Precision Polymer Synthesis by Degenerative Transfer Controlled/Living Radical Polymerization Using Organotellurium, Organostibine, and Organobismuthine Chain-Transfer Agents

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Received March 31, 2009

Contents

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1. Introduction

Structurally well-defined macromolecules are ubiquitous in nature, with enzymes as prime examples. They are admired not only for the beauty of their structures but also for their ability to catalyze a variety of chemical transformations under mild conditions. For example, nitrogenase catalyzes nitrogen fixation under physiological conditions,[1,2] whereas the same reaction in a chemical reactor by the Haber-Bosch process requires ultrahigh pressures and temperatures. The key to the functions of enzymes is the monodispersity and completely controlled amino acid (monomer) sequences of the polymer chain in the biomacromolecule, leading to highly ordered three-dimensional structures. This control combined with the existence of polar functional groups on the amino acid residues precisely located near the active center orchestrates the activity of enzymes.

By extrapolating from the structural and functional features of enzymes, one should be able to create new polymers with new properties and/or functions based on precise control of macromolecular structures, namely, molecular weight, molecular weight distribution (MWD), monomer sequence, topology, functional groups, and stereochemistry (tacticity). Controlling all of these factors is a formidable challenge, but significant advances have been made toward this goal since the advent of controlled/living radical polymerization (LRP). Living anionic,[3,4] cationic,[5] and coordination polymerization[6−8] have already been used to control molecular weights and MWDs of the resulting polymers and monomer sequences through block copolymer synthesis. However, these

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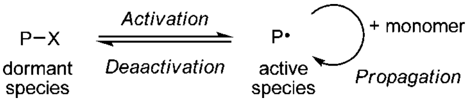
10.1021/cr9001269 CCC: $71.50

Scheme 1. General Mechanism of LRP; P Denotes Polymer End Species



methods usually require stringent reaction conditions to avoid the occurrence of undesirable side-reactions involving protic solvents, oxygen, and/or polar functional groups. On the contrary, radical polymerization can take place in the presence of various polar functional groups, because radicals are neutral, "soft", and highly reactive species. Furthermore, the high reactivity of radical species usually ensures that polymerization occurs under mild thermal conditions. Therefore, the living version of radical polymerization is now meeting the challenge for creating well-controlled but highly complex macromolecules with the hope that they will lay the essential foundation for new polymeric materials with improved and/or new properties and functions.

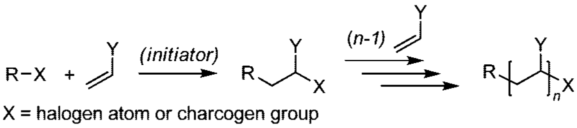
Conventional radical polymerization proceeds through four elemental steps: initiation, propagation, termination, and chain-transfer reactions. Once the initiating radical is formed by various stimuli, e.g., thermolysis, photolysis, and redox processes, successive addition of the radical to vinyl monomers occurs to grow the polymer chains (propagation). The resulting polymer end radical undergoes termination reactions by recombination or disproportionation reactions to give dead polymers. The propagating radical also undergoes a chain-transfer reaction to generate a new propagating radical and a dead polymer. Since radical generation occurs irreversibly and the termination usually occurs at near diffusion-controlled rates, the generated radicals are quickly and irreversibly deactivated to dead polymers.

The difference between LRP and conventional radical polymerization is that the radical end does not deactivate during the polymerization period. Although the living end in LRP is a carbon-centered radical in a strict sense, the radicals in solution usually homocouple or disproportionate at near diffusion-controlled rates, giving dead polymers as in conventional radical polymerization. Therefore, all of the LRPs so far reported rely on the reversible generation of carbon-centered radicals from a so-called dormant species, which possesses appropriate functional groups at the polymer end for radical generation (Scheme 1).[9−11] This "pseudo" deactivation of the polymer end radicals to the dormant species decreases the concentration of radical species in solution and minimizes undesirable side reactions, leading to dead polymers. Furthermore, the rapid deactivation makes it possible to elongate all of the polymer chains with similar chain lengths. In theory, the faster deactivation leads to higher control of MWD,[11] whereas sufficiently high activation is required for the polymerization to progress. This concept was initially proposed by Otsu in 1982 as the "iniferter" (initiator−transfer agent−terminator).[12,13] However, more than a decade passed before this concept was realized.

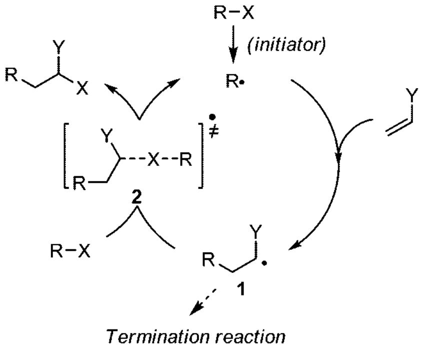
LRPs that have been widely used include nitroxide-mediated radical polymerization (NMP),[14] atom-transfer radical polymerization (ATRP),[15−18] and reversible addition−fragmentation chain-transfer radical polymerization (RAFT).[19−21] Organotellurium-,[22−29] organostibine-,[30−33] and organobismuthine-mediated[29,34] LRP (TERP, SBRP, and BIRP, respectively)[35,36] are relatively new methods developed by the author's research group. New variants of LRP have also emerged, such as cobalt-mediated polymerization,[37−49] single-electron transfer LRP,[50−53] titanium-catalyzed polymerization,[54] and reversible chain-transfer-catalyzed polymerization.[55,56] Each method utilizes unique chemical structures and activation/deactivation mechanisms of the dormant species, and these differences make each LRP method unique both mechanistically and synthetically.

Scheme 2. (a) Chemical Equation and (B) Mechanism for Atom- and Group-Transfer Radical Addition Reaction to Alkenes

(a) Mono and multi addition reactions



(b) Radical chain mechanism of the addition reaction



This review surveys the mechanistic and synthetic aspects of TERP, SBRP, and BIRP. Organoiodine-mediated living radical polymerization (IRP) is mechanistically similar to TERP, SBRP, and BIRP; however, IRP was extensively reviewed recently.[57] Therefore, this review mainly deals with TERP, SBRP, and BIRP. Recent developments in LRP under different methods are also reviewed in this special issue.

2. Background

2.1. Atom and Group-Transfer Radical Addition Reactions of Organoheteroatom Compounds to Alkenes and Alkynes

Radical-mediated atom-transfer addition reactions of haloalkanes to alkenes in the presence of a radical initiator were first reported by Kharasch in 1945,[58] and the results of early investigations of this type of reaction were summarized in a book chapter in 1963 (Scheme 2a).[59] Radical-mediated reductive C−C bond-formation reactions of these heteroatom compounds to alkenes in the presence of a reducing agent, such as the tin hydride-mediated method, have also been developed and widely used in organic synthesis.[60−62] Atom and group-transfer addition reactions have a synthetic advantage over the reductive methods because the heteroatom functionality present in the product can be used for further synthetic transformations. However, atom-transfer reactions were forgotten by synthetic chemists until the rediscovery of the iodine group-transfer radical reaction in 1986 by Curran.[61,63,64] Phenylselenyl group-transfer and phenyltellanyl group-transfer radical addition reactions of organoselenides and organotellurides, respectively, were subsequently reported by Byers,[65] Curran,[66] Kambe and Sonoda,[67,68] Crich,[69,70] Engmann,[71,72] and Schiesser.[73,74]

The reaction proceeds by a radical chain reaction, and carbon-centered radical R generated from an organoheteroatom compound, R−X, reacts with an alkene or alkyne to generate a new carbon-centered radical (**1**), which reacts with R−X to regenerate radical R through transition state **2** (Scheme 2b). The rate-control step is the heteroatom-transfer step, in which radical **1** undergoes homolytic substitution at the heteroatom X. If this step is slow, radical **1** undergoes a chain-breaking termination reaction. Therefore, this step should be sufficiently fast to achieve high synthetic yields.

The rate constant of the homolytic substitution reaction has been studied by kinetic experiments, and the rate constants for the halogen-atom or chalcogen-group-transfer reactions become 10 and 100 times faster going from third row (Cl, SPh) to fourth row elements (Br, SePh) and further going to fifth row elements (I, TePh).[75,76] Therefore, it is not surprising that heavier heteroatom compounds are generally used for this type of reaction. On the contrary, the rate constants of the halogen atoms and chalcogen groups in the same row are reported to be similar, though Kambe and Sonoda have reported that the phenyltellanyl group has a higher reactivity than an iodine atom does.[67] The synthetic advantages of organotellurium compounds over organoiodine compounds as well as organoseleniums were unknown when we started our program using organotellurium compounds as precursors for carbon-centered radicals.[77]

2.2. Brief History of Organoheteroatom-Mediated LRP

Repetition of atom- or group-transfer addition reactions to alkenes leads to the formation of living polymers possessing heteroatom functionality X at the ω-polymer end (Scheme 2a). Tatemoto was the first to observe the effects of organoiodine compounds in controlling the molecular weight and MWD in radical polymerization.[78] Tatemoto observed that the MWD during the copolymerization of 1,1-difluoroethene and perfluoropropene was significantly controlled by the addition of organoiodine compounds, e.g., $(CF_3)_2CFI$, and obtained copolymers with low MWDs ($M_w/M_n = 1.1-1.6$, where M_w and M_n correspond to weight-averaged molecular weight and number-averaged molecular weight, respectively). The living nature of the copolymerization was supported by the linear increase in the molecular weight versus the conversion and the synthesis of block copolymers. The drawback of IRP is its low versatility, and other conventional monomers, such as styrene and (meth)-acrylate derivatives, have been used with only limited success (see section 3.5.1).[79,80] However, because of its simplicity and the availability of organoiodine dormant species, IRP is still often employed. For example, Kamigaito and co-workers have used IRP to control the tacticity in the polymerization of vinyl acetate in fluoroalcohol solvent[81] and in manganese-mediated photoinduced polymerization.[82−84] In situ generation of the organoiodine chain-transfer agents (CTAs) and their applications to the polymerization of conventional vinyl monomers have been carried out by Lacroix-Desmazes and co-workers.[85−90] Goto and co-workers have recently developed a modified version of IRP, in which several inorganic and organic halides in the presence of conventional organoiodine CTAs increase the control of MWD in IRP (see section 3.5.1).[55,56,91] They call this method reversible chain-transfer-catalyzed polymerization (RTCP), because inorganic or organic radicals generated from the additives reversibly activate organoiodine chain-transfer agents.

Kwon and co-workers have utilized diaryldiselenides as photoiniferters[92−94] or radical-trapping agents,[95] which generate organoselenium dormant species in situ by the reaction of the monomers. They also employed phenylselenyl-substituted chain-transfer agents for the polymerization of styrene under photoirradiation.[96] The polymerization showed living character as judged from a linear increase of M_n upon monomer conversion and successful synthesis of block copolymers. However, the control of MWD was insufficient, and polymers with considerably high MWDs were obtained ($M_w/M_n > 1.5$). This is due to the low reactivity of organoselenides toward homolytic substitution reaction with polymer end radicals and also due to high reactivity of arylselenyl radical to monomers initiating a new polymer chain (see section 3.4).

The same group also reported the effect of diphenylditelluride on the conventional azobisisobutyronitrile (AIBN)-initiated radical polymerization of styrene.[97] They found that MWD becomes narrow ($M_w/M_n = 1.26-1.18$) with the addition of more than 0.5−2.0 equiv of diphenylditelluride to AIBN, whereas the addition of more ditelluride led to the formation of polystyrene with lower M_n. They also propose the existence of a phenyltellanyl-substituted ω-polymer end group, but there was no direct evidence to support the end group structure.

On the basis of our discovery of reversible radical generation from organotellurium compounds via carbon−tellurium bond thermolysis and photolysis,[98,99] we developed new organotellurium-group-transfer radical-coupling reactions.[100−107] During the course of our investigations, we discovered that several organotellurium compounds were excellent CTAs for LRP.[22,23,26] Furthermore, we recently found that organostibines[30] and organobismuthines[34] also promote highly controlled LRP. These methods are versatile and produce a variety of well-defined polymers with several different functional groups. The details of these methods are discussed below.

3. Organoheteroatom-Mediated LRP

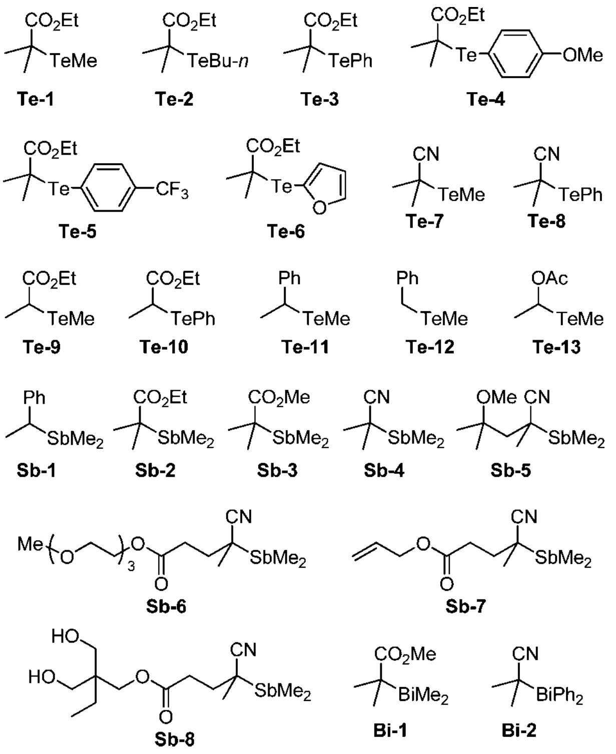
3.1. Chain-Transfer Agents (CTAs)

3.1.1. Synthesis

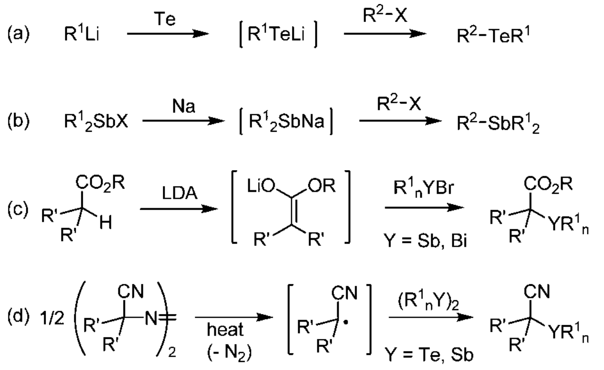
The availability of CTAs is a key issue with respect to practical applications of LRPs. Many of the organoheteroatom CTAs shown in Scheme 3 are easily prepared on large scales and easily purified by simple vacuum distillation. Though heteroatom CTAs are moderately air (oxygen) sensitive, they can be stored for long periods under a nitrogen atmosphere and are handled using standard syringe techniques. Organotellurium derivatives are the easiest to synthesize due to the availability of the starting materials and are the most resistant to oxidation by air among these CTAs.

Organotellurium CTAs are usually prepared under basic conditions as shown in Scheme 4a. The reaction of alkyl or aryl lithium reagents with tellurium metal affords the corresponding organotellanyl lithium species,[108] which reacts with organochlorides, bromides, and iodides to give the desired CTA.[22] CTAs **Te-1**−**Te-13** are prepared by using this route. Since many organolithium reagents and organohalogen compounds are readily available, this is a practical and scalable synthetic route to organotellurium CTAs. More than 20 g of CTAs **Te-1**−**Te-3** are routinely prepared in our laboratory starting from commercially available methyl-, butyl-, or phenyllithium, tellurium powder, and ethyl-2-bromo-2-ethylpropionate.

Scheme 3. Structures of Organoheteroatom CTAs



Scheme 4. Synthetic Route to Organoheteroatom-Transfer Agents



The reaction of an organostibanyl anion, which was reductively generated from the diorganostibanyl bromide and sodium metal, with 1-phenylethyl bromide afforded the organostibanyl transfer agent **Sb-1**.[31] However, because of the difficulty to generate the stibanyl anions and their low reactivities, the synthetic scope of this route is limited.

Organostibanyl transfer agents **Sb-2** and **Sb-3** were prepared by the reaction of lithium ester enolate generated from ethyl 2-methyl-2-propanoate and lithium diisopropylamide with dimethylstibanyl bromide as an electrophile (Scheme 4c).[31] The same method was used for the cyano-derivative **Sb-3** starting from 2-methyl-2-propionitrile. Organobismuthine transfer agents **Bi-1** and **Bi-2** were also prepared via this route using dimethylbismuthanyl bromide as an electrophile.[34]

Despite the high synthetic efficiencies of the routes shown in Scheme 4a−c, it is difficult to introduce polar functional groups into the CTAs. As the heteroatom functional groups in the CTAs are moderately sensitive to oxygen and also reactive under various conditions, post modifications to introduce functional groups starting from the existing CTAs are limited. In addition, as synthesis of the CTAs requires basic conditions, many polar functional groups are not compatible. The fourth method shown in Scheme 4d, which relies on the reaction of a radical generated from an azo-initiator with ditellurides[26] and distibines,[32] proceeds under neutral conditions and is applicable to the synthesis of functional CTAs. The reaction of an azo-initiator with iodine has been also used for the in situ synthesis of organoiodine chain-transfer agents.[56,85,86,89,90]

Scheme 5. Structural Effect of CTA on the Control of LRP

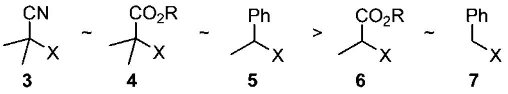


Table 1. Structural Effect of Organotellurium,[22,27,28] Organostibine,[30] and Organobismuthine[34] Chain-Transfer Agents (CTAs) on the Polymerization of Styrene (100 equiv) under Thermal Conditions

CTA	BDE (kJ mol^{-1})[a]	yield (%)	M_n	M_w/M_n
Te-1	114	88	11500	1.18
Te-2		99	10300	1.25
Te-3		88	12200	1.08
Te-4		90	9400	1.09
Te-5		81	9100	1.06
Te-6		88	7800	1.23
Te-7	120	98	9400	1.15
Te-9[b]	142	70	3100	1.33
Te-11	123	91	9100	1.18
Te-12	142	86	8300	1.34
Sb-1		99	9300	1.22
Sb-2	121	99	8700	1.14
Sb-4		95	9000	1.17
Bi-1	113	99	10500	1.07

[a] Bond dissociation energy calculated by the B3LYP/6-31G*(H,C,N,O)+LANL2DZ(Te,Sb,Bi). [b] Polymerization was carried out with 30 equiv of styrene.

Organotellurium CTAs **Te-7** and **Te-8** were prepared by reacting AIBN with dimethyl- and diphenylditelluride, respectively, but in low yields (8%−18%).[26] This route has the practical advantage that both AIBN and ditellurides are stable in air and can be handled without special precautions. Furthermore, the air sensitive CTAs formed can be directly used for polymerization without purification because the only side product is a dimer of AIBN-derived radicals, which does not affect the polymerization reaction. Despite the simplicity of this procedure, the use of purified initiators is the method of choice for obtaining living polymers with the highest level of control of MWD.

The reaction of azo-initiators with tetramethyldistibine, on the other hand, took place with high coupling efficiencies.[32] Yields of the CTAs were about 60% when a 1:1 mixture of an azo initiator and the distibine was employed. Since about 40% of the radicals generated from the azo initiators dimerize within a solvent cage,[109] the result indicates that almost all the radicals that diffused from the cage were captured by the distibine. Organostibine CTAs **Sb3**−**Sb8** were prepared via this route starting from the corresponding azo initiators. Ester, ether, terminal alkene, and alcohol groups were incorporated into the CTAs. α-Functional polymers were synthesized starting from these functional CTAs (see section 3.5.3).

3.1.2. Structural Effect of CTAs on the Control of LRP

Structural effects of the CTAs on MWD are summarized in Scheme 5 and Table 1.[22,26,33] The control is usually higher with the CTAs from left to right; cyano- and ester-substituted tertiary heteroatom compounds **3** and **4** and phenyl-substituted secondary heteroatom compound **5** generally show excellent control in the polymerization of conjugated monomers. Less-substituted analogues **6** and **7** are less efficient than **3**, **4**, and **5** but still exhibit sufficient control in the polymerization. For example, among organotellurium CTAs with a methyltellanyl group (X = TeMe) in styrene polymerization, the use of **Te-1**, **Te-7**, and **Te-11** afforded polystyrene with a narrow MWD ($M_w/M_n = 1.15-1.18$), whereas **Te-9** and **Te-12** gave polystyrene with a slightly wider MWD ($M_w/M_n = 1.33$). Other organotellurium compounds with general structures **3** and **4** (**Te-2**–**Te-6** and **Te-8**) were also excellent CTAs giving narrow MWD polystyrenes ($M_w/M_n = 1.08-1.25$). Organostibine and organobismuthine CTAs with general structures **3** and **4** (**Sb-1**, **Sb-2**, **Sb-4**, and **Bi-1**) also afforded polystyrene with a narrow MWD ($M_w/M_n = 1.07-1.22$).[30,34]

In general, the initiation reaction has to be faster than or at least similar to the propagation reaction to obtain well-controlled polymers in living polymerization. Therefore, generation of an initiating radical from a CTA has to be sufficiently fast compared to that from a polymer-end dormant species in LRP. The radical species generated from **3**, **4**, and **5** are about 20 kJ/mol more stable than those from **6** and **7**, as indicated by the bond dissociation energies (BDEs) of methyltellanyl derivatives (X = TeMe, Table 1). In addition, the reactivities of the radical species generated from these CTAs to monomers are similar. Therefore, CTAs with lower BDEs usually give higher control than those with higher BDEs. This trend is not limited to TERP, SBRP, and BIRP, and the same structural effects on the control of MWD have also been observed in NMP,[110,111] ATRP,[112] and RAFT.[113] The effects of heteroatom species and substituent on the heteroatom will be discussed in the mechanistic section (section 3.4). It should be noted that control of the MWD does not directly correlate to the BDEs of CTAs as well as those of dormant species because bond homolysis is not the main mechanism of the activation of dormant species in TERP, SBRP, and BIRP. This point also will be discussed in the mechanistic section.

3.2. Polymerization Conditions

Three conditions have been developed for conducting TERP, SBRP, and BIRP. One, which we call the first generation, is a purely thermal condition, in which a CTA and a monomer are typically heated between 80 and 110 °C (condition A in Table 2).[22,23] The second method, which we call the second generation, is a ternary system in which radical initiators, typically azo initiators, are added to a mixture of a CTA and a monomer (condition B in Table 2).[27] The polymerization conditions depend on the decomposition temperature of the azo initiator used, but it usually proceeds at lower temperature than that of the first generation. The third method, which we call the third generation, proceeds under photo irradiation of a mixture of an organotellurium CTA and a monomer (condition C in Table 2).[29] The polymerization proceeds under much milder conditions, such as temperatures in the range of 0 °C to room temperature, than the first and second generations. These differences depend on the mechanism of the polymerization reaction, as discussed in section 3.4.

Table 2. Polymerization of Styrene (St), *n*-Butyl Acrylate (BA), and Methyl Methacrylate (MMA) under Different Conditions

monomer	condition[a]	temp (°C)	time (h)	yield (%)	M_n	M_w/M_n
BA	A	100	24	69	8300	1.12
	B	60	0.5	92	10700	1.17
	C	0	4	86	10500	1.16
St	A	100	98	98	9400	1.15
	B	60	11	94	11300	1.17
	B[b]	40	23	82	7400	1.21
MMA[c]	A	80	13	81	8300	1.12
	B	60	2	98	9600	1.15

[a] Conditions. (A) A mixture of chain-transfer agent (**Te-1**) and monomer (1:100) was heated.[22] (B) A mixture of AIBN, chain-transfer agent (**Te-1** or **Te-7**), and monomer in a ratio of 1:1:100 was heated.[27] (C) A mixture of chain-transfer agent (**Te-3**) and monomer was irradiated with a 500 W high-pressure Hg lamp through a cutoff filter.[29] [b] 2,2′-Azobis(4-methoxyvaleronitrile) was used instead of AIBN. [c] One equiv of dimethyl ditelluride was added.

Effects of the conditions on the polymerization of *n*-butyl acrylate (BA), styrene (St), and methyl methacrylate (MMA) in the presence of organotellurium CTAs **Te-1**, **Te-3**, and **Te-7** are summarized in Table 2. Polymerization of BA (100 equiv) under condition A was sluggish, and monomer conversion reached 70% after being heated at 100 °C at 24 h. Despite the slow polymerization rate, poly(butyl acrylate) (PBA) with a narrow MWD ($M_w/M_n = 1.12$) was obtained. Polymerization under condition B, on the other hand, completed within 0.5 h at 60 °C and gave well-controlled polymers ($M_w/M_n = 1.17$). Polymerization proceeded even at 0 °C under condition C, and PBA with a narrow MWD ($M_w/M_n = 1.16$) was also obtained with high monomer conversion. Polymerization of St and MMA also proceeded under condition B, of which the conditions are much milder than those of condition A. Polymerization of St and MMA under condition A proceeded in the temperature range of 80–100 °C, and that under condition B with AIBN as an initiator proceeded at 60 °C with a high monomer conversion. Polymerization of St using condition B took place at 40 °C with 2,2′-azobis(4-methoxyvaleronitrile) as an initiator, which decomposes at a lower temperature than AIBN does. Uncontrolled free radical polymerization did not compete with LRP even in the presence of azo-initiators, and the same level of control of MWD ($M_w/M_n = 1.12-1.21$) was observed regardless of the method used. Since polymerization takes place at lower temperatures and with shorter reaction times under conditions B and C than under condition A, these methods should be suitable for monomers that undergo unwanted side reactions at high temperatures. The high energy efficiencies of conditions B and C should also be useful for industrial applications.

Since thermolysis of the dormant species is the rate-determining step in condition A (see section 3.4 in detail), the rate of polymerization is strongly affected by the strength of the carbon–heteroatom bond of the dormant species. Assuming that the BDEs of polymer-end dormant species with structurally related CTAs are similar, the PBA-dormant species has a higher BDE than the polystyrene (PSt)- and PMMA-dormant species do. Therefore, the polymerization of BA required a higher temperature and a longer reaction time than those of St and MMA. Conversely, the rate control step is the propagation reaction in condition B because the initiating radicals are provided from azo-initiators. Therefore, the rate of polymerization is similar to the propagation rate; BA is the fastest followed by MMA and then St.

3.3. Confirmation of the Livingness

The living character of TERP of St under first-generation conditions was ascertained by performing several control

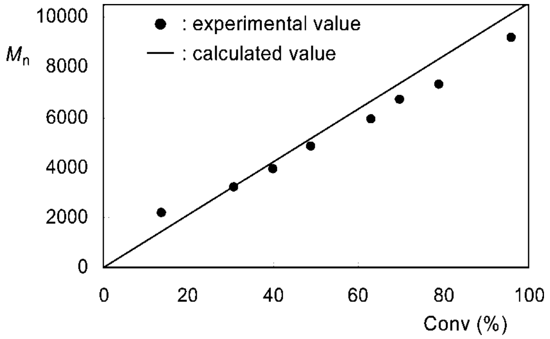
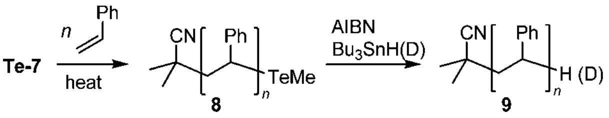


Figure 1. Correlation of experimental and theoretical M_n of polystyrene in the bulk polymerization of 100 equiv of St using **Te-11** as a function of the conversion of St. Reprinted with permission from ref 35. Copyright 2005 John Wiley & Sons, Inc.

Scheme 6. Reduction of Methyltellanyl Polymer End Group with Tributyltin Hydride or Deuteride



experiments.[22] First, M_n increased linearly with an increase in the conversion of St (Figure 1). Second, M_n also increased linearly with an increase in the amount of St used. Monodisperse PSts with an M_n close to the theoretical value calculated from the ratio of St/CTA and a narrow MWD were obtained in all cases ($M_n = 9200-62600$, $M_w/M_n = 1.17-1.30$). The same linear correlations were also observed under second-generation conditions using AIBN as an additive.

The existence of a carbon−tellurium bond in the ω-polymer end group was confirmed by labeling experiments. PSt **8** prepared using **Te-7** and St (30 equiv) was reduced quantitatively using either tributyltin hydride or tributyltin deuteride to yield the end-protonated **9** or deuterated polystyrene **9**-d$_1$, respectively (Scheme 6).[22,26] Selective incorporation of the deuterium atom in the polymer was confirmed from MALDI-TOF mass spectra of **9** and **9**-d$_1$ as silver adducts (Figure 2). The ^{2}H NMR spectrum of **9**-d$_1$ further supported the selective incorporation of deuterium at the benzylic position ($\delta = 2.36$ ppm, broad singlet). These results clearly demonstrate the existence of an organotellurium ω-polymer end group in **8**. The difference between the main mass peaks was 104 in the MALDI-TOF mass spectrum, which corresponds to the molecular mass of St, and there were no significant peaks arising from impurities. These observations strongly suggest the highly controlled character of TERP, in which the polymerization is initiated by a radical generated from **Te-7** and proceeds in the absence of unfavorable side reactions. The labeling experiments in SBRP and BIRP also confirmed the living character of these methods.

3.4. Mechanism

Studies on the kinetics involved in the activation and deactivation of dormant species have revealed the existence of two mechanisms: reversible termination (RT, Scheme 7a) and degenerative chain transfer (DT, Scheme 7b).[27,33,114] Although NMP and ATRP proceed exclusively via the RT mechanism and RAFT proceeds via the DT mechanism, TERP, SBRP, and BIRP proceed through the two mechanisms. Involvement of the two mechanisms makes these LRP methods unique, and it is the origin of three polymerization conditions described in the previous section. Recent investigation of cobalt-mediated LRP revealed that this reaction also takes place by the RT and DT mechanisms.[41,43,44]

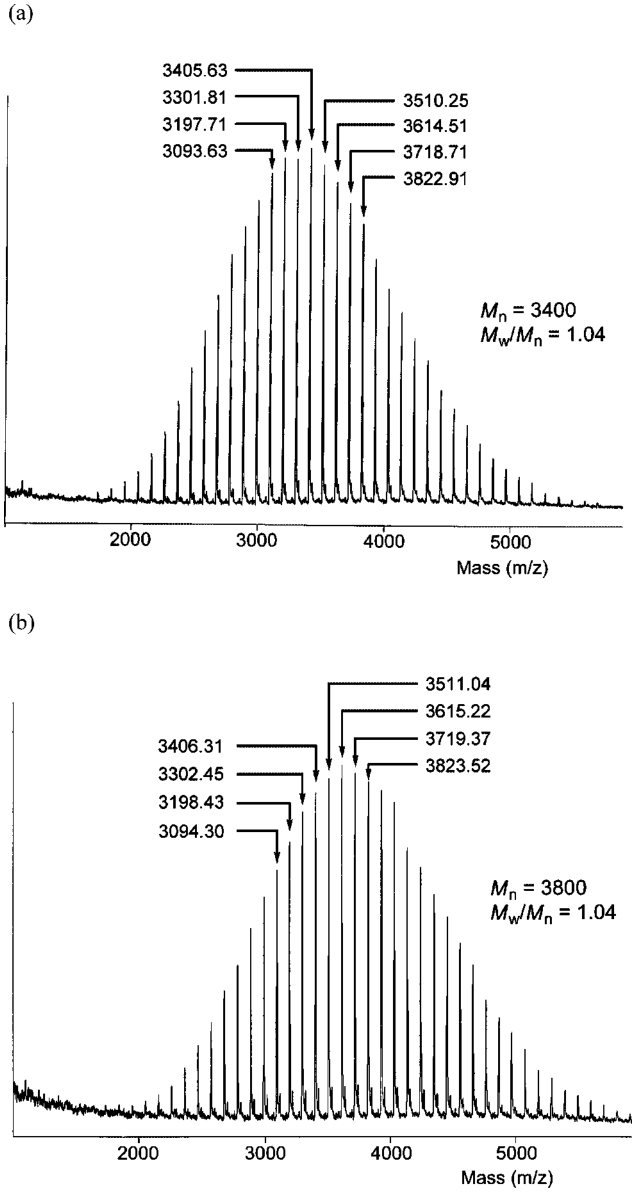


Figure 2. MALDI-TOF mass spectra of (a) end-protonated polystyrene **9** and (b) end-deuterated polystyrene **9**-d$_1$. The molecular ions were observed as silver ion adducts [$m/z = (M + \mathrm{Ag})^+$]. Reprinted with permission from ref 26. Copyright 2003 American Chemical Society.

Scheme 7. Activation/Deactivation Mechanisms Involved in TERP, SBRP, and BIRP

(a) Reversible termination (RT) mechanism

$$\mathrm{P{-}X} \overset{k_d}{\rightleftharpoons} \mathrm{P}\bullet + \bullet\mathrm{X}$$

(b) Degenerative transfer (DT) mechanism

$$\mathrm{P{-}\mathbf{X}} + \mathrm{P'}\bullet \overset{k_{ex}}{\rightleftharpoons} \mathrm{P}\bullet + \mathbf{X}\mathrm{{-}P'}$$

The first-order rate constant for the activation of the dormant species via RT (k_d) and the second-order rate constant for the activation via DT (k_{ex}) in TERP,[27,28,114] SBRP,[30,33] and BIRP[34] are summarized in Table 3. The rate constants of IRP[115] and RAFT[116] are also listed as a reference.

Table 3. Kinetic Parameters for the Activation of Organotellurium,[27,28,114] Organostibine,[30,33] Organobismuthine,[34] Organoiodine,[115] and Dithiocarbonyl[116] Dormant Species at 60 °C in Homopolymerization[a]

P-X[b]	k_d (s^{-1})	k_{ex} (M^{-1} s^{-1})	k_p (M^{-1} s^{-1})	C_{ex}
PSt-TeMe	1×10^{-5} (2×10^{-4})[c]	5.7×10^3	3.4×10^2	17
PSt-TeBu-*n*	1×10^{-5}	3.4×10^3		10
PSt-TePh	1×10^{-5}	9.6×10^3		28
PSt-TeC$_6$H$_4$OMe-*p*	4×10^{-5}	1.2×10^4		35
PSt-TeC$_6$H$_4$CH$_3$-*p*	5×10^{-5}	1.4×10^4		41
PSt-SbMe$_2$	~0	1.1×10^4		32
PSt-BiMe$_2$	(3×10^{-4})[c]	1.8×10^4		53
PSt-I	~0	1.2×10^3		3.5
PSt-SC(=S)Me	~0	6.1×10^{14}		180
PMMA-TeMe	5×10^{-6}	3.0×10^3	8.3×10^2	3.6
PMA-TeMe	$\leq 1 \times 10^{-3}$	4.6×10^5	2.4×10^4	19
PVAc-TeMe (H-T)[c]	~0	$1.0 (\pm 0.3) \times 10^6$	9.5×10^3	110 ± 30
PVAc-TeMe (H−H)[c]	~0	1.1×10^4		1.2

[a] The k_d, k_{ex}, and k_p are the rate constant for reversible termination (Scheme 7a), degenerative transfer (Scheme 7b), and propagation, respectively. C_{ex} is the degenerative chain-transfer constant ($= k_{ex}/k_p$). [b] Abbreviation: PSt = polystyrene, PMMA = poly(methyl methacrylate), PMA = poly(methyl acrylate), PVAc = poly(vinyl acetate). [c] Data obtained at 100 °C.

For example, the k_d and k_{ex} for TERP using the methyltellanyl derivative (X = TeMe) at 60 °C in St polymerization are 1.2×10^{-5} s^{-1} and 5.7×10^3 M^{-1} s^{-1}. The activation energy of DT was also experimentally determined to be 30 kJ mol^{-1}, whereas that for RT of PSt-TeMe is estimated from the BDE of polymer-end mimetic CTA **Te-11** to be around 120 kJ mol^{-1}. Therefore, DT is the predominant mechanism in TERP. Although the rate constants are affected by the heteroatom species and the substituents on the heteroatom, the contribution of the RT mechanism is always considerably smaller than that of the DT mechanism. Therefore, once the initiating radical species have formed, they predominantly undergo the DT-mediated polymerization reaction in all cases.

Under the first-generation conditions (condition A), the initiating radicals form via the thermolysis of the heteroatom CTA. In other words, the high temperatures and long reaction times required for the polymerization are due to the high activation energy required for the thermolysis. Conversely, the initiating radicals are generated from azo-initiators under mild thermal conditions, i.e., the second-generation conditions (condition B), and the polymerization proceeds exclusively via the DT mechanism at temperatures where the azo-initiators decompose. Under the third-generation conditions (condition C), direct C−Te bond photolysis occurs to afford the initiating radicals from the dormant species. Since photochemical reactions do not require heat, polymerization also proceeds at low temperatures exclusively via DT. It is worth noting that, as the rate of polymerization becomes slower at lower temperatures, heating is sometimes necessary to complete the polymerization within a reasonable time scale when monomers with slow propagation rates are employed.

MWD of polymers prepared via DT can be estimated by using eq 1 under steady state conditions without any side reactions leading to dead polymers, where c is the monomer conversion, C_{ex} ($= k_{ex}/k_p$) is a DT constant, and k_p is the rate constant for the propagation reaction.[9]

$$M_w/M_n = 1 + (2/c - 1)/C_{ex} \qquad (1)$$

Since the propagation rate constant is the same when the same monomer is considered, a faster k_{ex} and thus a higher C_{ex} leads to lower MWD of the resulting polymer at the same monomer conversion.

Kinetics studies showed that C_{ex} of a methyltellanyl group-transfer reaction at PSt polymer-end radical and PSt−TeMe dormant species in St polymerization (C_{ex} = 17) was approximately five times larger than that of an iodine atom-transfer reaction at PSt−I (C_{ex} = 3.5)[115] and ca. 10 times lower than that of RAFT polymer end PSt−SCSMe (C_{ex} = 180).[116] These results are consistent with the observation that TERP is more controllable than IRP but slightly less controllable than RAFT.

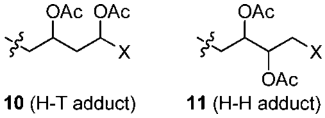
Although C_{ex} (= 10) of the butyltellanyl group-transfer reaction is slightly smaller than that of the methyltellanyl group-transfer reaction, it is still faster than that of the iodine atom-transfer reaction. DT in the phenyltellanyl, *p*-methoxyphenyltellanyl, and *p*-trifluoromethylphenyltellanyl group-transfer reactions take place much faster than that in methyltellanyl group-transfer reactions. The C_{ex} are ca. 10 times higher than that of the iodine atom-transfer reaction, and this difference is identical to that reported by Kambe and Sonoda.[67] The kinetic data are consistent with the observed higher MWD control using CTAs **Te-3**−**Te-5** possessing aryl substituents than that using methyltellanyl derivative **Te-1** (Table 2).

High values of k_{ex} and C_{ex} were also observed in dimethylstibanyl and dimethylbismuthanyl group-transfer reaction in SBRP (C_{ex} = 32) and BIRP (C_{ex} = 53) in St polymerization. Among the same methyl-substituted heteroatom groups, bismuth is the fastest followed by antimony and then tellurium for the DT reaction. Although organotellurium and iodine compounds have been recognized as being the most reactive heteroatom compounds toward the DT reaction,[75,76] the results clearly show that organostibine and bismuthine compounds are more reactive than these heteroatom compounds. Therefore, these heteroatom compounds should find significant use in the synthetic radical chemistry of small molecules. The kinetic data are also consistent with the general trend that organostibine, such as **Sb-2** and **Sb-4**, and organobismuthine CTAs, such as **Bi-1**, show higher MWD control than organotellurium CTAs **Te-1** and **Te-7** do.

The contribution of RT is small compared to DT, but it plays a crucial role under the first-generation conditions especially in TERP and BIRP (Table 3).[114] The results indicate that CTAs in TERP and BIRP also serve as radical initiators. As the rate of thermal dissociation of organobismuth compounds is about 2 times faster than that of organotellurium compounds, the former is the best radical initiator among the heteroatom compounds.

The kinetic parameters of the polymerization of MMA, methacrylate (MA), and vinyl acetate (VAc) involving an organotellurium dormant species with a methyltellanyl group are also summarized in Table 3.[114] The DT mechanism is the predominant activation mechanism in all cases. The rate of DT of poly(methyl methacrylate) (PMMA) polymer-end radical with a PMMA dormant species (PMMA−TeMe) takes place about 2 times slower than that of a PSt polymer end species, and the propagation rate of the MMA polymerization is ca. 2.5 times faster than that of St. Consequently, C_{ex} (= 3.6) of the MMA polymerization becomes ca. 5 times smaller than that of the St polymerization. This C_{ex} value is too small to yield PMMAs with narrow MWDs (M_w/M_n <

Scheme 8. Head-to-Tail (H−T) and Head-to-Head (H−H) *ω*-Polymer End Group Structure in PVAc



10 (H-T adduct) **11** (H-H adduct)

1.28). The result is consistent with the fact that the MWD control of the TERP of MMA was not sufficient ($M_w/M_n > 1.35$), and the addition of ditellurides was required to yield PMMA with a narrow MWD ($M_w/M_n \approx 1.1$),[23] as discussed in the following section (section 4.1). SBRP and BIRP of MMA gave PMMA with a low MWD ($M_w/M_n < 1.25$) without the addition of additives. The results suggest that the C_{ex} values under these conditions must be larger than that under TERP, as in the polymerization of St, and that organostibines and bismuthines generally have a higher reactivity in the DT reaction than organotellurium compounds have.

The rate of propagation of MA is ca. 70 times faster than that of St. However, as the rate of DT of the MA polymer end species is ca. 80 times faster than that of PSt, the C_{ex} ($= 19$) in MA polymerization was similar to that in St polymerization. The result is also consistent with the fact that the polymerization of acrylates usually gives resulting polymers with a low MWD ($M_w/M_n < 1.2$).

TERP and SBRP of VAc afforded poly(vinyl acetate) (PVAc) with a low MWD when the degree of polymerization was low, but the control decreased as the increase of the degree of polymerization (see also section 3.5.1). This has also been reported for IRP[117] and iron-catalyzed ATRP of VAc.[118] It is known that a small amount of head-to-head (H−H) addition (ca. 2%) occurs during the propagation of VAc. This leads to the formation of dormant species **11** derived from H−H addition, whereas normal head-to-tail (H−T) addition gives dormant species **10** (Scheme 8). Kinetic experiments revealed that DT of the PVAc polymer end radical species with H−T adduct **10** in TERP (X = TeMe) was very fast with $k_{ex} = 1.0 \times 10^6$ M^{-1} s^{-1}.[114] Although the propagation rate constant of VAc ($k_p = 9.5 \times 10^3$ M^{-1} s^{-1}) is relatively high, C_{ex} was 110, a value large enough to give PVAc with a narrow MWD. In contrast, k_{ex} of H−H adduct **11** (X = TeMe) was ca. 100 times slower than that of **10**, indicating that the activation from the H−H adduct was insufficient. C_{ex} was determined to be 1.2, a value too small to give PVAc with a narrow MWD. Since the H−H adduct gradually accumulated in the reaction mixture as the polymerization progressed, the MWDs gradually increased with an increase in the degree of polymerization. Therefore, the formation of the H−H adduct is responsible for the loss of control as the progress of polymerization.

Although RAFT also proceeds by DT polymerization,[19,21] the microscopic energy profiles of DT in RAFT are completely different from those of IRP, TERP, SBRP, and BIRP, as schematically shown in Figure 3. DT in RAFT proceeds stepwise with the addition of radical P to thiocarbonyl compound **12** (a RAFT reagent) to form intermediate radical **13** (Figure 3a). Subsequent fragmentation of the S−P′ bond in **13** generates RAFT reagent **12′** and radical P′. All the elementary processes are reversible, and the addition of radical P′ to **12′** also generates radical P and **12** through intermediate **13**.[119] It is well-recognized that the lifetime of **13** should be short in order to minimize unwanted radical−radical termination processes. However, capture of intermediate **13** in acrylate polymerization occurs as ascertained by Monteiro[120] and Fukuda,[121,122] and this chain-breaking reaction causes the rate retardation in acrylate polymerization using phenyl substituted RAFT CTA (Z = Ph). Stability of **13** is strongly affected by Z substituent because it directly attaches to the radical center, while effects of P and P′ radicals on **13** are marginal. When the same Z group is considered, relative stability and, thus, concentration of **13** increase as the polymer-end radical P and P′ become less stable, as shown in the gray line. This enhances the probability of **13** undergoing the chain-breaking reaction. Therefore, appropriate choice of Z group is necessary depending on the monomer families being polymerized so as to undergo efficient degenerative transfer reaction. In other words, there is no universal CTA in RAFT.

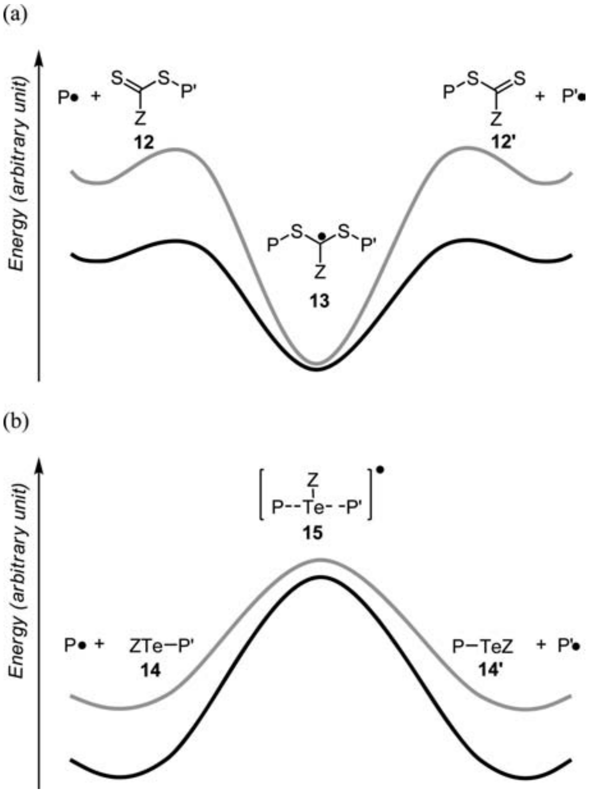
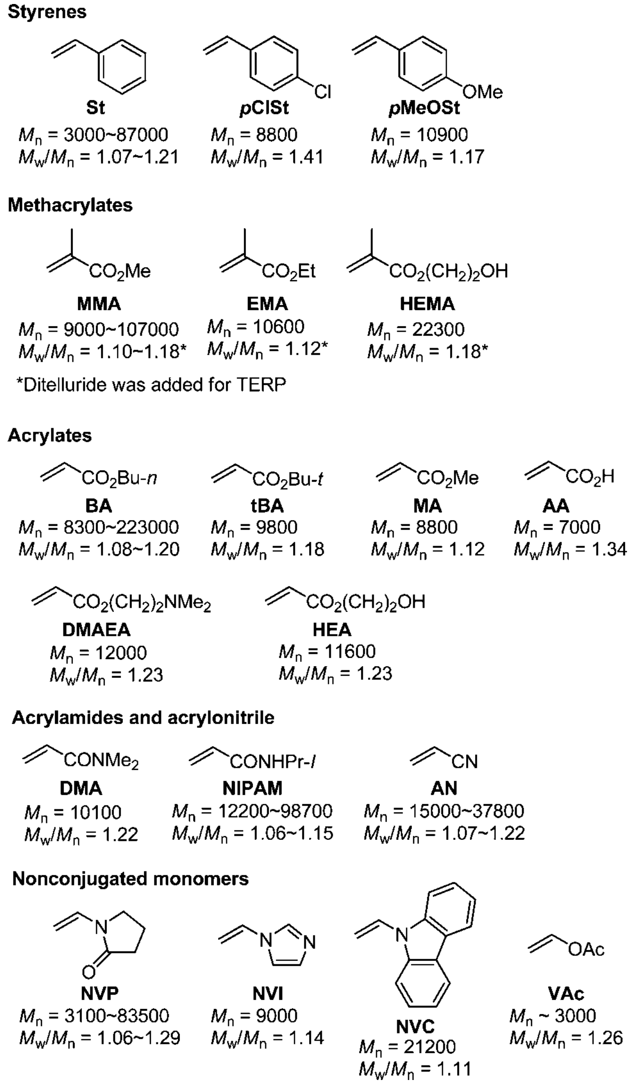


Figure 3. Hypothetical energy diagram of the DT of (a) RAFT and (b) TERP. The lines in gray show the energy diagram when less stabilized radicals P and P′ are involved.

In sharp contrast, DT in TERP proceeds through hypervalent tellurium intermediate or transition state **15**, which forms by the reaction of radical P with organotellurium dormant species **14** to generate radical P′ and new dormant species **14′** (Figure 3b). Although the existence of a trivalent tellurium radical intermediate is still a controversial issue,[104,123−125] the intermediate, if any, should be very close in energy to the transition state. Therefore, DT in TERP virtually proceeds in a concerted manner, and involvement of a long-lived intermediate, which may cause unwanted side reactions, is unlikely. In addition, since the DT process becomes faster when less stable polymer-end radicals are involved as shown in the gray line, CTAs with the same Z group can be used for controlling LRP (see section 3.5). Energy profiles of SBRP, BIRP, and IRP should be very similar to TERP, though more experimental and theoretical investigations are needed.[126,127]

Scheme 9. Selected Monomers Polymerized by Using TERP, SBRP, and BIRP; Polymerization Data (M_n and M_w/M_n values) Were Taken from the Data Obtained Using CTAs Having General Structures 3, 4, and 5



3.5. Synthetic Scope

3.5.1. Homopolymerization

A synthetic advantage of TERP, SBRP, and BIRP is their high versatility in polymerizing a variety of monomer families using the same CTAs. Selected monomers polymerized in a controlled manner by using these methods are summarized in Scheme 9. M_n and MWD data were taken from the polymerization using CTAs with general structures **3**, **4**, and **5**. The monomer conversions are usually high (>90%), and polymers with narrow MWDs were obtained in all cases.

St was polymerized under first- and second-generation conditions, and structurally well-defined PSt with M_n close to the theoretical values and low MWDs was formed.[22,26−28,34] M_n increased linearly with an increase in the St/CTA ratio, and PSts with M_n in the range of 3 000−87 000 and narrow MWDs (M_w/M_n < 1.3) were prepared. *p*-Chlorostyrene (*p*ClSt) and *p*-methoxystyrene (*p*MeOSt) were also successfully polymerized.[22] Although the MWD control in *p*ClSt polymerization was less efficient than those in St and *p*MeOSt polymerizations, presumably due to the higher propagation rate of the former than the latter, the level of control was still acceptable.

IRP of St was less successful than TERP, SBRP, and BIRP, and PSt with considerable broad MWD was obtained even when the targeted molecular weight was low ($M_n \approx$ 6 500, $M_w/ M_n \approx 1.4$) using 1-phenylethyl iodide as a CTA.[80] This is primarily due to the low exchange constant C_{ex} in IRP versus that in other methods as discussed in section 3.4. Polymerization under RTCP conditions, on the other hands, significantly increases the MWD control.[55,56,91] Polymerization of St in the presence of an organoiodine CTA and a catalytic amount of inorganic or organic halides, such as SnI_4, GeI_4, Tolyl-GeI_3, PI_3, *N*-iodosuccimide, and organic hydride, such as $(RO)_2P(=O)H$, gave PSt with narrow MWDs (M_n = 4 800−27 000, M_w/M_n = 1.16−1.48).

Although methacrylates could be polymerized under first- and second-generation conditions, the control of MWD was inefficient via TERP. Polymerization of MMA using organotellurium CTAs resulted in the formation of PMMAs with considerably broad MWDs (M_w/M_n > 1.37) due to the small C_{ex}, as described previously (section 3.4). However, the control increased with the addition of ditellurides as a catalyst, such as dimethyl, dibutyl, and diphenylditelluride, and PMMAs with narrow MWDs (M_w/M_n = 1.12−1.16) and M_n in the range of 8 600−79 400 were obtained depending on the monomer/CTA ratio.[23,26] A catalytic amount of ditelluride was effective when the targeted molecular weight was small, but substoichiometric to excess amounts of ditelluride were used when the targeted molecular weight was large. SBRP and BIRP exhibited higher MWD control than TERP, and PMMAs with narrow MWDs (M_w/M_n = 1.10−1.25) and M_n in the range of 10 000−100 000 were obtained without the addition of additives. Distibines are also effective in controlling the MWD in SBRP, and the effects of distibine are discussed in section 4.1.[32] IRP of MMA afforded PMMAs with broad MWDs (M_w/M_n > 1.5),[80,86] but RTCP of MMA gave PMMAs with narrow MWDs (M_n = 6 300−10 300, M_w/M_n = 1.22−1.38).[91]

Acrylates were polymerized under first-generation conditions with good MWD control, but high temperatures and long reaction times were required to reach high monomer conversion due to inefficient generation of the initiating radicals from the dormant species.[23] The high temperatures were also unsuitable because a considerable amount of branching occurred due to a backbiting reaction.[128−130] Therefore, the second-[33] and third-generation[29] conditions at low-to-ambient temperature are more suitable for acrylate polymerizations. Poly(butyl acrylate)s (PBAs) with narrow MWDs (M_w/M_n = 1.10−1.20) and M_n in the range of 11 000−122 000 were successfully synthesized at 60 °C by using BIRP under the second-generation conditions with AIBN as the initiator. Polymerization of BA proceeded in the temperature range of 0−50 °C by using TERP under UV−vis irradiation (third-generation conditions), and PBAs with narrow MWDs (M_w/M_n = 1.08−1.19) and M_n in the range of 13 000−223 000 were synthesized. IRP of acrylate, on the other hand, were uncontrolled (M_w/M_n > 1.6).[80,85]

Since TERP, SBRP, and BIRP are performed under thermal or photochemical conditions without catalysts that are incompatible with the functionalities of the monomers, controlled polymerization of various monomers possessing functional groups can be achieved. For example, methacrylates and acrylates with a free hydroxyl group, such as hydroxyethyl methacrylate (HEMA) and hydroxyethyl acrylate (HEA), a carboxylic acid group, such as acrylic acid (AA), and an amine group, such as *N*,*N*-dimethylaminoethyl acrylate (DMAEA), were polymerized by using TERP in a controlled manner.[23,29] Acryl amides, such as *N*,*N*-dimethylacrylamide (DMA) and *N*-isopropylacrylamide (NIPAM), and acrylonitrile (AN) also gave the corresponding controlled polymers. Protection of the acidic proton in the hydroxyl, carboxylic acid, and amide groups was not necessary because polymerization proceeded under neutral conditions and carbon−heteroatom bonds in the dormant species are resistant to polar functional groups. RTCP is also compatible with several polar functional groups, and the controlled polymerizations of HEMA, DMAEA, glycidyl methacrylate, and poly(ethylene glycol) methacrylate were reported.[56,91]

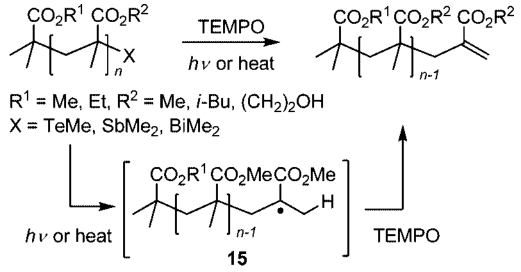
The most notable feature of these LRP methods is that they can control the polymerization of both conjugated and unconjugated monomers using the same CTAs used for the controlled polymerization of conjugated monomers, such as **Te-2**, **Te-3**, **Sb-2**, and **Bi-1**.[24,29,30,34] For example, TERP, SBRP, and BIRP of *N*-vinylpyrrolidone (NVP) afforded poly(NVP)s (PNVPs) with M_n in the range of 3 100−83 500 and narrow MWDs (M_w/M_n = 1.06−1.29) under second- and third-generation conditions. *N*-Vinylimidazole (NVI) and *N*-vinylcarbazole (NVC) were also polymerized in a controlled manner by using TERP under photo irradiation. Polymerization of vinyl acetate (VAc) by using TERP[114] and SBRP[30] gave the controlled poly(vinyl acetate)s (PVAcs), but the control was limited to low molecular weight polymers (M_n < 5000), as discussed in the mechanistic section (section 3.4). IRP showed better control than TERP and SBRP, and PVAcs of M_n ranging from 4 000−34 000 were synthesized under a controlled manner (M_w/M_n < 1.5).[117] Kamigaito and co-workers have recently shown that PVAcs with considerably high molecular weights were synthesized with narrow MWD ($M_n \approx$ 45 000, M_w/M_n < 1.5) by IRP carrying out the polymerization in a fluoroalcohol solvent.[81] While fluoroalcohols were used to control the tacticity by coordination to VAc,[131] they also perturb the monomer reactivity and decrease the formation of the H−H adduct (Scheme 8). Since the H−H adduct serves as a dead polymer, its reduction leads to the increased control of VAc polymerization. The simultaneous control of molecular weight, MWD, and tacticity has been a topic in LRP, and recent developments have been reviewed recently, including this thematic issue.[132,133]

3.5.2. Solvents

TERP, SBRP, and BIRP are routinely carried out without solvent (bulk polymerization), but several solvents have also been used. Polar solvents, such as *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF), were used for the polymerization of NIPAM, AN, NVC, and AA.[23,29,30,34] TERP of NIPAM was also carried out in a DMF/water mixture at 20 °C under third-generation conditions.[29] Desired polymers with controlled structures were obtained in all cases, as shown in Scheme 9.

Because of the high compatibility of water, TERP was applied to mini-emulsion conditions by Okubo.[25] Polymerization of MMA, St, and BA were carried out under the second-generation conditions with organotellurium CTA **Te-2** and AIBN as an initiator in an aqueous solution containing sodium dodecyl sulfate at 60 °C. In the case of MMA polymerization, dibutylditelluride was added to increase the MWD control. The polymerization proceeded in a controlled manner with a high monomer conversion and afforded stable latexes with controlled sizes, though the MWDs of the resulting polymers were broader (M_w/M_n = 1.23−1.76) than those obtained under homogeneous conditions, as shown in Scheme 9. Diblock copolymers composed of St, MMA, and BA were prepared by using a two-step procedure, both of which were carried out in an aqueous dispersed system. Okubo also reported recently that TERP of BA could be carried out in emulsifier-free emulsion polymerization conditions.[134] The results demonstrate the applicability of TERP in aqueous heterogeneous systems.

Scheme 10. Synthesis of *ω*-Vinylidene Polymethacrylates



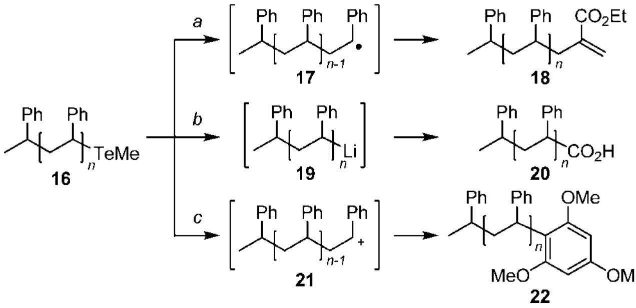
3.5.3. End-Group Transformations

A characteristic advantage of the TERP, SBRP, and BIRP is the versatility of the transformations that can be carried out on the polymer end groups. Radical-mediated reduction of organoheteroatom *ω*-end groups, as shown in Scheme 6, is the simplest route to *ω*-protonated and deuterated polymers.[22,26,30,34] Not only tin hydrides, which pose environmental concerns, but also arylthiols can be used as reducing agents.[135] Although thiols are inefficient reducing agents for organohalogen compounds, organotellurium, stibine, and bismuthine compounds are excellent substrates for thiol reduction due to their high reactivities toward radicals.

Treatment of polymethacrylates, which were prepared by using BIRP, SBRP, and TERP, with 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) under thermal or photochemical conditions gave the corresponding *ω*-vinylidene-functionalized polymethacrylates (Scheme 10).[136] The same protocol could be used for the synthesis of *ω*-vinylidene-functionalized polymethacrylonitrile. ^1H NMR spectroscopy, gel permeation chromatography (GPC), MALDI TOF MS, and thermogravimetric analyses showed that the products had a highly controlled and defined structure in terms of molecular weight, MWD, and the *ω*-polymer end structure. The reaction proceeds through the thermal or photochemical generation of polymer-end radical **15**, followed by the abstraction of a *β*-hydrogen adjacent to the radical center by TEMPO. The high end-group fidelity must be due to the high efficiency of radical generation by direct carbon−heteroatom homolysis, as discussed in the mechanistic section (section 3.1). The reaction requires efficient generation of radical **15** via the RT mechanism (Scheme 7b). Therefore, application of organobismuthine dormant species under thermal conditions and organotellurium dormant species under photochemical conditions is suitable for this transformation.

Although the same functionalized polymers were prepared by catalytic chain-transfer polymerization using cobalt catalysts[37,137] and by conventional radical polymerization in the presence of α-heteroatom functionalized methacrylates,[138−141] the control of molecular weight and MWD was insufficient. *ω*-Vinylidene-functionalized PMMAs with narrow MWDs were recently prepared by ruthenium[142] and copper[143] catalyzed ATRP, followed by reaction with TEMPO,

Scheme 11. Transformation of Organotellurium *ω*-Polymer End Groups; Conditions: (a) Ethyl 2-[(Tributylstannyl)methyl]acrylate (3 equiv), AIBN (0.1 equiv), $C_6H_5CF_3$, 80 °C; (b) *n*-BuLi (1.5 equiv), THF, −78 °C, then CO_2 (excess), H_3O^+; (c) PhTeOTf (1.5 equiv), 1,3,5-$(MeO)_3C_6H_3$ (10 equiv), rt



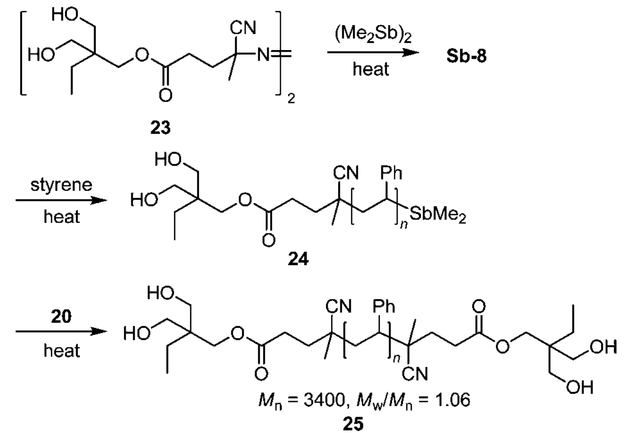
but the efficiency of the end-group transformation was not sufficient (~80%). Highly controlled polymerization of methacrylates by using TERP, SBRP, and BIRP combined with the high efficiency of the generation of radical **12** are responsible for the observed high control of the macromolecular structure and the polymer end group.

Organotellurium compounds are excellent precursors for carbon-centered radicals, carbanions, and carbocations.[77,108,144] The treatment of PSt **16** prepared by using TERP of ethyl 2-[(tributylsnanyl)methyl]acrylate[145] in the presence of AIBN in trifluoromethylbenzene as a solvent produced enoate-functionalized polymer **18** via polymer-end radical **17** (Scheme 11a).[22,136] Tellurium−lithium transmetalation[146,147] was achieved by the treatment of **16** with butyllithium to give benzyllithium **19**, which was trapped with an electrophile, such as carbon dioxide, giving carboxylic acid **17** after treatment with acid (Scheme 11b).[22] The carboxylic acid could be further transformed to different functional groups by using standard techniques, such as esterification. Treatment of **16** with phenyltellanyl triflate in the presence of 1,3,5-trimethoxybenzene afforded Friedel−Crafts product **22** through benzilic cation **21**.[148]

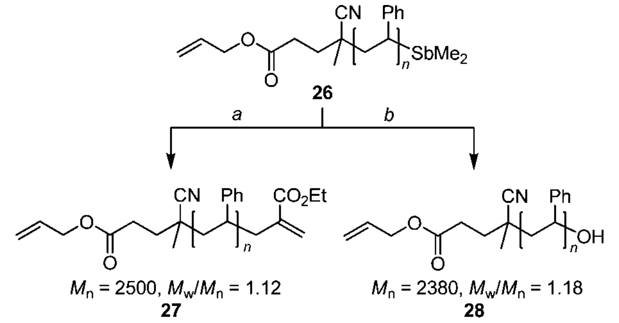
The synthetic chemistry of organostibines has not been well-established, but several transformations of organostibine polymer end groups have been reported recently, leading to the introduction of functional groups at the *ω*-polymer end. These methods combined with the use of functional CTAs, such as **Sb-7** and **Sb-8**, have led to the synthesis of structurally well-controlled telechelic polymers.[32]

The reaction of living polymers prepared by using RAFT with an excess amount of AIBN has recently been reported to form the bisfunctionalized polymers by Perrier,[149] and this method can be applied to organstibine-substituted living polymers.[32] For example, the reaction of diazo initiator **23** with tetramethyldistibine gave CTA **Sb-8**, as described in Scheme 4d. PSt **24**, which was prepared by using SBRP of St with **Sb-8**, was treated with 40 equiv of **23** to give α,*ω*-bisfunctionalized PSt **25**. Although the molecular weight and MWD of **25** were controlled, *ω*-protonated PSt also formed as a side product due to the disproportionation reaction of the polymer end radical derived from **24** and a carbon-centered radical generated from **23**. These results indicate that not only homotelechelic polymers but also heterotelechelic polymers, which possess different functional groups at their α-polymer and *ω*-polymer ends, can be synthesized by arbitrary choice of the azo initiator for preparation of the CTA and the subsequent *ω*-polymer end transformation.

Scheme 12. Synthesis of Diol-Functionalized Telechelic Polystyrene



Scheme 13. Synthesis of Telechelic Polymers with Different Functional Groups at α- and *ω*-Polymer Ends by Organostibanyl End-Group Transformation; Conditions: (a) Ethyl 2-[(Tributylstannylmethyl]acrylate (4 equiv), AIBN (0.1 equiv), $C_6H_5CF_3$, 80 °C; (b) Air (1 atm), $C_6H_5CF_3$, rt



However, as this *ω*-end functionalization method does not completely avoid disproportionation products, more selective reactions are needed to obtain telechelic polymers with high fidelity of the polymer end group. The results also suggest that the disproportionation product would form regardless of the LRP method used because it is formed from the radical species rather than the dormant species (Scheme 12).

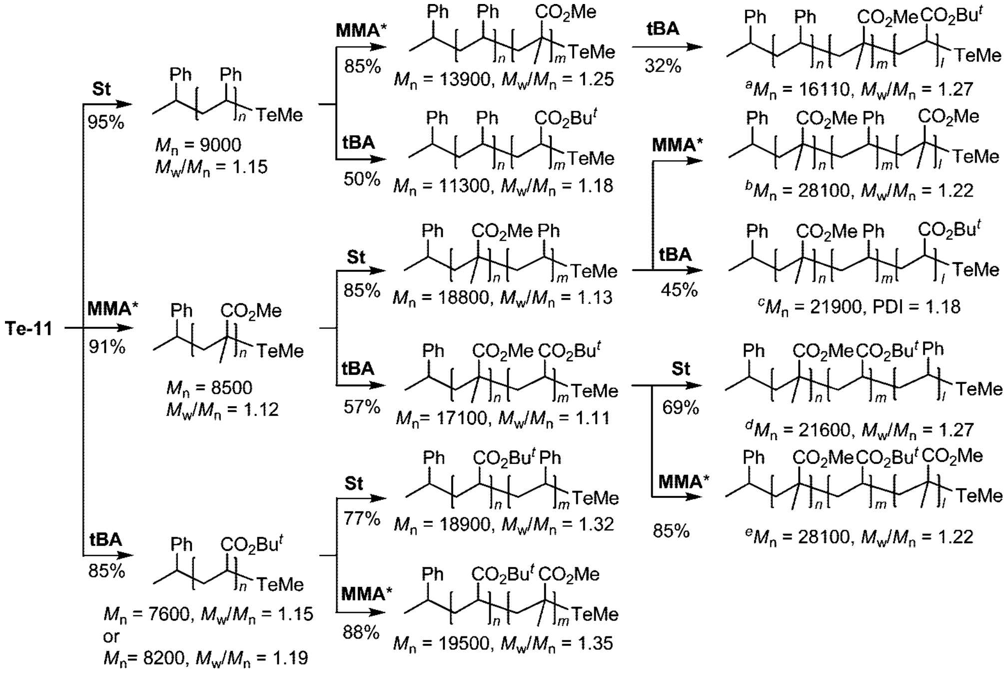
The radical-mediated allylation reaction shown in Scheme 11a can be applied to organostibine living polymers.[32] For example, PSt **26**, prepared from **Sb-7** and St, was heated with ethyl 2-[(tributylstannyl)methyl]acrylate in the presence of AIBN at 80 °C to give telechelic polymer **27** as the sole product (Scheme 13a). Aerobic oxidation of an organostibanyl group to a hydroxyl group has been reported,[150] and application of this procedure to **26** resulted in the selective formation of *ω*-hydroxylated PSt **28** (Scheme 13b). The different functional groups at the α-polymer and *ω*-polymer ends of these PSts should be useful for further selective synthetic transformations.

Though synthetic transformations of the polymer end groups of BIRP are not yet well-elucidated, they should have similar versatility to those of TERP and SBRP because the reactivity of organobismuthine compounds is similar to those of organotellurium and organostibine compounds.

3.5.4. Block Copolymer Syntheses

Another notable feature of TERP, SBRP, and BIRP is their versatility in the synthesis of block copolymers. Although the success of block copolymer synthesis is, in general, highly dependent on the order of monomer addition, espe-

Scheme 14. Syntheses of AB-block, ABA-triblock, and ABC-triblock Copolymers Using St, MMA, and tBA; 100 equiv of Each Monomer was used to Synthesize Diblock Copolymer, and M_n and MWD of the Diblock Macro CTAs for the Synthesis of Triblock Copolymers were as follows: (a) M_n = 12 600, M_w/M_n = 1.30, (b) M_n = 18 700, M_w/M_n = 1.18, (c) M_n = 19 000, M_w/M_n = 1.13, (d) M_n = 11 500, M_w/M_n = 1.09, and (e) M_n = 11 000, M_w/M_n = 1.11

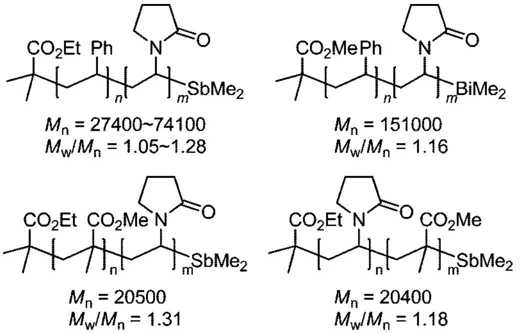


*(MeTe)$_2$ [1 equiv] was added.

cially when different families of monomers are used, these methods are more tolerant toward the order of addition than other LRP methods.[151−154] For example, blocking of the PSt macro CTA was successfully carried out for MMA and tBA, and the desired AB-diblock copolymers with narrow MWDs were obtained in both cases (Scheme 14).[23] The essentially complete disappearance of the starting macro CTAs and the formation of the desired diblock copolymers were observed. The addition of ditelluride is necessary when MMA is used as a monomer, as is also the case for the homopolymerization of MMA. The controlled syntheses of AB-diblock copolymers starting from a PMMA macro CTA with St and tBA, or from a poly(*t*-butyl acrylate) (PtBA) macro CTA with St and MMA, were also carried out by the subsequent addition of a second monomer. The desired diblock copolymers with narrow MWDs were obtained in all cases. Because of the stronger carbon−tellurium bonds found in PBA dormant species compared with those found in PSt and PMMA species, the MWD control of diblock copolymers initiated by the PtBA CTA was slightly less efficient than that starting from PSt and PMMA, but still at an acceptable level ($M_w/M_n < 1.35$).

Because the order of monomer addition is less important in TERP compared to that in other LRP methods, it was possible to prepare ABA and ABC triblock copolymers starting from diblock macro CTAs (Scheme 14). Treatment of PMMA-*block*-PSt and PMMA-*block*-PtBA macro CTAs with MMA gave the desired ABA triblock copolymers with narrow MWDs. ABC-triblock copolymers with different monomer sequences of St, MMA, and tBA, namely, PSt-*block*-PMMA-*block*-PtBA, PMMA-*block*-PSt-*block*-PBA, and PMMA-*block*-PtBA-*block*-PSt, were also synthesized in a controlled manner by the successive addition of each monomer. These triblock copolymers were all obtained in a highly controlled manner with narrow MWDs.

Scheme 15. Chemical Structures of Diblock Copolymers Containing a PNVP Segment Prepared by SBRP and BIRP



Block copolymers composed of conjugated and unconjugated monomers were also synthesized in a controlled manner by using TERP, SBRP, and BIRP.[24,30,31,34] Synthesis of these block copolymers is more difficult than that from both conjugated monomers because stabilities and reactivities of the dormant species and polymer-end radicals derived from conjugated and unconjugated monomers are quite different. Polymerization of organostibine and organobismuthine PSt macro CTAs with NVP in the presence of AIBN in DMF at 60 °C resulted in the complete consumption of the CTAs and the formation of desired PSt-*block*-PNVP in high monomer conversion (Scheme 15). The diblock copolymers composed of different compositions of PSt and PNVP segments were successfully synthesized in a controlled manner (M_w/M_n = 1.05−1.28) by altering the molecular weight of PSt macro CTAs and the amount of NVP. PMMA-*block*-PNVP was also synthesized in a controlled manner (M_n = 20 500, M_w/M_n = 1.31) by treating an organostibine−PMMA macro CTA with NVP in the presence of AIBN. Although the blocking reaction of PNVP macro CTA to St was inefficient, that to MMA proceeded smoothly in the presence of AIBN to give highly controlled PNVP-*block*-

PMMA with a narrow MWD ($M_w/M_n = 1.18$). These are the first examples of the successful block copolymerization of both conjugated and unconjugated monomers. Since these block copolymers are composed of hydrophobic PSt or PMMA and hydrophilic PNVP blocks, their physical properties will be of great interest. Synthesis and solution properties of poly(*N*-isopropylacrylamide) (PNIPAM)-*block*-PNVP are discussed in section 5.1.

The insensitivity toward the order of monomer addition in TERP was partly verified via kinetic studies on the block copolymerization of St and MMA, i.e., activation rate constants of PMMA−TeMe macro CTA in the St polymerization and the reverse reaction were determined.[114] C_{ex} for PMMA polymer-end radical to PMMA−TeMe CTA (homopolymerization) and PSt−TeMe CTA (block copolymerization) are similar (17 vs 31), and those for PSt radical to PSt−TeMe CTA (homopolymerization) and PMMA−TeMe CTA (block copolymerization) are also similar (3.6 vs 2.8). The results indicate that the transfer of PSt block to MMA, as well as that of PMMA block to St, occurs efficiently to give the second PMMA or PSt block.

Although RAFT also proceeds via the DT mechanism, the order of monomer addition is important, and a monomer that generates a more stable polymer-end radical must be used prior to the one generating a less stable polymer-end radical.[154] C_{ex} values for RAFT polymerization have been reported by Fukuda, and they are significantly different depending on the combination of CTA and monomer.[155] Although the C_{ex} values for PSt polymer-end radical to PSt−SCSMe CTA and PMMA−SCSMe CTA are similar (220 vs 420), those for PMMA polymer-end radical to PMMA−SCSMe CTA (homopolymerization) and PSt−SCSMe CTA (block copolymerization) are very different (40 vs 0.83). These results are consistent with the fact that the block copolymerization of MMA to a PSt−SCSMe macro CTA is less successful than that of St to the PMMA−SCSMe macro CTA.

The origin of the monomer dependence of the kinetic parameters between TERP and RAFT is not clear at this moment. However, the difference in the DT mechanism between TERP and RAFT, as shown in Figure 3, namely, a concerted-like single-step pathway in TERP and a stepwise mechanism involving stable intermediate radical in RAFT, may well contribute to the observed differences.

4. Diheteroatom Compounds in Organoheteroatom-Mediated LRP

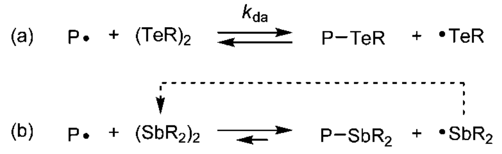
4.1. Ditellurides and Distibines

Addition of ditellurides and distibines in TERP and SBRP, respectively, is effective for increasing MWD control especially in methacrylate polymerization, as mentioned in the previous section.[23,32] The effects of dimethylditelluride and tetramethylstibine in TERP and SBRP, respectively, are summarized in Table 4. Although MWD control was moderate for TERP of MMA using CTA **Te-7** ($M_w/M_n = 1.37$), it increased with the addition of 1 equiv of dimethyl ditelluride ($M_w/M_n = 1.15$).[26] CTA **Te-11** also showed high MWD control in the polymerization of MMA in the presence of dimethyl ditelluride.[23] The same effect on MWD control was observed under both first- and second-generation conditions.[27] Although ditellurides react with radical species generated from the azo initiator to form a CTA (Scheme 4d), the efficiency is low.[26] In addition, ditellurides are virtually inert to monomers and do not initiate new polymer chains.[156] Therefore, the M_n of PMMA is determined by the ratio of monomer/CTA. PMMAs of M_n's up to 80 000 were prepared in a controlled manner by the addition of 1−2 equiv of ditelluride. A catalytic amount of ditelluride is sufficient when the degree of polymerization is low, but substoichiometric-to-excess amounts of ditelluride are usually used.

Table 4. Effect of Dimethylditelluride and Tetramethylstibine on MMA Polymerization by TERP[23,26] and SBRP[32]

CTA	additive	(equiv)	MMA (equiv)	yield (%)	M_n	M_w/M_n
Te-7	none	0	100	74	8600	1.37
	$(MeTe)_2$	1.0	100	98	9600	1.15
Te-11		1.0	100	92	9700	1.18
		1.0	200	83	16200	1.14
		2.0	500	79	36300	1.18
		2.0	1000	83	79400	1.14
Sb-4	none	0	100	100	11000	1.24
	$(SbMe_2)_2$	0.1	100	87	8600	1.05
		0.5	100	74	6600	1.06
		1.0	100	70	6400	1.08
		0.1	500	69	34700	1.05
		0.1	1000	75	74200	1.08
		0.1	2000	63	122900	1.15

Scheme 16. Deactivation/Activation Mechanism of Polymer End Radical P by (a) Ditelluride and (b) Distibine

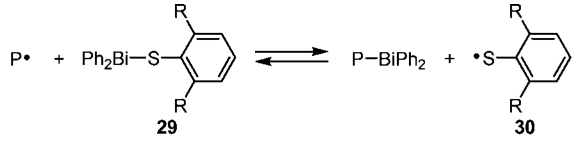


Organostibine CTAs are reasonably effective for the controlled polymerization of methacrylates, but the addition of a catalytic amount of tetramethylstibine further improves the MWD control. For example, SBRP of MMA using **Sb-4** proceeded with reasonable MDW control ($M_w/M_n = 1.24$), and that in the presence of 0.1 equiv of tetramethylstibine afforded PMMA with highly controlled structures ($M_w/M_n = 1.05$). The addition of further distibine, on the other hand, had virtually no effect on the MWD control, and significant rate retardation of the polymerization was observed. In addition, the M_n's were slightly lower than the theoretical values, presumably due to in situ formation of the CTA via the reaction shown in Scheme 4c. PMMAs of higher molecular weights ($M_n = 34\,700−122\,900$) and very narrow MWDs ($M_w/M_n = 1.05−1.15$) were prepared by increasing the ratio of MMA to **Sb-4** in the presence of 0.1 equiv of tetramethyldistibine. It is worth mentioning that the use of a tiny amount of distibine is effective (0.1 equiv to the CTA and $10^{-3}−10^{-5}$ equiv to the monomer) for achieving a high M_n and MWD control.

Ditellurides and distibines are also effective for increasing the MWD control in St polymerization, but their synthetic advantages have not been well-established.[23,114] Addition of ditelluride has a negative effect on the polymerization of acrylates, and significant rate retardation has been observed.[26]

Kinetic studies have revealed that polymer-end radicals are effectively deactivated by ditelluride via a homolytic substitution reaction to form the dormant species (Scheme 16a).[114] The second-order rate constant (k_{da}) for the deactivation of PSt polymer-end radical by dimethylditelluride is $3.4−6.8 \times 10^5$ M^{-1} s^{-1}, the value of which is ca. 100 times faster than the rate constant of DT (k_{ex}) of PSt polymer-end radical with PSt dormant species, which is identical to the deactivation rate constant of PSt polymer-end radical to the

Scheme 17. Deactivation/Activation Mechanism of Polymer End Radical P by Thiobismuthine 29



a: R = 2,6-dimesitylphenyl (Mes), **b**: R = H

corresponding dormant species (Table 3). k_{da} for the deactivation of PMMA polymer-end radical by dimethylditelluride is $1.2-2.4 \times 10^5$ M^{-1} s^{-1}, the value of which is also 40−80 times faster than the DT rate constant k_{ex} of PMMA polymer-end radical by PMMA dormant species.

The addition of dimethylditelluride also increases the activation rate of organotellurium dormant species.[114] The apparent second-order activation rate constant (k^{app}) of the PSt dormant species due to the addition of ditelluride in St polymerization is 0.2 M^{-1} s^{-1}. The k^{app} of PMMA dormant species in MMA polymerization is 8.8 M^{-1} s^{-1}. Control experiments suggest that these rate enhancements originate from the activation of an organotellurium dormant species by the tellanyl radical, and this reaction regenerates a polymer end radical and a ditelluride. This is the first experimental evidence for the occurrence of a homolytic substitution reaction of tellurium-centered radicals with organotellurium compounds, though this type of reaction has often been proposed.[73] Despite the observed high reactivity toward the activation of dormant species, the tellurium-centered radicals show low reactivity toward addition reactions to alkynes and alkenes.[156] Thus, the tellanyl radical generated from ditelluride does not initiate polymerization. If it did, the observed high controllability would not be realized. These seemingly conflicting reactivities of tellurium-centered radicals also play crucial roles in the control of MWD in TERP in the presence of ditellurides.

Though there are no kinetic studies on the effects of distibines in SBRP, the increased MWD control in the presence of distibine can also be ascribed to the higher efficiency of the deactivation of the polymer-end radical by distibine via a homolytic substitution reaction (Scheme 16b). The effect on the control using distibine is more noticeable than ditelluride, and this may be attributed to the higher reactivity of distibine than ditelluride, as in the DT reaction of polymer-end dormant species (Table 3).[32] The observed rate retardation in the presence of distibine is likely to shift the equilibrium from the polymer-end radical to the dormant species. This shift is probably due to the low reactivity of the dimethylstibanyl radical compared to that of an organostibine dormant species. In such a case, the stibanyl radical may dimerize to a distibine.

4.2. Thiobismuthines

Dibismuthines cannot be used as an additive for BIRP due to their low thermal stability.[157] However, diphenyl(2,6-dimesitylphenylthio)bismuthine **29a** is an effective additive to increase MWD control especially in the synthesis of high molecular weight polymers (Scheme 17).[158]

For example, BIRP of St (1 000 equiv) using CTA **Bi-1** proceeded with reasonable MWD control ($M_w/M_n = 1.21$) and high monomer conversion. However, a black precipitate appeared in the reaction mixture, indicating the loss of organobismuthine polymer end. The same polymerization in the presence of **29a**, on the other hand, afforded colorless PSt with a narrow MWD ($M_w/M_n = 1.11$). Both low and high molecular weight PSts with M_n's in the range of $1.0 \times 10^4-2.0 \times 10^5$ and narrow MWDs ($M_w/M_n = 1.07-1.15$) were synthesized by adding a catalytic amount of **29a** to the CTA. The addition of sterically less demanding **29b** in BIRP of St also afforded a colorless PSt, but the polymerization was less controlled ($M_w/M_n = 1.27$) than that in the presence of **29a**.

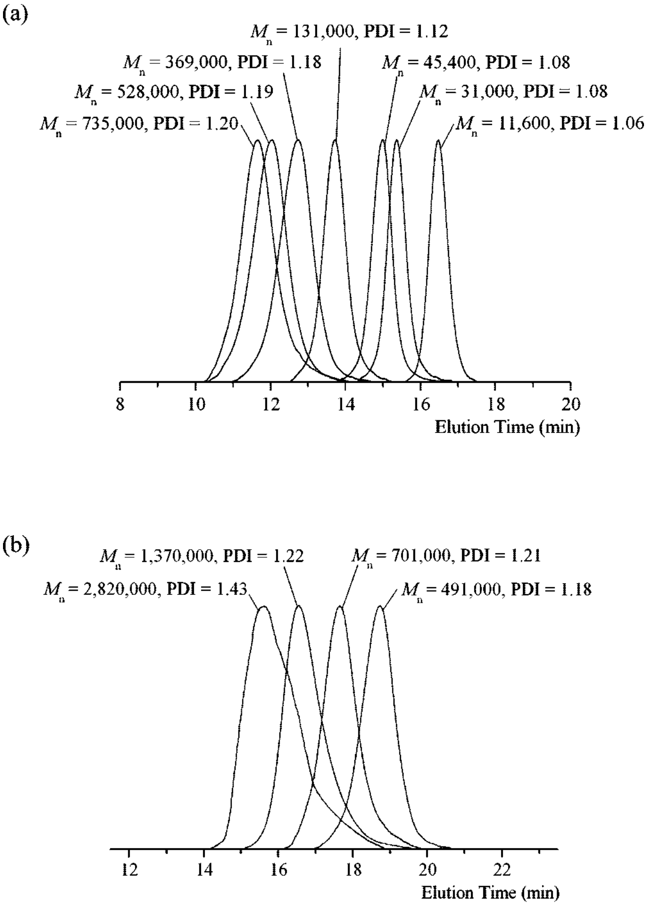


Figure 4. GPC traces of PBA samples prepared by varying the BA/Bi-**1** ratio in the presence of **29a** measured by GPC columns with exclusion limits of (a) 2×10^6 and (b) 2×10^7. Reprinted with permission from ref 158. Copyright 2009 American Chemical Society.

The effects of **29a** were more remarkable in BA polymerization than in St polymerization, and PBAs with M_n's in the range of $1.2 \times 10^4-2.8 \times 10^6$ and narrow MWDs ($M_w/M_n = 1.06-1.43$) were prepared under mild thermal conditions. The GPC traces of all of the PBAs were unimodal, and the peak maxima shifted to higher molecular weights as the targeted molecular weight increased (Figure 4). A PBA with an M_n of 1.4×10^6 and a narrow MWD ($M_w/M_n = 1.22$) was obtained at 47% monomer conversion when 20 000 equiv of BA was employed. Moreover, a PBA with an M_n of 2.8×10^6 was obtained at 41% monomer conversion when 50 000 equiv of BA was employed. Although the MWD was slightly large ($M_w/M_n = 1.43$), it is still acceptable.

A significant drawback of LRP is the synthesis of high molecular weight polymers because the polymer-end radicals are always subject to irreversible termination reactions.[159] Only a few examples have been reported for the synthesis of ultrahigh molecular weight polyacrylates and polymethacrylates with M_n's exceeding 1×10^6 and with narrow MWDs: RAFT[160] and ATRP[161,162] under high-pressure

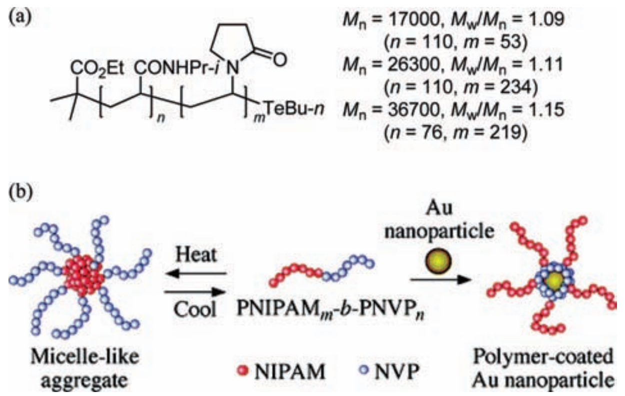


Figure 5. (a) Chemical structure of thermoresponsive diblock copolymer PNIPAM-*block*-PNVP and (b) schematic illustration of the micellization of the block copolymer as a function of temperature and the formation of a polymer-coated gold nanoparticle. Reprinted with permission from ref 24. Copyright 2007 American Chemical Society.

conditions, single-electron transfer LRP using a copper catalyst,[51] and ATRP under mini-emulsion conditions.[163] Therefore, BIRP in the presence of **29a** provides a new route to structurally well-defined ultrahigh molecular weight polymers.

The role of thiobismuthine **29a** is to react reversibly with the polymer-end radical to generate an organobismuthine dormant species and 2,6-dimesitylphenylthiyl radical **30a** (Scheme 18).[164] Chain-termination reactions involving the polymer-end radicals and loss of the bismuthanyl polymer end group do not occur in this reaction. The bulky 2,6-dimesitylphenyl group attached to the sulfur atom may prevent the addition of thiyl radicals to the vinyl monomers generating a new polymer chain, as thiyl radicals are reactive toward alkenes.[165] Since thiyl radicals are highly reactive toward organobismuthines,[135] the liberated thiyl radical **30a** would react with the orgnobismuthine dormant species to regenerate the polymer end radical P and **29a**.

5. Synthesis of Functional Polymers by TERP

5.1. Thermosensitive Micelles

Yusa and co-workers have reported the synthesis of diblock copolymers composed of PNIPAM and PNVP and their solution properties in water.[24] PNIPAM is a representative thermosensitive polymer and has a lower critical solution temperature (LCST) in water,[166] and PNVP is a water-soluble polymer.[167,168] Therefore, the block copolymers reversibly form micelles in water depending on the solution temperature (Figure 5).

The synthesis was achieved by treating PNIPAM organotellurium macro CTA ($M_n = 10\,900$, $M_w/M_n = 1.09$), which was prepared from **Te-2** and NIPAM in DMF with 100% monomer conversion, with NVP (300 equiv) in the presence of AIBN. The blocking reaction proceeded cleanly, and the desired diblock copolymer formed with 76% monomer conversion and a narrow MWD ($M_n = 36\,700$, $M_w/M_n = 1.15$). By changing the amount of each monomer, diblock copolymers with different block lengths were also prepared in a controlled manner ($M_n = 17\,000-26\,300$, $M_w/M_n = 1.09-1.11$) (Figure 5a).

Heat-induced association of the diblock copolymers was confirmed by using ^{1}H NMR, turbidity, and light scattering studies as a function of temperature. The diblock copolymer dissolves in water as a unimer below the aggregation temperature (T_a), but it starts to aggregate near the LCST of PNIPAM. T_a is a function of the chain length of each polymer block, and it becomes lower as the block length of PNVP becomes shorter. On the other hand, the T_a becomes higher as the block length of PNIPAM becomes shorter. Each block copolymer reversibly forms spherical core−corona micelles above T_a with unique aggregation numbers (300−27 000) depending on the block lengths of each segment.

Although there have been a number of reports concerning the synthesis of thermoresponsive block copolymers containing PNIPAM segment,[169−171] this is the first example of the synthesis of diblock copolymer composed of PNIPAM and PNVP. Since PNVP is a water-soluble and biocompatible polymer, this block copolymer is a good candidate for several biological applications, such as in thermosensitive drug delivery vehicles.[172]

The same diblock copolymer encapsulates gold nanoparticles in water via coordination of the PNVP block to the gold particle, as schematically shown in Figure 5b.[173] The polymer-coated gold nanoparticles show a temperature-dependent color change of the solution from pink to bluish-purple above the LCST of PNIPAM determined on the basis of the surface plasmon band. The polymer-coated gold nanoparticles may be separately dissolved in water when the temperature is below the LCST for the PNIPAM block. However, they may associate with each other due to hydrophobic interactions between the dehydrated PNIPAM blocks at temperatures above LCST, inducing a color change. This phenomenon may be applied to colloidal sensors.

5.2. Polymer Monoliths

Kanamori and co-workers have reported that TERP of 1,4-divinylbenzene in the presence of poly(dimethylsiloxane) and 1,3,5-trimethylbenzene gave macroporous cross-linked polymeric gels (Figure 6a).[174] Well-defined macroporous monolithic dried gels with bicontinuous structures on the micrometer scale were obtained after removing poly(dimethylsiloxane) and 1,3,5-trimethylbenzene by simple washing and drying (Figure 6b). Inside the skeletons that comprise the macroporous structure, "skeletal pores" with various sizes on the nanometer scale were found. The controlled pore formations are based on polymerization-induced phase separation by spinodal decomposition in the course of the homogeneous network formation during LRP. An unreactive polymeric agent present in solution during the polymerization induces spinodal decomposition during gelation to give a well-defined bicontinuous porous structure. Pore size and volume can be independently controlled by changing the starting composition.[175]

Conventional free-radical polymerization in the presence of a "porogen", which is usually a poor solvent for the network-forming components and induces phase separation, is widely used for the preparation of porous polymeric materials (polymer monoliths).[176−178] Polymer monoliths thus prepared have been applied especially as liquid-phase separation or reaction media.[179,180] However, fine-tuning of the pore properties, such as pore size, volume, and morphology, is relatively difficult because the pores are formed in-between segregated microgel particles that aggregate at random. Since the more homogeneous macroporous morphology with a bicontinuous structure obtained from spinodal decomposition will improve liquid transport throughout the media, liquid-

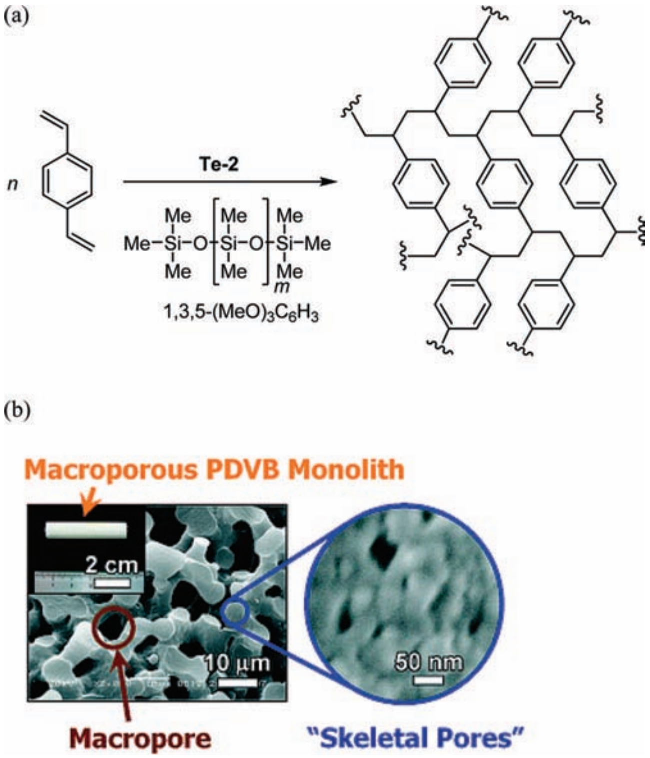


Figure 6. (a) Synthesis and (b) morphology of polydivinylbenzene (PDVB) gel prepared by using TERP of 1,4-divinylbenzene. Reprinted with permission from ref 174. Copyright 2009 American Chemical Society.

phase applications, such as chromatography and catalyst supports, are expected.

The same group has recently reported the synthesis of rigid cross-linked polyacrylamide monoliths with well-defined macropores derived from *N*,*N*-methylenebis(acrylamide) by using TERP accompanied by spinodal decomposition with polyethylene oxide as a porogen.[181] They are promising materials with highly hydrophilic polyacrylamide surfaces and have enough strength to withstand the surface tension arising from repetitive swelling and drying, which is inevitable in many applications. Kanamori has also reported the synthesis of polymer monoliths with controlled pore properties by using NMP of 1,4-divinylbenzene[182] and ATRP of 1,3-glycerol dimethacrylate.[183] Therefore, the synthesis of polymer monoliths with controlled pore sizes is not limited to TERP. However, the synthetic advantages of TERP, such as high functional compatibility and high versatility of polymerizable monomer families, should be beneficial for the future design of new monoliths with various functionalities.

5.3. Adhesives, Dispersants, and Compatibilizers

Otsuka Chemical Co. recently announced that they had started selling several adhesives prepared by using TERP (http://chemical.otsukac.co.jp/advanced/about01.html). Although detailed polymer compositions and chain lengths are not shown, control of MWD and the distribution of the cross-linking functionality of the polymer is the key for improving the properties. For example, a model random copolymer was formed by TERP with an M_w of 581 600 with a narrow MWD ($M_w/M_n = 1.24$), whereas a control polymer prepared by conventional radical copolymerization had a broad MWD ($M_w = 703\,800$, $M_w/M_n = 3.44$). A model adhesive prepared from the model polymer by cross-linking reaction had about 10 times stronger holding power than a control adhesive prepared from the control polymer, although they had similar adhesive powers. The properties of adhesives, such as the adhesive power and the tack, are easily tuned by changing the composition of functional groups and/or chain lengths. Otsuka Chemical Co. has also succeeded in the development of polymer compatibilizers and pigment dispersants consisting of block copolymers prepared by TERP.

6. Conclusion

Degenerative transfer polymerization using organotellurium, organostibine, and organobismuthine compounds, namely, TERP, SBRP, and BIRP, are versatile and robust methods for the preparation of structurally well-controlled macromolecules. Characteristic features of these methods include wide applicability to the polymerization of a variety of monomer families, high functional group compatibility, and a strong ability for the syntheses of block copolymers and end-modified polymers. These features clearly demonstrate that TERP, SBRP, and BIRP could rival current LRP methods for the preparation of functionalized macromolecules with well-defined structures, although more work is needed to clarify the full scope of these methods.

One potential disadvantage of these methods for practical applications may be the instability of the CTAs toward oxygen, and care should be taken in handling and manipulating them. Therefore, the development of oxygen-resistant CTAs or new conditions applicable to air-stable heteroatom compounds is clearly needed. The nature of the heteroatoms determines the stability and reactivity of each CTA and the level of control of each LRP method. Because an in-depth understanding is still lacking, the factors affecting the reactivities of each element must be determined in order to design new heteroatomic CTAs having superior properties to those of the current CTAs. Further efforts are also clearly needed to overcome the scientific and technical problems hindering industrial applications and creating complex functional macromolecules, which may exhibit functions similar to those of enzymes.

7. Acknowledgments

The author deeply appreciates the contributions of collaborators and co-workers whose names appear in the references. The author also gratefully acknowledges the financial support of a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, and Sports, the Japan Science and Technology Agency, the Mitsubishi Science Foundation, the Toray Science Foundation, and the Nagase Science Foundation.

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CR9001269