, the reaction mixture was poured into 300 ml ice water. Organic materials were extracted twice with hexane, and the combined organic layers were dried over $MgSO_4$, filtered, and evapolated. The residue was purified by column chromatography with hexane as an eluant followed by distillation (bp = 85 °C/10.4 mmHg) to give 22.9 g (74 %) of MU as an oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 0.89 (t, 6 H), 1.26 (m, 8 H), 1.42 (m, 4 H), 1.99 (t, 4 H), 4.69 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 14.30, 22.01, 27.70, 31.89, 36.24, 108.51, 150.70.

Typical procedure for copolymerization under thermal conditions. Synthesis of poly(MA-*co*-MU). A solution of MA (0.26 g, 3.0 mmol), MU (0.50 g, 3.0 mmol), V-601 (4.6 mg, 0.020 mmol) and **1** (15.5 μl, 0.10 mmol) was heated at 60 °C for 12 h with stirring under a nitrogen atmosphere in a glove box. A small portion of the reaction mixture was withdrawn and dissolved in CDCl$_3$. The conversion of the monomer (MA: 89%, MU: 23%) was determined by using ^{1}H NMR spectroscopy. PhSH (12.0 μl, 0.13 mmol) was added to the reaction mixture, and the resulting solution was stirred at 80 °C for 2 h. The mixture was concentrated under reduced pressure to give the crude product (0.64 g). The MF$_{MU}$ = 0.22 was determined by using ^{1}H NMR spectrometry, and the M_n = 3400 and the PDI = 1.26 were determined by GPC calibrated against PMMA standards.

Typical procedure for copolymerization under photo irradiation conditions. Synthesis of poly(MA-*co*-MU). A solution of MA (0.26 g, 3.0 mmol), MU (0.50 g, 3.0 mmol), **3** (1.2 g, 3.0 mmol), and **1** (15.5 μl, 0.10 mmol) was irradiated by 500 W high-pressure mercury lamp through a > 470 nm cutoff filter at 60 °C for 6 h. A small portion of the reaction mixture was withdrawn and

dissolved in CDCl$_3$. The conversion of the monomer (MA: 93%, MU: 46%) was determined by using ^{1}H NMR spectroscopy. PhSH (12.0 µl, 0.13 mmol) was added to the reaction mixture, and the resulting solution was stirred at 80 °C for 2 h. The mixture was concentrated under reduced pressure to give the crude product (0.47 g). The MF$_{MU}$ = 0.32 was determined by using ^{1}H NMR spectrometry, and the M_n = 5100 and the PDI = 1.24 were determined by GPC calibrated against PMMA standards.

Synthesis of poly[(MA-*co*-MU)-*block*-St]. A solution of **1** (15.5 µl,, 0.10 mmol), MA (0.26 g, 3.0 mmol), MU (0.50 g, 3.0 mmol), and **5** (0.49 g, 2.9 mmol) was irradiated by 500 W high-pressure mercury lamp through a > 520 nm cutoff filter at 20 °C for 24 h to give poly[MA-*co*-(MU)] with M_n = 5000 and PDI = 1.18. Conversion of MA (95 %) and the MF$_{MU}$ = 0.31 was determined by ^{1}H NMR spectroscopy. St (3.1 g, 30 mmol) and V-601 (4.8 mg, 0.021 mmol) were added, and the resulting solution was heated at 60 °C for 40 h. The monomer was removed under reduced pressure to give the block copolymer (2.7 g, 72 % conversion of St was determined by ^{1}H NMR spectroscopy) with M_n = 21900 and PDI = 1.41.

Synthesis of poly[(MA-*co*-MU)-*block*-NVP]. A solution of **1** (15.5 µl,, 0.10 mmol), MA (0.26 g, 3.0 mmol), MU (0.51 g, 3.0 mmol), and **5** (0.51 g, 3.0 mmol) was irradiated by 60 W black lamp at 20 °C for 60 h to give poly[MA-*co*- (MU)] with M_n = 4000 and PDI = 1.22. Conversion of MA (96 %) and the MF$_{MU}$ = 0.31 was determined by ^{1}H NMR spectroscopy. NVP (2.2 g, 20 mmol) was added, and the resulting solution was irradiated by 500 W high-pressure mercury lamp through a filter (> 580 nm) which can proceed polymerization smoothly at 60 °C for 110 h. The monomer was removed under reduced pressure to give the block copolymer (3.6 g, 82 % conversion of NVP) with M_n = 31000 and PDI = 1.22.

Synthesis of end deuterided poly(TFEA-*co*-MU). A solution of **1** (7.7 µl,, 0.050 mmol), TFEA (0.12 g, 0.75 mmol), MU (1.3 g, 7.5 mmol), **5** (0.13 g, 0.75 mmol) was irradiated by 60 W black lamp at 60 °C for 10 h. A small portion of the reaction mixture was taken and dissolved in

CDCl$_3$. The conversion was of monomer (TFEA: 100 %, MU: 9 %) was determined by ^{1}H NMR spectroscopy. Volatile materials were removed under vacuum and isolated by preparative/recycling GPC.   The isolated poly[TFEA-*co*-(MU)] was dissolved in trifluoromethylbenzene (1 ml) and to this solution was added tributyltin deuteride (34 µl, 0.13 mmol) and V-601 (2.5 mg, 0.011 mmol). The resulting solution was stirred at 80 °C for 2 h. Volatile materials were removed under reduced pressure and the crude polymer was purified by GPC to give the copolymer (0.21 g) with M_n = 4800 and PDI = 1.24. The MF$_{MU}$ (0.47) was determined by ^{1}H NMR spectroscopy. The polymer showed two broad singlet signals at 1.2 and 2.3 ppm in ^{2}H NMR spectra measured in CHCl$_3$ (Figure 3a).

Synthesis of end deuterided poly(TFEA-*co*-octene). A solution of **1** (15.5 µl,, 0.10 mmol), TFEA (0.23 g, 1.5 mmol), 1-octene (1.7 g, 15 mmol), **5** (0.25 g, 1.5 mmol) was irradiated by 60 W black lamp at 60 °C for 43 h. A small portion of the reaction mixture was taken and dissolved in CDCl$_3$. The conversion was of monomer (TFEA: 78 %, Oct: 6 %) was determined by ^{1}H NMR spectroscopy. The mixture was vaccumed in the grove box, the reaction mixture was dissolved in trifluorobenzene (1 ml), and to this solution was added tributyltin deuteride (68 µl, 0.25 mmol) and V-601 (2.3 mg, 0.011 mmol) and the resulting solution was stirred at 80 °C for 2 h. Volatile materials were removed under reduced pressure, and the crude polymer was purified by GPC to give the product (0.12 g) with M_n = 2800 and PDI = 1.21. The MF$_{oct}$ (0.45) was determined by ^{1}H NMR spectroscopy. The polymer showed broad singlet at 1.2 and 2.4 ppm in ^{2}H NMR spectra measured in CHCl$_3$ (Figure 3b).

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Chapter 5

Diastereoselective Addition Reaction of Allylsilane to α-Alkoxy Carbocations through Neighboring Group Participation.

Abstract

β-Vinyloxy ester or amide **6**, which possess a chiral center at α position, were synthesized and used as precursors for alkoxy carbocations, which are reactive intermediates in cationic polymerization of vinyl ethers. The cation reacted with allyltrimethylsilane to give the corresponding allylating products with up to 96% diastereoselectivity. Involvement of a cyclic cationic intermediate formed by the intramolecular neighboring participation of the ester and amide groups was suggested by control experiments. The formation of this intermediate would be the origin of observed high diastereoselectivity.

Introduction

Control of stereoregularity (tacticity) is one of the most important subjects in polymer synthesis, because stereochemistry of the polymer backbone influences their physical properties. Highly stereoregular polymerization has been already reported in living anionic polymerization of methacrylates initiated by *t*-BuMgBr and *t*-BuLi/alkylaluminum,[1] coordination polymerization of simple alkenes catalyzed by Zieglar-Natta or metallocene catalysts,[2,3] and radical polymerization by using methacrylates bearing bulky substituents or under constrained polymerization conditions.[4-9] In contrast, although cationic polymerization occupies important class of vinyl polymerization method, general procedures for the control of stereoregularity are lacking. For example, synthesis of highly isotactic poly(isobutyl vinyl ether) (PIBVE) with the meso dyad (m) = 92% was reported by employing bulky Lewis acid by Samamoto and coworkers (Scheme 1),[10] its generality has not well established. Therefore, a new strategy to control stereoregularity in cationic polymerization has been awaited.

Scheme 1. Synthesis of isotactic PIBVE by using bulky titanium Lewis acid.
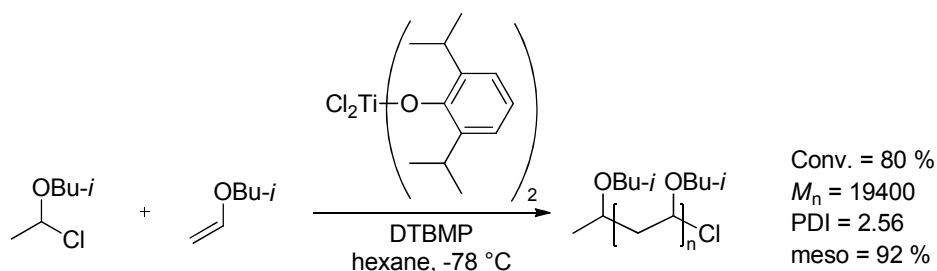
We are interested in utilizing the neighboring group participation to control the stereoregularity in cationic polymerization, because it has been widely used to control the stereochemistry involving carbocation species in organic synthesis, especially in glycosylation reaction.[11] For example, 2-acyl protecting groups in hexoses direct the incoming nucleophile, such

as an alcohol, to *trans* to the protecting group (Scheme 2). This is because the acyl group "participates" to the α-alkoxy carbocation to form a cyclic intermediate **1** by neighboring participation, to which a nucleophile (*Nu*) attacks in a S_N2 manner giving 1,2-*trans* adduct **2**. The "stereodirecting groups" are not limited to acyl groups, and our group recently found that phosphates also serve as excellent "stereodirectors" and applied to the stereoselective glycosylation reactions.[12]

Scheme 2. Diastereoselective glycosylation through neighboring group participation.
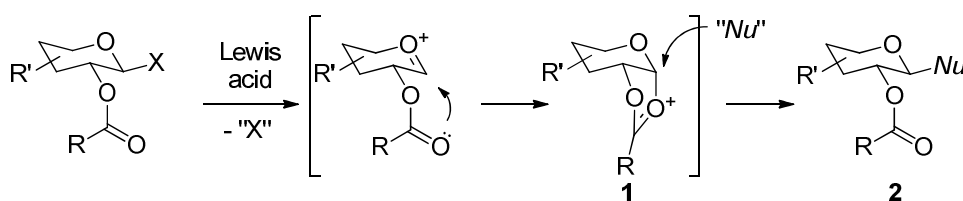
However, despite of the widespread use of the neighboring group participation in cyclic system, its use in acyclic system has been limited. Devine and coworkers have reported highly stereoselective addition of phenol derivatives (up to 99% diastereoselectivity [ds.]) when α-bromo ester bearing amide group **3** was used as a starting material (Scheme 3).[13] The reaction took place the elimination of bromine followed by the neighboring group participation of amide to the resulting cationic species to form cyclic intermediate **4**, in which methyl and R substituents occupy thermodynamically stable equatorial position. Addition of phenoxide occurred in a S_N2 manner from *anti* to the methyl group to avoid steric bulkiness, giving **5** with high yield and high steleoselectivities.

Scheme 3. Highly stereoselective synthesis of 2-aryloxy ester through neighboring group participation.
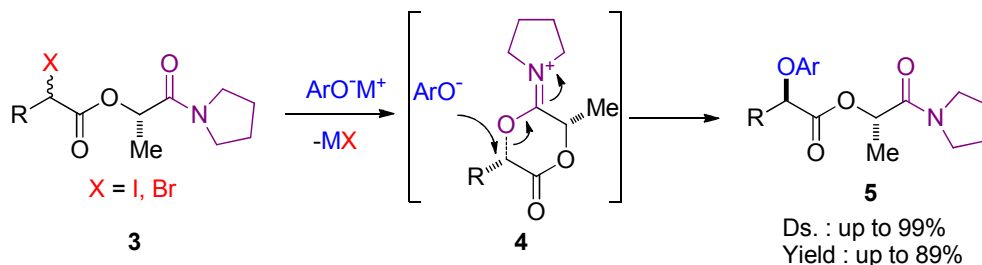
These results prompted us to design α-vinyloxy ester or amide monomer **6** for cationic polymerization. When electrophile attacks to **6**, intramolecular neighboring participation of the adjacent ester or amide group to generated α-alkoxy cation **7** would occur to give cyclic intermediate **8**. An alkene (monomer) would add to **8** from the less hindered side to **6** giving addition product **9** with control of the relative configuration of the newly formed chiral center. If second monomer adds to **9** in the same manner, relative configuration of polymer backbone would be controlled regardless of the stereochemistry of the penultimate unit.

Scheme 4. Working hypothesis for stereoregulated living cationic polymerization through neighboring group participation.
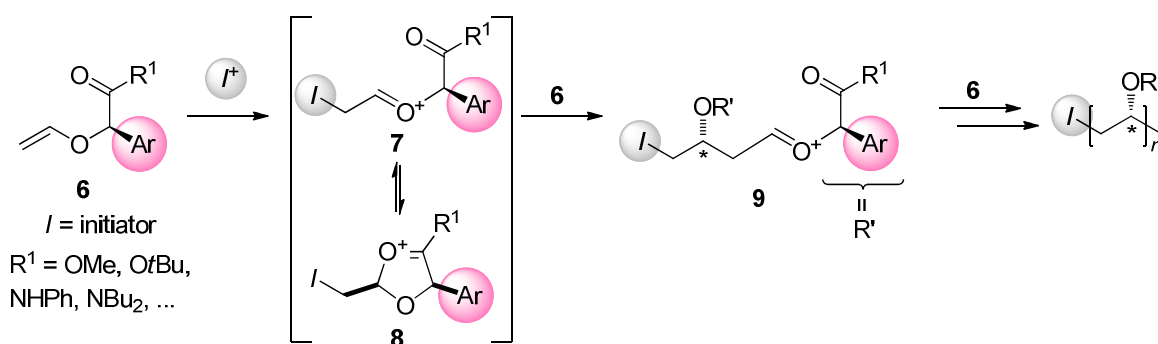
We synthesized vinyl ethers **6** and examined the proof of principle experiments by taking a single alkene addition to a cation generated from **6** and its analogues. Highly diastereoselective addition of allylsilane was observed by proper choice of the pendant ester group and an activator, a Lewis acid. Though stereochemical outcome could not be determined yet, involvement of the desired cyclic intermediate was suggested from several control experiments.

Results and discussions

Synthesis of vinyl ethers. Since enantiomerically pure monomer is needed for the stereoregulated polymerization reaction, we synthesized optically active vinyl ether **6a** starting from (*R*)-Mandelic acid. Thus, Ir catalyzed exchange reaction between (*R*)-Mandelic acid methyl ester and vinyl acetate in the presence of Na_2CO_3 under reflux in toluene to give **6a** in good yield.[14] 4-Methoxyphenyl-, 4-fluorophenyl, and 2,4,6-trimehylphenyl derivatives **6b~6d** were also prepared starting from the corresponding α-hydroxycarboxylic acid methyl esters **10b~10d**, respectively. Racemic starting materials were used because enantiomerically pure substrates are not required for the model reaction.

Scheme 5. Synthesis of vinyl ethers **6a-d**.

$$\text{Ir(cod)Cl]}_2 \text{ (0.02 eq)}$$
$$Na_2CO_3 \text{ (1.0 eq)}$$
toluene
reflux, 10-32 h

10   (3 equiv)

Ar = (R)-Ph (**a**)
4-OMeC$_6$H$_4$ (**b**)
4-FC$_6$H$_4$ (**c**)
2, 4, 5-(Me)$_3$C$_6$H$_2$ (**d**)

6a: 78%
6b: 69%
6c: 75%
6d: 72%
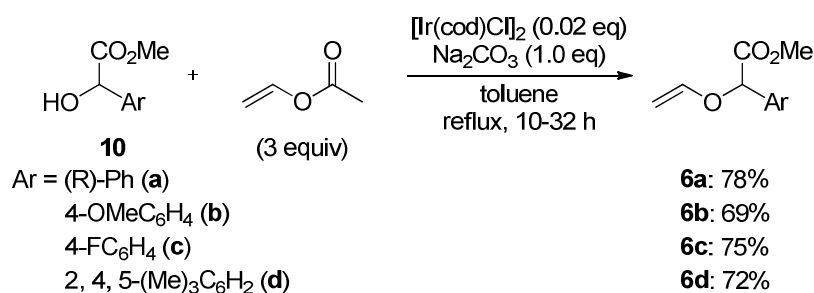
Methyl ester in **6a** was transformed to the corresponding *tert*-butyl ester **6e** and amides **6f** and **6g** by standard synthetic methods (Scheme 6).

Scheme 6. Synthesis of vinyl ethers **6e-g** with various substituents.
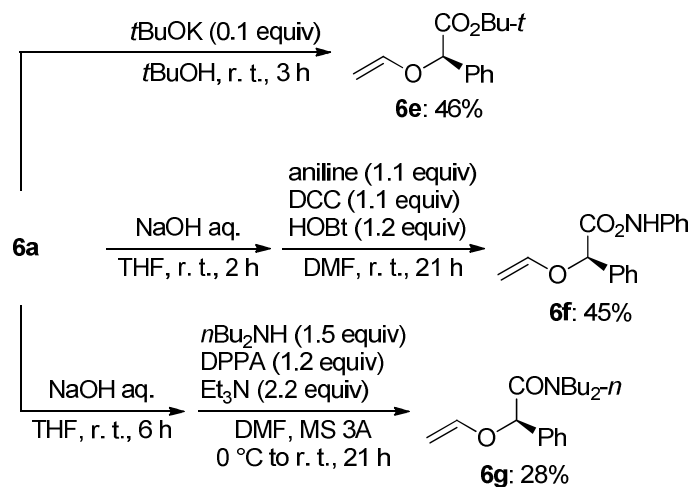
Diastereoselective addition of allylsilane to vinyl ethers. To generate α-alkoxy carbocation, e.g., **7** from the vinyl ether, it was converted to α-chloroether **11** which was further treated with a Lewis acid. Thus, treatment of **6a** with HCl (1.0 M in Et$_2$O, 2 equiv) at -24 °C for 10 min gave **11a** quantitatively. After excess amount of HCl and Et$_2$O was removed, allyltrimethylsilane (1.2 equiv) followed by Lewis acid (1.1 equiv) were added to the CH$_2$Cl$_2$ solution of **11a** at -78 °C. The yields and products analyzed by ^{1}H NMR were summarized in Table 1. When ZnCl$_2$, BF$_3$·OEt$_2$, or AgOTf were used as a Lewis acid, the yields of the desired allylated product **12** were moderate but considerably high diastereoselectivities were observed especially when AgOTf was employed (runs 1~3). We next examined the "preactivation method", in which **11** and AgOTf was treated at -78 °C before the addition of allyltrimethylsilane. The yield of **12** increased to 61% and, more importantly, the diastereoselectivity of **12** considerably increased to 94% (run 4). When the temperature raised to 0 °C after the addition of allyltrimethylsilane, the yields of **12** further increased to 79 and 83% though the diastereoseletivity was slightly decreased (88~91%, runs 6 and 7). The use of silver salt with different counter anion, such as NTf$_2$ and B(C$_6$F$_5$)$_3$ instead of OTf, or different solvent, such as toluene and propionitrile, did not increase either the yield of **12** or its diastereoselectivity (runs 7~10).

Table 1. Diastereoselective addition of allylsilane to vinyl ethers.[a]
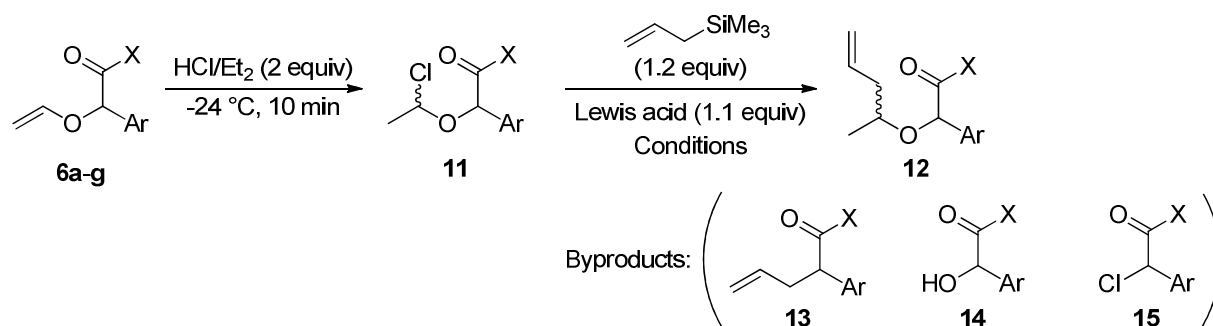

Run	Vinyl ether	Solvent	Lewis acid	Condition (°C/h)	Yield (%)[b]				Dr. of **12**[d]
					12	**13**[c]	**14**[c]	**15**[c]	
1	**6a**	CH$_2$Cl$_2$	ZnCl$_2$	-78/3	46	-	-	-	70:30
2	**6a**	CH$_2$Cl$_2$	BF$_3$·OEt$_2$	-78/2	30	-	-	-	77:23
3	**6a**	CH$_2$Cl$_2$	AgOTf	-78/1	50	-	-	-	82:18
4	**6a**	CH$_2$Cl$_2$	AgOTf	-78/1	61	-	-	-	94:6
5	**6a**	CH$_2$Cl$_2$	AgOTf	-78~0/1.5	79	-	-	-	87:13
6	**6a**	CH$_2$Cl$_2$	AgOTf	-78~0/6	83 (61)[c]	-	-	-	91:9
7	**6a**	CH$_2$Cl$_2$	AgNTf$_2$	-78/1	46	-	-	-	88:12
8	**6a**	CH$_2$Cl$_2$	AgB(C$_6$F$_5$)$_4$	-78/1	0	-	-	-	-
9	**6a**	toluene	AgOTf	-78~0/6	36	-	-	-	76:24
10	**6a**	EtCN	AgOTf	-78~0/6	68	-	-	-	89:11
11	**6b**	CH$_2$Cl$_2$	AgOTf	-78~0/6	0	41	1	15	-
12	**6c**	CH$_2$Cl$_2$	AgOTf	-78~0/6	32(29)[c]	0	30	0	81:19
13	**6d**	CH$_2$Cl$_2$	AgOTf	-78~0/6	78(60)[c]	0	9	<30	96:4
14	**6e**	CH$_2$Cl$_2$	BF$_3$·OEt$_2$	-78/3	0	-	-	-	-
15	**6f**	CH$_2$Cl$_2$	BF$_3$·OEt$_2$	-78/3	0	-	-	-	-
16	**6g**	CH$_2$Cl$_2$	AgOTf	-78~0/6	0	-	-	-	-

[a]Vinyl ether and 2 equivalents HCl (1.0 M in Et$_2$O) solution was reacted under nitrogen atmosphere at -24 °C for 10 min to obtain chloro adduct **11**. After excess amount of HCl and Et$_2$O was removed under vacuum at this temperature, CH$_2$Cl$_2$ was added in the **11**, and then the solution was cooled to -78 °C. Then, 1.1 equivalents Lewis acids and 1.2 equivalents of allyltrimethylsilane were added to the solution and reacted at -78 °C. [b]Determined by ^{1}H NMR using internal standard. [c]Isolated yield. [d]Diastereomeric ratio determined by ^{1}H NMR spectra.

We next examined the substituent effects on the aryl ring. When **6b** possessing electron donating methoxy group was used, no desired product **12b** formed. Instead, α-allylated ester **13b** formed as a major side product in moderate yield (run 11). The result may suggest the formation of desired cyclic intermediate **8b**, in which the benzylic position is activated by the neighboring group participation (Scheme 7). Direct addition of allylsilane to the benzilic position of **8b** or an elimination of acetaldehyde followed by addition of allylsilane to **16** resulted the formation of **13b**. **14b** may form by the addition of water to either **8b** or **16** during the work up.

Scheme 7. Possible mechanism for the formation of **13b** and **14b** from **11b**.
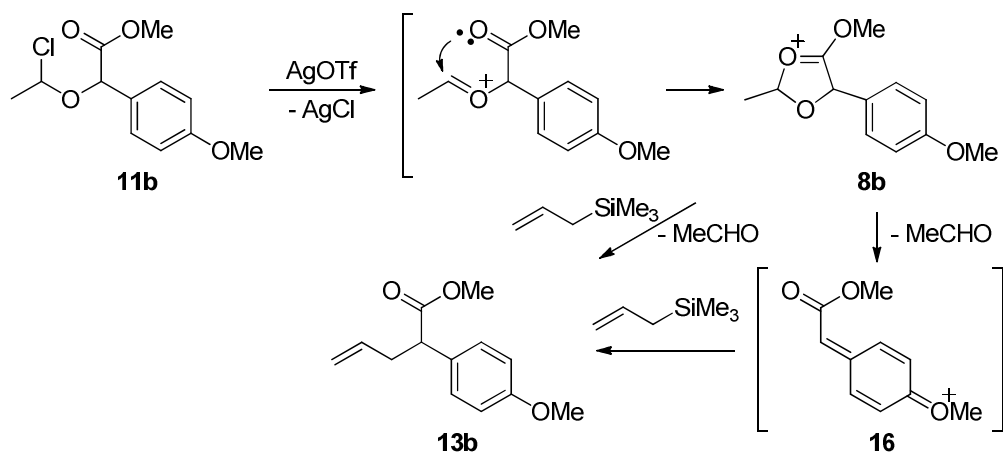
On the contrary, **6c** possessing electron withdrawing fluorine atom gave a mixture of **12c** and α-hydroxy ester **14c** (run 12). The diastereoselectivity of **12c** (81%) was much lower than the one starting from **6a** probably due to the less participation of the ester group to the cation due to the electron withdrawing fluorine atom. When **6d** having bulky trimethylphenyl group was used, **12d** was obtained with high diastereoselectivity (96:4). The reactions of vinyl ethers **6f** and **6g** which have amide instead of ester group were complex and gave no desired product but complex mixtures (Table 1, runs 15 and 16).

When vinyl ether **6e** which has *tert*-buthyl ester was used as a substrate, a mixture of α-chloroether **11e** and cyclic acetal **17** in 37 and 44% yields, respectively, by the treatment of HCl (Scheme 8). Furthremore, when the mixture of **11e** and **17** was subjected allylation reaction by employing BF$_3$·OEt$_2$ in the presence of allyltrimethylsilane, **11e** was completely transformed to **17** (Table 2, run 1). Cyclic acrtal **17** was also predominantly formed when ZnCl$_2$ and AgOTf were used as a Lewis acid (Table 2, runs 2 and 3). The formation of **17** can be explained by the occurrence of neighboring group participation; α-alkoxy cation **7e** is generated either protonation of **6e** or elimination of chlorine atom from **11e**, and subsequent intramolecular participation of ester group to form cyclic intermediate **8e**. Nucleophilic attack of chloride anion to the *tert*-butyl group of **8e** gives **17**. These results strongly suggest the importance of cyclic intermediate, e.g., **8** for the diastereoselective allylation when **6** was employed.

Scheme 8. Possible mechanism for the formation of cyclic acetal **17** from **6e** and **11e**.
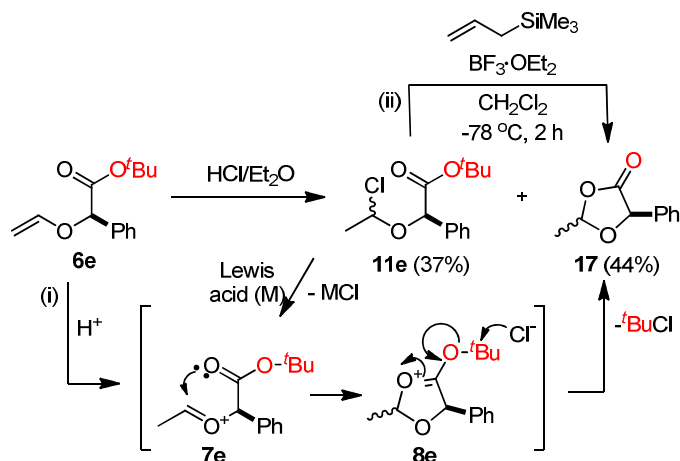
Table 2. Formation of cyclic acetal **17** form **6e (11e)**.[a]

run	Lewis acid	Yield (%)[b]
1	$BF_3 \cdot OEt_2$	99
2	$ZnCl_2$[c]	87
3	AgOTf	61

[a]Allyltrimethylsilane (1.2 equiv) and Lewis acid (1.1 equiv) were added to the reaction mixture of **11e** and **17**, and the resulting solution was stirred for 2 h at -78 °C. [b]Determined by ^{1}H NMR. [c]The reaction was carried out in 1.0 M Et_2O solution.

Conclusions

Highly diastereoselective allylation occurred to α-alkoxy cation generated from α-alkoxychloride **11** prepared from vinyl ether **6**. Involvement of a cyclic intermediate, e.g., **8** was suggested by the formation of α-allylester **12** and cyclic acetal **17**, and formation of the cyclic intermediate must be the origin of the observed high diastereoselectivity. The results would open new possibilities to design monomers for stereoregular cationic polymerization.

Experimental Section

General. All reaction conditions dealing with air- and moisture sensitive compounds were carried out in a dry reaction vessel under nitrogen or argon atmosphere. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured for a $CDCl_3$ solution of a sample. ^{1}H NMR spectra are reported in parts per million (δ) from internal tetramethylsilane (0 ppm), ^{13}C NMR from $CDCl_3$ (77.2 ppm). IR spectra are reported in cm^{-1}. Preparative HPLC was performed with GPC equipped with polystyrene cross-linked gel (JAIGEL 1H and 2H columns) with $CHCl_3$ as an eluant.

Materials. Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. CH_2Cl_2, EtCN and DMF were distilled successively from P_2O_5 and

K_2CO_3 and stored over molecular sieves 4A. Toluene and triethylamine were distilled from CaH_2 and stored over molecular sieves 4A. Methanol and *tert*-butyl alcohol were distilled from Mg which was activated by I_2 and stored over molecular sieves 3A. 2-Hydroxy-2-(4-methoxyphenyl)acetic acid, 2-hydroxy-2-mesitylacetic acid[15] and 2-(4-fluorophenyl)-2-hydroxyacetic acid[16] were synthesized as reported.

Typical procedure for esterification of carboxylic acid 18. *p*-Toluenesulfonic acid (0.12 g, 0.01 equiv) was added to a solution of (*R*)-mandelic acid (9.1 g, 60 mmol) in methanol (243 ml, 100 equiv), and the mixture was refluxed at 70 °C with stirring for 3 h under a nitrogen atmosphere. After removal of methanol, aqueous $NaHCO_3$ solution and ethyl acetate were introduced. Water phase was separated and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with a saturated aqueous NaCl solution, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude oil. The resulting crude oil was purified by flash column chromatography (elution with 20 % ethyl acetate in hexane) affording (*R*)-mandelic acid methyl ester (**10a**)[17] in quantitative yield (7.8 g, 46.9 mmol) as a white solid.

Same transformation starting from **18b**, **18c**, and **18d** afforded the corresponding methyl esters **10b**,[18] **10c**,[19] and **10d**[20] in 96%, 89%, and 100% yields, respectively.

$$p\text{-TsOH (0.1-0.3 eq)}$$
$$\text{or}$$
$$H_2SO_4 \text{ (0.2 equiv)}$$

CO$_2$H		CO$_2$Me
HO⤙Ar	MeOH, reflux, 3 h	HO⤙Ar
18		
Ar = (*R*)-Ph (**a**)		**10a** : 100%
4-OMeC$_6$H$_4$ (**b**)		**10b** : 96%
4-FC$_6$H$_4$ (**c**)		**10c** : 89%
2, 4, 5-(Me)$_3$C$_6$H$_2$ (**d**)		**10d** : 100%
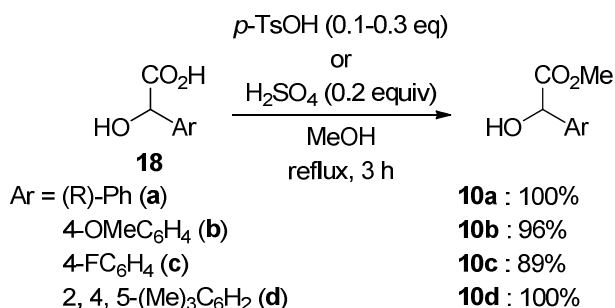
Typical procedures for the synthesis of vinyl ether 6.[14] Alcohol **10a** (9.5 g, 58 mmol) and vinyl acetate (16 g, 184 mmol) were added to a toluene solution (30 mL) of [Ir(cod)Cl]$_2$ (0.57 g, 0.85 mmol) and Na_2CO_3 (5.7 g, 54 mmol) under a nitrogen atmosphere. The reaction mixture was

stirred at 100 °C for 10 h. After the reaction mixture was quenched by the addition of Et$_2$O, the product was isolated by flash column chromatography (elution with 7 % ethyl acetate in hexane) followed by vacuum distillation (90 °C, 2.1 mmHg) to give vinyl ether **6a** in 78% yield.
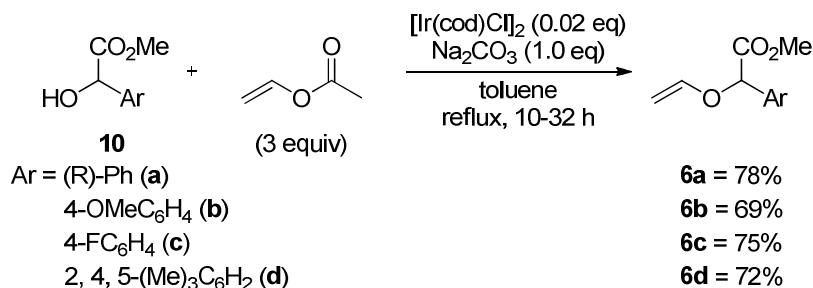
(*R*)-methyl-2-phenyl-2-(vinyloxy)acetate (6a). 78% yield; d = 1.07 g/ml; bp. = 90 °C/2.1 mmHg ; Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) 3.74 (s, 3 H), 4.17 (dd, *J* = 2.4 Hz, 6.8 Hz, 1 H), 4.31 (dd, *J* = 2.4 Hz, 14.4 Hz, 1 H), 5.32 (s, 1 H), 6.50 (dd, *J* = 6.8 Hz, 14.4 Hz, 1 H), 7.36-7.41 (m, 3 H), 7.49 (d, *J* = 2.0, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) 52.80, 78.57, 89.77, 127.21, 128.95, 129.20, 135.20, 149.89, 170.35. HRMS (EI) *m/z*: Calcd for C$_{11}$H$_{12}$O$_3$ (M+), 192.0786; Found 192.0788.

Methyl 2-(4-methoxyphenyl)-2-(vinyloxy)acetate (6b). 69% yield; d = 1.15 g/ml; bp. = 104 °C/2.2 mmHg; Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) 3.74 (s, 3 H), 3.81 (s, 3 H), 4.15 (d, *J* = 2.8 Hz, 6.8 Hz, 1 H), 4.29 (d, *J* = 2.8 Hz, 14.0 Hz,1 H), 5.26 (s, 1 H), 6.48 (dd, *J* = 6.8 Hz, 14.0 Hz, 1 H), 6.91 (d, *J* = 8.0, 2 H), 7.39 (d, *J* = 8.4, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) 52.64, 55.44, 78.25, 89.63, 114.30, 127.27, 128.64, 149.88, 160.26, 170.48; . HRMS (EI) *m/z*: Calcd for C$_{12}$H$_{14}$O$_4$ (M+), 222.0892; Found 222.0885.

Methyl 2-(4-fluorophenyl)-2-(vinyloxy)acetate (6c). 75% yield; d = 1.23 g/ml; bp. = 40 °C/0.6 mmHg; Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) 3.74 (s, 3 H), 4.18 (dd, *J* = 1.2 Hz, 6.8 Hz, 1 H), 4.29 (d, *J* = 14.4 Hz, 1 H), 5.30 (s, 1 H), 6.48 (dd, *J* = 6.8 Hz, 14.4 Hz, 1 H), 7.07 (t, *J* =

8.4 Hz, 2 H), 7.46 (t, *J* = 7.2 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) 52.81, 77.94, 89.96, 115.95, 129.06, 149.79, 161.99, 164.46, 170.15; HRMS (EI) *m/z*: Calcd for C$_{11}$H$_{11}$FO$_3$ (M+), 210.0692; Found 210.0694.

Methyl 2-mesityl-2-(vinyloxy)acetate (6d). 72% yield; d = 1.11 g/ml; bp. = 84 °C/2.2 mmHg; Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) 2.26 (s, 3 H), 2.39 (s, 6 H), 3.73 (s, 3 H), 4.09 (d, *J* = 6.0 Hz, 1 H), 4.33 (d, 14.4 Hz, 1 H), 5.69 (s, 1 H), 6.37 (dd, *J* = 6.8 Hz, 14.0 Hz, 1 H), 6.86 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) 20.40, 21.08, 52.65, 75.41, 89.94, 129.45, 130.10, 137.55, 138.61, 149.76, 170.61; HRMS (EI) *m/z*: Calcd for C$_{14}$H$_{18}$O$_3$ (M+), 234.1256; Found 234.1266.

Synthesis of (R)-*tert*-butyl 2-phenyl-2-(vinyloxy)acetate (6e). *t*BuOH solution (100 mL) of pottasium *tert*-butoxide (0.28 g, 2.5 mmol) and **6a** (1.0 g, 5.2 mmol) was stirred at room temperature for 3 h. The reaction mixture was evaporated to give a crude colorless oil. Purification by flash column chromatography (elution with 3 % ethyl acetate in hexane) afforded **6e** in 46 % yield (0.59 g, 2.5 mmol). d = 1.29 g/ml. ^{1}H NMR (400 MHz, CDCl$_3$) 1.41 (s, 9 H), 4.15 (dd, *J* = 2.4 Hz, 6.8 Hz, 1 H), 4.29 (dd, *J* = 2.4 Hz, 14.4 Hz, 1 H), 5.17 (s, 1 H), 6.51 (dd, *J* = 6.8 Hz, 14.4 Hz, 1 H), 7.34-7.40 (m, 3 H), 7.47 (d, *J* = 6.4 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) 28.01, 78.96, 82.53, 89.25, 127.14, 128.26, 128.86, 135.72, 150.08, 168.89; HRMS (EI) *m/z*: Calcd for C$_{14}$H$_{18}$O$_3$ (M$^+$), 234.1256; Found 234.1254.

Synrhesis of (R)-*N*-phenyl-*O*-[2-phenyl-2-(vinyloxy)acetyl] hydroxylamide (6f). 6a (1.0 g, 5.2 mmol) was slowly added to a THF solution (17 mL) of 10 % aqueous NaOH (0.20 g, 0.20 mmol in 1.8 ml H$_2$O) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 h to give the corresponding carboxylic acid as yellow solid in 81% yield (4.2 mmol). (The product was dissolved in DMF solution (150 ml), and aniline (0.42 g, 4.6 mmol) was added. The resulting mixture was cooled to 0 °C.) After addition of DMF (150 mL) and aniline (0.42 g, 4.6 mmol) to the crude carboxylic acid, *N*,*N*'-dicyclohexylcarbodiimide (DCC; 1.0 g, 4.6 mmol) and

1-hydroxybenzotriazole (HOBt; 0.71 g, 5.0 mmol) was added at 0 °C , and the resulting mixture was stirred at room temperature for 21 h. Ethyl acetate was added, and the resulting solution was cooled to -30 °C. The precipitates formed was removed, and residual organic phase was washed with 3 times with satuated aqueous $NaHCO_3$ and NaCl solutions, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a crude white solid. Purification by flash column chromatography (elution with 17 % ethyl acetate in hexane) followed by recrystallization from a mixture of CH_2Cl_2 and hexane afforded **6f** in 45 % yield (2 step; 0.59 g, 2.3 mmol) as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) 4.27 (dd, $J = 2.4$ Hz, 6.8 Hz, 1 H), 4.50 (dd, $J = 2.4$ Hz, 14.4 Hz, 1 H), 5.31 (s, 1 H), 6.48 (dd, $J = 6.8$ Hz, 14.4 Hz, 1 H), 7.13 (t, $J = 7.6$ Hz, 1H), 7.31-7.42 (m, 5 H), 7.50 (d, $J = 7.6$ Hz, 2 H), 7.57 (d, $J = 8.4$ Hz, 2 H), 8.27 (br, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$) 80.97, 92.17, 120.01, 124.90, 126.78, 128.92, 128.97, 129.22, 136.01, 137.20, 149.11, 167.51; HRMS (EI) *m/z*: Calcd for $C_{16}H_{15}NO_2$ (M+H), 254.1181; Found 254.1187.

Synthesis of (R)-*N, N*-dibutyl-2-phenyl-2-(vinyloxy)acetamide (6g). THF solution (5 mL) of aqueous NaOH (0.59 g, 14 mmol in 6.0 ml H_2O) and **6a** (0.99 g, 5.0 mmol) was stirred at room temperature for 6 h. The reaction mixture was evaporated to give a crude solid.(DMF (150 ml) was added to the product,) The crude carboxylic acid was dissolved in the DMF solution, and dibutylamine (1.0g, 7.7 mmol), diphenyl phosphorazidate (DPPA; 1.7 g, 6.1 mmol), and triethylamine (1.1 g, 11 mmol) were added at 0 °C. After the mixture was stirred at room temperature for 21 h, water and CH_2Cl_2 was added, the organic phase was washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a crude white solid. Purification by flash column chromatography (elution with 15 % ethyl acetate in hexane) followed by preparative GPC afforded **6g** in 28 % yield (2 step; 0.20 g, 0.69 mmol) as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) 0.82-0.93 (m, 6 H), 1.12-1.53 (m, 8 H), 3.09-3.41 ppm (m, 4 H), 4.16 (dd, $J = 1.6$ Hz, 6.8 Hz, 1 H), 4.40 (d, $J = 14.4$ Hz, 1 H), 5.53 (s, 1H), 6.51 (dd, $J = 6.8$ Hz, 14.4 Hz, 1 H),

7.30-7.45 (m, 5 H); ^{13}C NMR (100 MHz, CDCl$_3$) 13.96 and 14.04, 20.19 and 20.35, 29.43 and 30.67, 45.93 and 46.86, 80.03, 89.70, 126.94, 128.67, 128.89, 135.94, 150.42, 168.40; HRMS (EI) *m/z*: Calcd for C$_{18}$H$_{27}$NO$_2$ (M+), 289.2042; Found 289.2038.

Typical procedure for diastereoselective addition of allylsilane to vinyl ethers (Table 1, run 4). A solution of HCl in Et$_2$O (1.0 M, 0.40 ml) was slowly added to **6a** (38 mg, 0.20 mmol) at -24 °C, and the mixture was stirred for 10 min at this temperature to give **11a**, a quantitative formation of which was ascertained by ^{1}H NMR analysis by a separated experiment. After excess amount of HCl and Et$_2$O was removed, CH$_2$Cl$_2$ (1.0 ml) was introduced. The solution was cooled to -78 °C, this solution was added through cannula to AgOTf (59 mg, 0.23 mmol) suspension (CH$_2$Cl$_2$; 1.0 ml), and the mixture was stirred for 10 min at this temperature. Allyltrimethylsilane (27 mg, 0.24 mmol) was added, and the resulting solution was stirred at this temperature for 1 h. The reaction was quenched by addition of Et$_3$N (0.3 ml) followed by saturated aqueous NaHCO$_3$ solution. The organic phase was separated, and the aqueous phase was extracted with ethyl acetate. The combined organic extracts were washed with saturated aqueous NaCl solution, dried over MgSO$_4$, filtered, and concentrated under reduced pressure to give a crude oil containing **12a**. The yield (61%) and diastereoselectivity (96:4) were determined by ^{1}H NMR. Characterization of **12a** was done after purification by flash column chromatography (elution with 5 % ethyl acetate and 5 % CH$_2$Cl$_2$ in hexane)

11a: ^{1}H NMR (400 MHz, CDCl$_3$) 1.80 and 1.89 (d, *J* = 5.2 and 5.2 Hz, 3 H), 3.71 and 3.74 (s, 3 H), 5.33 (s, 1 H), 5.45 and 5.85 (q, 1 H), 7.26-7.44 (m, 5 H).

12a. Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) (major diastereomer) 1.24 (d, *J* = 6.0 Hz, 3 H), 2.21-2.42 (m, 2 H), 3.54-3.58 (m, 1 H), 3.71 (s, 3 H), 5.02 (d, *J* = 3.2 Hz, 2 H), 5.06 (s, 1 H), 5.72-5.79 (m, 1 H), 7.24-7.46 (m, 5 H).

12c. Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) (main diastereomer) 1.24 (d, J = 6.0 Hz, 3 H), 2.20-2.40 (m, 2 H), 3.52-3.56 (m, 1 H), 3.71 (s, 3 H), 5.01 (br, 2 H), 5.06 (s, 1 H), 5.71-5.78 (m, 1 H), 7.04 (m, 2 H), 7.42 (m, 2 H).

12d. Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) (main diastereomer) 1.25 (d, J = 6.0 Hz, 3 H), 2.14-2.34 (m, 2 H), 2.26 (s, 3 H), 2.38 (s, 3 H), 3.49-3.54 (m, 1 H), 3.68 (s, 3 H), 4.98 (br, 2 H), 5.01 (s, 1 H), 5.61-5.71 (m, 1 H), 6.84 (s, 2 H) ; ^{13}C NMR (100 MHz, CDCl$_3$) 19.56, 20.38, 21.08, 41.21, 52.29, 73.88, 74.14, 111.13, 129.88, 131.22, 134.95, 137.57, 137.88, 172.57.

13b. Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) 2.45-2.83 (m, 2 H), 3.59 (t, J = 7.6 Hz, 1 H), 3.65 (s, 3 H), 3.79 (s, 3 H), 5.00 (d, J = 10.0 Hz, 1 H), 5.07 (d, J = 17.2 Hz, 1 H), 5.68-5.74 (m, 1 H), 6.86 (d, J = 8.8 Hz, 2 H), 7.23 (d, J = 8.4 Hz, 2 H).

15b. Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) 3.77 (s, 3 H), 3.81 (s, 3 H), 5.34 (s, 1 H), 6.90 (d, J = 8.8 Hz, 2 H), 7.42 (d, J = 8.4 Hz, 1 H).

15d. Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) 2.27 (s, 3 H), 2.38 (s, 3 H), 5.42 (s, J = 8.4 Hz, 1 H), 6.88 (s, 2 H).

17. Colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) (diastereomer) 1.65 or 1.70 (d, J = 5.2 or 4.8 Hz, 3 H), 5.25 or 5.43 (s, 1 H), 5.84 or 5.92 (qd, J = 1.2, 5.2 or 0.8, 5.2 Hz, 1 H), 7.40-7.47 (m, 5 H); ^{13}C NMR (100 MHz, CDCl$_3$) 20.71 and 21.75, 75.56, 102.09 and 102.99, 126.04, 127.03, 128.96, 129.13, 129.15, 171.69 and 171.87.

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Concluding Remarks

This thesis entitled in "**Organoheteroatom-Mediated Living Vinyl Polymerization under Acidic Condition**" described new and powerful methods for the precise control of macromolecular structures in terms of molecular weights, molecular weight distributions, and monomer sequence based on organoheteroatom-mediated living cationic and radical (co)polymerization under acidic conditions. By developing new conditions for living cationic and radical (co)polymerization involving organoheteroatom chain transfer agents and dormant species, this author succeeded in synthesizing several new alternating, random, and block copolymers with controlled molecular weights and molecular weight distributions. Furthermore, preliminary investigations to control stereoregularity in cationic polymerization by using neighboring group participation of heteroatom groups were attempted.

Chapter 1 describes the development of new Lewis acidic activator of organotellurium compounds. Phenyltellanyl triflate was prepared and characterized for the first time, and it was used for the activation of various organotellurium compounds generating corresponding carbocations. The Friedel–Crafts reaction took place in good to excellent yields when the activation was carried out in the presence of aromatic compounds. Application to polymer-end organotellurium compounds affording the end-functionalized polymers was also demonstrated.

Chapter 2 describes the use of organotellurium compounds for chain transfer agents for both living cationic and living radical polymerizations. Polymerization of vinyl ethers in the presence of organotellurium initiator and Lewis acid, such as $In(OTf)_3$ and $BF_3 \cdot OEt_2$, proceeded in a living manner and afforded well controlled poly(vinyl ether)s. Hybrid block copolymers were successfully synthesized starting from poly(meth)acrylates prepared by TERP followed by living cationic polymerization.

Chapter 3 describes random and alternating copolymerizations of (meth)acrylates and vinyl ethers under TERP, SBRP, and BIRP conditions. Structurally well-controlled random and alternating copolymers with controlled molecular weights and PDIs were synthesized. Syntheses of new block copolymers were also demonstrated by combining the living copolymerization and living radical or living cationic polymerizations.

Chapter 4 describes controlled copolymerizations of (meth)acrylates with α-olefines under TERP condition. Structurally well-controlled random and nearly alternating copolymers with controlled molecular weights and low PDIs were synthesized. Addition of Brønsted acids, such as $1,3\text{-}C_6H_4[C(CF_3)_2OH]_2$ and $(CF_3)_2CHOH$, increased the insertion rate of alkylethylenes in the copolymer while keeping low PDIs. The copolymers were successfully used as macro initiators for block copolymer synthesis.

Chapter 5 describes model reactions for the control of stereoregularity in cationic polymerization by using intramolecular neighboring group participation. α-Aryl-β-vinyloxyesters and amides were synthesized, and they were used as a precursor of α'-alkoxy carbocation which is the polymer end reactive species in cationic polymerization of vinyl ethers. The reaction of the cation with allyltrimethylsilane, which is a model monomer of vinyl ether, gave allylated product with up to 96% diastereoselectivity.

These results not only considerably expand the availability of structurally well controlled macromolecules with rich functionality and the ability of macromolecular engineering for the design and production of functional polymeric materials in materials science. The results also shed new lights on the basic chemistry involving carbocations and carbon-centered radicals. This author believe that, with further progress of these works, these methods developed by this author will become powerful methods for creating new polymer materials in both academic and industrial areas.

List of Publications

1. "Phenyltellanyl Triflate (PhTeOTf) as a Powerful Tellurophilic Activator in the Friedel-Crafts Reaction"
   Yamada, T.; Mishima, E.; Ueki, K.; Yamago, S. *Chem. Lett.* **2008**, *37*, 650-651.
   Chapter 1

2. "Precision Synthesis of Hybrid Block Copolymers by Organotellurium-Mediated Successive Living Radical and Cationic Polymerizations"
   Mishima, E.; Yamada, T.; Watanabe, H.; Yamago, S. *Chem. Asian J.* **2011**, *6*, 445-451.
   Chapter 2

3. "Controlled Alternating Copolymerization of (Meth)acrylates and Vinyl Ethers by Using Organoheteroatom-Mediated Living Radical Polymerization"
   Mishima, E.; Yamago, S. *Macromol. Rapid Commun.* **2011**, *32*, 893-898.
   Chapter 3

4. "Highly Controlled Random and Alternating Copolymerization of (Meth)acrylates, Acrylonitrile, and (Meth)acrylamides with Vinyl Ethers by Organotellurium, Organostibine, and Organobismuthine Mediated Living Radical Polymerization Reactions"
   Mishima, E.; Yamago, S. *J. Polym. Sci. Part A: Polym. Chem.* in press.
   Chapter 3

5. "Controlled Copolymerization of Acrylate and 6-Methyleneundecane by Organotellurium-Mediated Living Radical Polymerization (TERP)"
   Mishima, E.; Tamura, T.; Yamago, S. submitted to *Macromolecules*.
   Chapter 4

6. "Diasteroselective Addition of Allylsilane to α-Chloroethers through Neighboring Group Participation"
   Mishima, E.; Fujita, T.; Yamago, S. manuscript in preparation.
   Chapter 5

Other Associated Publication

1. "Solvolysis of Methoxy-substituted Diaryliodonium Tetrafluoroborates: Attempted Generation of a Stabilized Aryl Cation"
    Fujita, M.; Mishima, E.; Okuyama, T. *J. Phys. Org. Chem.* **2007**, *20*, 241-244.

2. "Kinetics of Living Anionic Polymerization of Polystyrenyl Lithium in Cyclohexane"
    Mishima, E.; Matsumiya, Y.; Yamago, S.; Watanabe, H. *Polym. J.* **2008**, *40*, 749-762.