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Organotellurium-Mediated Radical Polymerization (TERP)

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1. INTRODUCTION

Controlled radical polymerization, also known as living radical polymerization, has made significant advances during the last three decades and has revolutionized the development of polymeric materials.[1,2] While atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization (RAFT) are the most popular methods, the present authors have independently developed organotellurium-mediated radical polymerization (TERP) and have implemented it in society through industry-academic collaborations.[3–6] TERP fulfills five important technological requirements, which are the keys to its success: 1) high versatility for applicable monomers with different reactivities, 2) high compatibility toward polar functional groups, 3) high flexibility in copolymer synthesis, 4) high diversity in end group transformations, and 5) high reliability in largescale synthesis. In this article, the features of TERP related to 1–4) will be discussed. Until recently, controlled radical polymerization was limited to synthesizing polymers with linear structures.

However, the authors have recently succeeded in synthesizing hyperbranched polymers with controlled structures by developing monomers that selectively induce branching. This result will also be discussed. The controlled radical polymerization methods reported so far cannot completely prevent the termination reaction. Therefore, it should be noted that IUPAC recommends not using the term “living radical polymerization” for this method but instead using the term reversible deactivation radical polymerization (RDRP).[7]

2. POLYMERIZATION MECHANISM AND POLYMERIZATION CONDITIONS

The key mechanism of RDRP is reversible radical formation from a radical precursor *P*-X (*P* = polymer, X = capping group or atom), called the dormant species (**Figure 1a**).[2,3] A P radical generated from the dormant species reacts with a monomer to form a chain-elongated P radical, which is then deactivated to a dormant species. This is different from the formation of dead polymers by the termination reaction in conventional radical polymerization in that the dormant species can regenerate radicals again after its deactivation. In other words, the propagating end is “living” in the form of the dormant species. The equilibrium is heavily shifted to the dormant species, which reduces the concentration of *P* radicals. Thus, the probability of the termination reaction occurring is significantly reduced (but not completely eliminated, as noted earlier). Furthermore, if the deactivation occurs faster than or as fast as the propagation reaction, all polymer chains grow at approximately equal rates. The molecular weight of the resulting polymer is predetermined by the monomer/chain transfer agent (or initiator) ratio with low dispersity (narrow molecular weight distribution), which is a characteristic feature of a living polymerization.

Two mechanisms are known to realize the equilibrium shown in **Figure 1a**: the dissociation-combination (DC) mechanism (**Figure 1b**) and the degenerative chain transfe (DT) mechanism (**Figure 1c**). In the DC mechanism, the formation of *P* and X radicals by C-X homolysis is the activation step, and the recombination of the formed radical pairs is the deactivation step. In the DT mechanism, on the other hand, the substitution reaction between a *P* radical and a dormant species results in simultaneous deactivation of the P radical and activation of the dormant species.

For example, ATRP proceeds by the DC mechanism (a high-valent metal formed by the reduction of a dormant species, e.g., Cu(II)X2, is the X-radical equivalent), and RAFT proceeds by the DT mechanism. TERP proceeds predominantly by the DT mechanism, but the DC mechanism can also be involved[8,9] depending on the polymerization conditions for TERP.

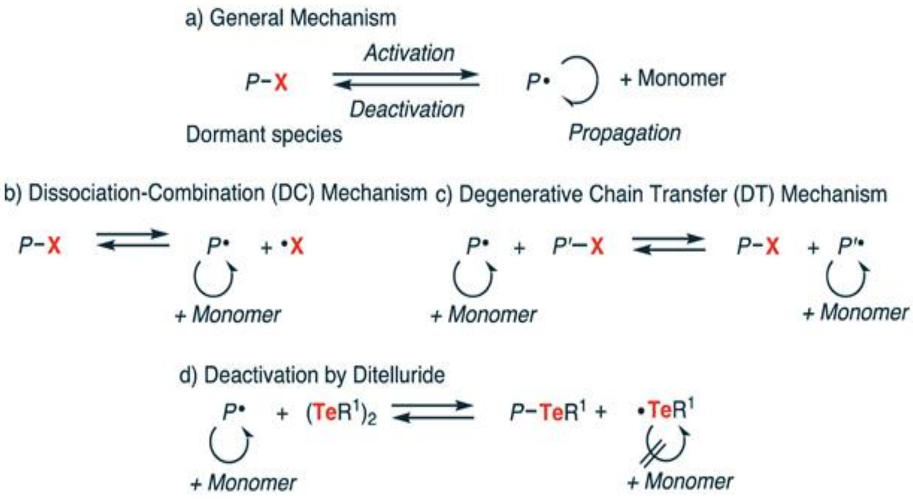


Figure 1. a) General mechanism of RDRP, b) DC mechanism, c) DT mechanism, and d) mechanism involving ditelluride. *P* and *P*' stand for polymer and **X** for capping group; in TERP **X** = TeR1.

TERP can be carried out under three conditions: 1) a thermal condition by heating the TERP chain transfer agent (CTA) and monomers,[4,10] 2) a thermal condition by adding an azo initiator to condition 1),[8] and 3) a photo condition by irradiating a mixture of TERP CTA and monomers with light.[11,12] In condition 1), the initiating radicals are supplied by thermal dissociation of the C-Te bond of the dormant species, i.e., the DC mechanism, and polymerization proceeds mainly by the DT mechanism. The condition is suitable for polymerizing styrene and dienes, which have a low C-Te bond dissociation energy for the dormant species and a slow propagation rate.[4,11] Under condition 2), thermal decomposition of the azo initiator provides the initiating radicals, and polymerization proceeds only by the DT mechanism. This condition is highly versatile since the polymerization temperature can be set according to the decomposition temperature of the azo initiator and the reactivity of the monomer. Under condition 3), the initiating radicals are supplied by photocleavage of the C-Te bond. Since it is important to keep a low concentration of radicals, low-intensity light, such as that from an LED with a power of several watts, is suitable.[11,13] In addition, polymerization can be carried out at low temperatures, even below room temperature, and the progress of polymerization can be controlled by turning the light on and off (**Figure 2**). Therefore, this condition has unique advantages.

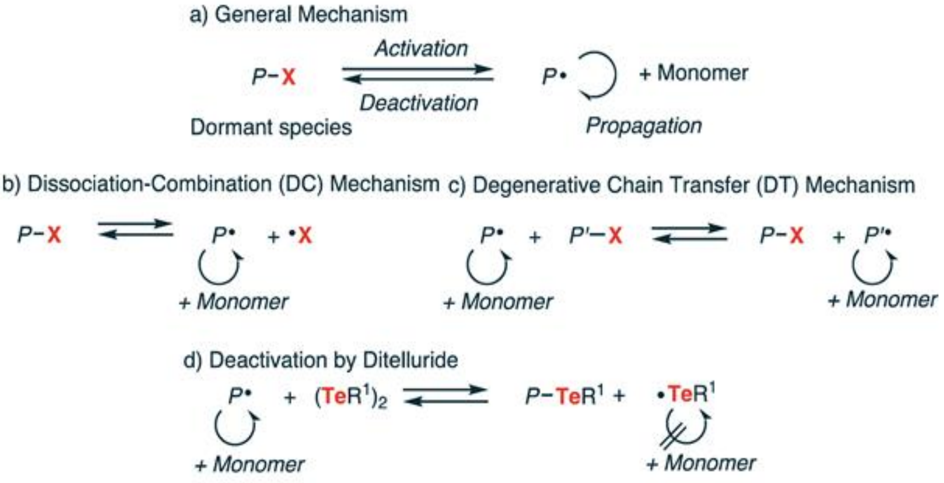


Figure 2. Time control of polymerization by turning the light on and off

Note that the addition of a ditelluride is necessary to achieve high polymerization control in the polymerization of methacrylates.[10] Ditelluride reacts with the propagating P radical and deactivates it to the dormant species about 100 times faster than the DT mechanism (Figure 1d).[14] In addition, the generated tellanyl radical (R1Te·) is virtually unreactive toward the monomer while reacting with the dormant species to regenerate the *P* radical and the ditelluride. This fast and selective deactivation allows for better control of polymerization in methacrylate polymerization. In contrast, polymerization of acrylate is greatly inhibited by the presence of ditelluride, since activation of the polyacrylate-dormant species by the tellanyl radical is insufficient.

3. TERP CHAIN TRANSFER AGENT (CTA)

The structures of typical CTAs of TERP are shown in Figure 3. To achieve controlled polymerization, the initiation reaction must occur as fast as or faster than the propagation reaction. Since the radicals generated from CTAs **1**, **2**, and **3** are stable and sufficiently reactive toward the monomer, these CTAs generally give excellent results.[4,10,15] Among these, **1** having a polymethacrylateend structure is the most frequently used CTA. On the other hand, **4** with a polyacrylic-end structure[16] and **5** with a poly(vinyl ether)-end structure[17] are less efficient than **1** for control because the radicals generated from them are less stable than that from **1**. However, polymerization using these CTAs can be reasonably well controlled. The substituent effect of R1 on tellurium is small.[18] Aromatic groups such as phenyl group show higher reactivity for the DT reaction than alkyl groups such as methyl and butyl groups, and thus, in principle, exhibit better polymerization control. However, since the difference in control is small, there is no need for extra caution in most cases. As for the ester substituent R2, methyl esters and ethyl esters (**1a**, **1b**) are often used in homogeneous polymerization.

On the other hand, by condensing the carboxylic acid of **1c** with various amines, various CTAs with functional groups can be synthesized, such as **6** with amino acids and multivalent CTA **7**. This allows for variation in the initiating end structure of the polymer (**Figure 3b**).[19] Furthermore, treatment of **1c** with a base, such as NaOH, generates water-soluble carboxylate **1d** for use in emulsion polymerization in water.[20] In addition, by immobilizing the CTA using silyl groups, **1e**[21] can be used for graft polymerization from a surface. **1~5** can be synthesized in a single step by tellanyl anions and corresponding organohalides. They are sensitive to oxygen but can be stored for a long time under an inert atmosphere. CTAs **1**, **2**, and **3** are now available from TCI, and we hope that this will expand the use of TERP.

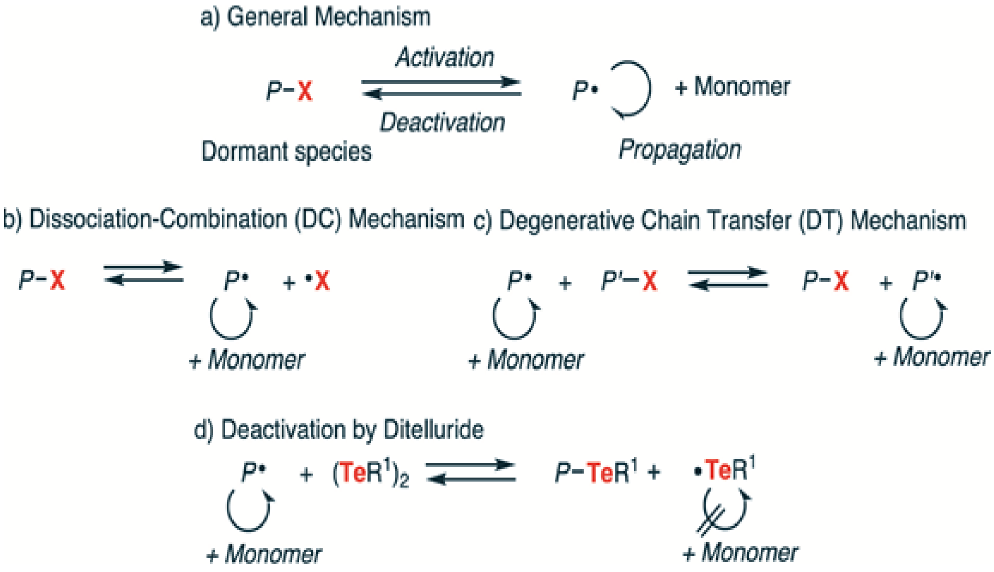


Figure 3. Chemical structures of a) typical CTAs and b) functional CTAs for TERP

4. POLYMER ENGINEERING WITH TERP

4.1 Synthesis of homopolymers under homogeneous Polymerization

The most significant feature of TERP is its high monomer versatility: monomers with different reactivities, from conjugated to non-conjugated monomers, can be polymerized in a controlled manner using the same CTA, resulting in a polymer with a molecular weight (*M*n) close to the theoretical value with narrow dispersity (*Đ*) (**Figure 4**).[4,8,10,11,21–28] This is the advantage of TERP, in contrast to ATRP and RAFT where the ligand of the catalyst and CTA must be appropriately selected according to the monomer. The monomer conversion usually reaches over 90%, which is also synthetically attractive. Even in the polymerization of ethylene, in which activation of the dormant species is most difficult, polymerization can be controlled under low ethylene pressure and mild thermal conditions.[27]

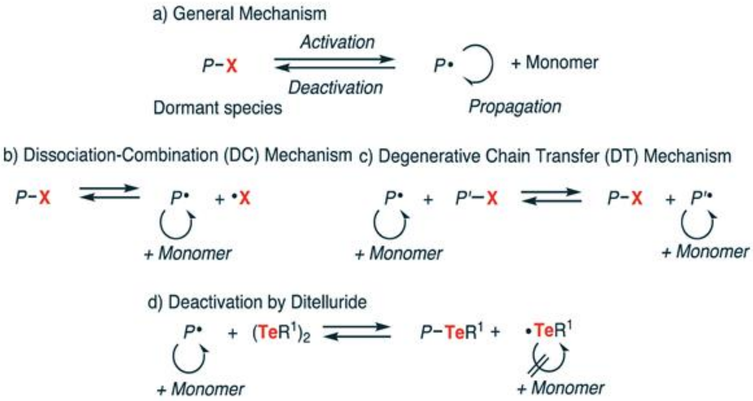


Figure 4. Typical examples of polymerization using TERP. The structure of the monomers and the number-average molecular weight (*M*n) and dispersity (*Đ*) of the resulting polymers are shown. *Ditelluride is added in the polymerization of methacrylate monomers.

TERP has excellent functional group compatibility, including a highly reactive isocyanate group.[8,11,16,25,29] Bronsted and Lewis acids are also compatible. Therefore, simultaneous control of stereochemistry and molecular weight is possible by TERP of acrylamides in the presence of a lanthanide triflate as a catalyst, which is effective for stereo-controlled polymerization of acrylamides (**Figure 5**).[30-32] The advantages of TERP have also been demonstrated in the synthesis of polymer monoliths and surface-initiated polymerization.[33–35]

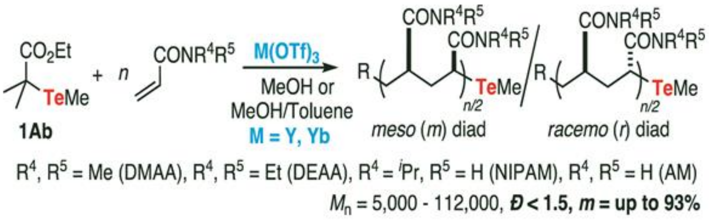


Figure 5. Dual control of stereochemistry and molecular weight

4.2. Emulsion TERP

TERP can be carried out by emulsion polymerization in water due to the high tolerance of organotellurium compounds to water. Microemulsion polymerization with hydrophobic TERP CTAs, such as **1B**,[36,37] polymerization-induced self-association (PISA) with macro-CTAs having hydrophilic oligomeric chains,[38–40] and *ab initio* emulsion polymerization using water-soluble CTA **1d** in the presence of a surfactant have been reported (**Figure 6**).[20,41] In the latter case, polymerization proceeds by irradiation with either low-intensity visible light or by thermal conditions. Traditionally, photopolymerization has been considered difficult because light does not penetrate emulsions. We believe that photo-induced emulsion polymerization becomes possible due to the high permeability of visible light and high photosensitivity of the organotellurium compounds.[19]

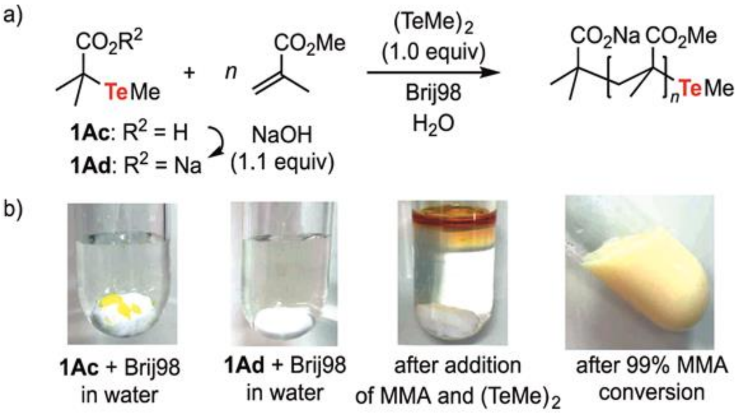


Figure 6. a) Polymerization of MMA by emulsion polymerization and b) solution behavior before and after polymerization *Brij® is a trademark of Croda Americas LLC.

Since the emulsion polymerization condition suppresses the termination reaction due to the segregation effect, high-molecular-weight polymers can be synthesized using emulsion TERP. In particular, the use of **1Dd** and **1Ed** with hydrophilic ethylene glycol groups instead of **1Ad** with a Me group as the R1 group is effective, and polymerization of butyl acrylate (BA)[41] and styrene[42] gives the corresponding homopolymers with *M*n over 500,000 and 1,000,000, respectively, and low dispersity. The high monomer conversion (>90%) is observed even in the synthesis of these ultra-high molecular weight polymers, and this is advantageous in practical use, including the synthesis of block copolymers shown in the next section.

4.3. Synthesis of Copolymers.

RDRP can be used to synthesize block copolymers by sequential addition of monomers, similar to other living polymerization methods, but the synthesis usually suffers from the order of monomer addition. However, TERP has fewer limitations than other RDRP methods. For example, when two monomers are selected from the representative conjugated monomers, i.e., styrene, acrylate, and methacrylate, all possible AB-diblock copolymers can be synthesized regardless of the order of monomers used.[10] The synthesis of block copolymers from conjugated and non-conjugated monomers is usually highly challenging due to the different reactivities of the monomers. However, even such a combination is possible with TERP, and several block copolymers have already been synthesized,[22,43][25] including a block copolymer consisting of *N*-vinylformamide (NVF) and *N*,*N*-dimethylacrylamide (**Figure 7a**).[28] Since the formyl group of PNVF can be selectively hydrolyzed under mild conditions, copolymers with polyvinylamine as a block can be synthesized without affecting the amide groups.[28]

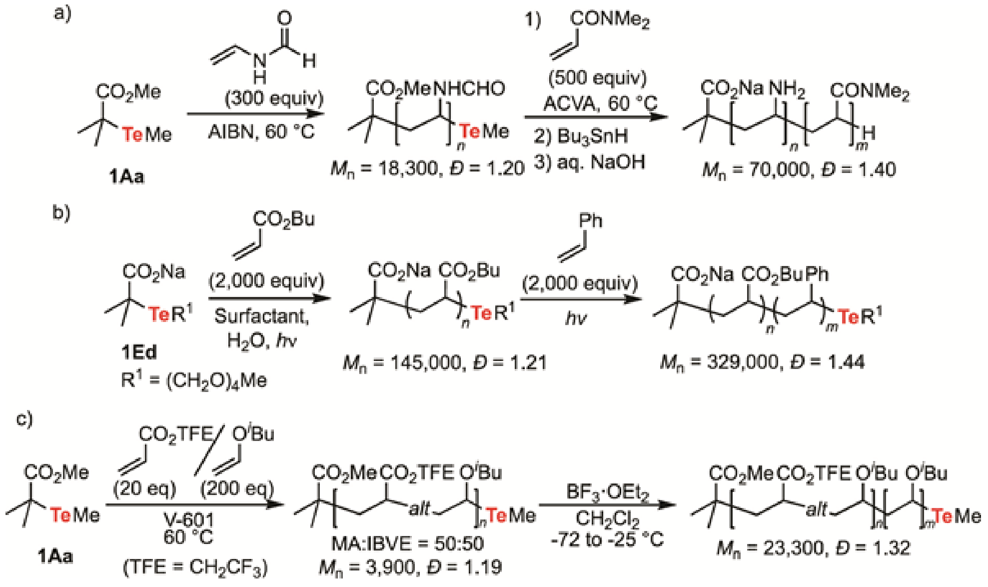


Figure 7. Typical results of block copolymer synthesis: a) block copolymer composed of conjugated and non-conjugated monomers, b) block copolymer with high molecular weight, and c) block copolymer with conversion of mechanism from radical to cationic polymerization.

High-molecular-weight polymers can be obtained not only by homopolymerization but also by block copolymerization using emulsion polymerization (**Figure 7b**).[20,41] Since the macro-CTA obtained in the first polymerization is dispersed in water as particles, there is no need to homogenize the macro-CTA and the second monomer, unlike in homogeneous conditions. Therefore, block polymerization can be started simply by adding the second monomer after the conversion of the first monomer. Vinyl ethers and α-olefins do not homopolymerize but copolymerize with acrylate monomers. TERP shows excellent polymerization control in such copolymerizations. For example, alternating copolymers with a controlled structure can be synthesized by copolymerization of vinyl ethers and acrylic monomers by using an excess amount of vinyl ethers (**Figure 7c**).[44,45]

Furthermore, since the copolymer has an alkoxy group at the propagating end, the addition of a Lewis acid, such as BF3·OEt2, initiates living cationic polymerization of the remaining vinyl ether, resulting in the formation of the corresponding block copolymer. Controlled copolymerization of α-olefins and acrylate monomers in the presence of a Brønsted acid also takes place, and the acid increases the feed of α-olefins into the copolymer.[46,47]

4.4. Convers ion of polymer ends

Since organotellurium compounds are excellent precursors not only for carbon-centered radicals but also for carbanions and carbocations, various transformations of the dormant end are possible (**Figure 8a**).[4] Such transformations usually proceed with high efficiency, thus various functional groups can be introduced at the polymer ends. The most popular reaction is the radical-mediated reduction. Not only tin hydride, a typical reducing agent,[4] but also thiols and tellurols, which are generally less efficient reducing agents, can be used due to the high reactivity of the organotellurium compounds.[48,49] The polymer end can be selectively deuterated by employing the corresponding deuterated reducing agents. The chain reaction proceeds by irradiation with low-intensity light or addition of an azo initiator. Radical-mediated allylation using allylstannane is also possible.[4] As the concentration of radicals generated from the dormant species increases with increasing light intensity, radical-radical coupling reactions take place by irradiation with high-intensity light, such as from a highpressure mercury lamp. For example, using functionalized TEMPO derivatives as the coupling partner, various functional groups can be introduced to the polymer end. [11,50–52] Diene-mediated dimerization also takes place when photo-activation of the dormant species is carried out in the presence of dienes, even those with functional groups.[53,54] For example, after coupling using a diene with hydroxy groups, the introduced hydroxy groups can be used for further synthetic transformations, such as the polymerization of lactide, giving a miktoarm polymer with a controlled structure (**Figure 8b**).

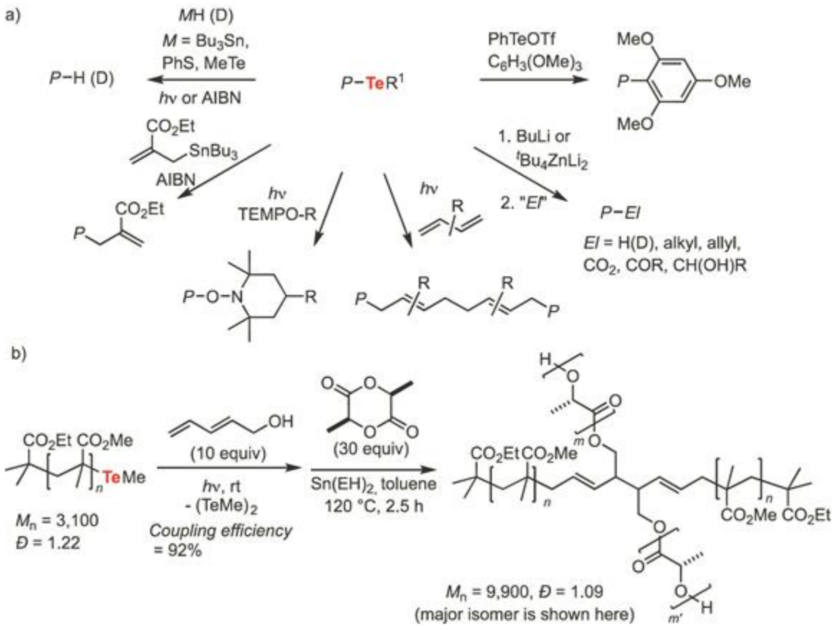
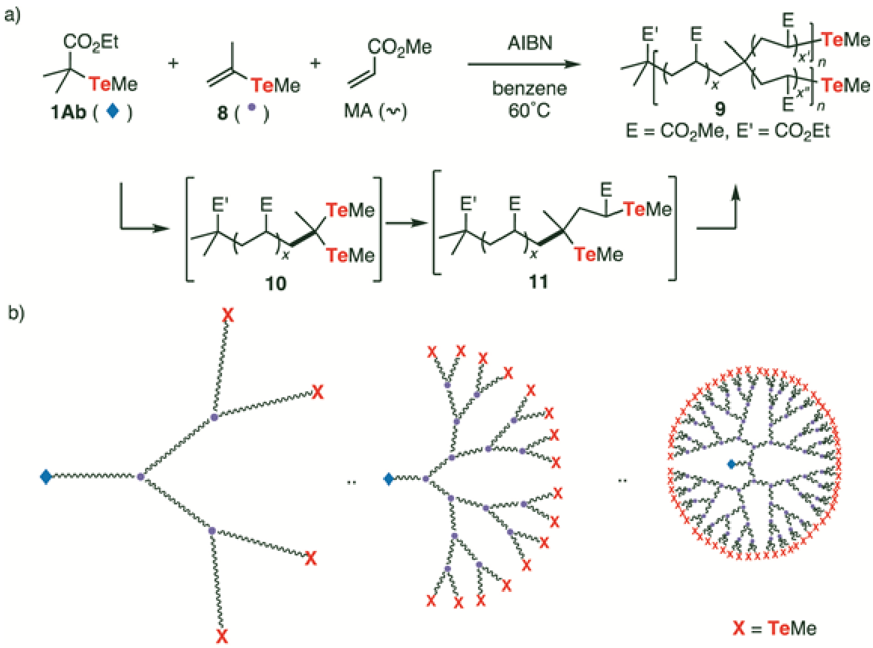


Figure 8: Versatility of polymer end group transformations. a) General schemes for conversions under radical or ionic conditions and b) synthesis of miktoarm polymer using radical coupling reactions and subsequent polymerization. *P* and "*El*" denote polymer and electrophiles, respectively.

Conversion of the dormant end to a carbanion is possible by a transmetallation reaction, even if the dormant polymers possess polar functional groups, such as poly(meth)acrylates and poly(meth)acrylamides, due to the high reactivity of the organotellurium group.[4,55,56] The resulting carbanions can react with various electrophiles, including carbonyl compounds and carbon dioxide, to introduce polar functional groups, which are difficult to introduce by radical reactions. Electrophilic activation is also possible, and the transformation using Friedel-Crafts reactions has already been reported.[57]

5. CONTROLLED SYNTHESIS OF HYPERBRANCHED POLYMERS

Hyperbranched polymers (HBPs) have characteristic properties such as smaller hydrodynamic volume, lower intrinsic viscosity, and a larger number of terminal substituents than linear polymers. Therefore, HBPs have attracted much attention in both basic and applied research.[58–61] Self-condensing polymerization using an inimer, a term coined for a monomer with an initiator function, has been used to synthesize HBPs under radical polymerization.[62–67] However, control of the threedimensional (3D) structure, including molecular weight, distribution, and branch structure, cannot be achieved except under special conditions. In contrast, the authors have developed a new method by designing vinyl telluride **8** as a branch-inducing monomer for the synthesis of HBP **9** with a controlled 3D structure (**Figure 9a**).[49]



$[\mathbf{1Ab}]_0/[\mathbf{8}]_0$	3	15	63
generation	2	4	6
M_n(theo)	41,200	39,600	34,600
M_n(SEC)	42,100	25,600	9,800
M_n(MALS)	53,700	57,300	53,900
$Đ$	1.55	1.71	1.99

Figure 9. a) Synthesis of HBP using vinyl telluride 8 and b) ideal schematic structure of product and polymerization results (using methyl acrylate [MA] as monomer)

The key feature of **8** is that the strength of its C-Te bond changes significantly after it has reacted as a monomer to form **10**. Since generation of the vinyl radical from **8** is unfavorable, **8** does not serve as an initiator. However, after **8** has acted as a monomer, the resulting **10** can generate stable alkyl radicals. Sequential activation of the C-Te bonds from **10** leads to the branched structure in **9** through intermediate **11**. Indeed, theoretical calculations suggest that the C-Te bond dissociation energies for **10** and **11** are about 50 kJ mol-1 lower than that for **8**. A characteristic feature of this method is that the number of branches and the branching density can be controlled arbitrarily by changing the ratio of CTA (**1**),**8**, and acrylate monomers. For example, controlling the “generation,” which is the hierarchical structure present in dendrimers, can be controlled by the **8**/**1** ratio, whereas the molecular weight can be controlled by the monomer/**1** ratio.

Figure 9b shows the ideal schematic structure of HBPs when varying the **8**/**1** ratio to 3, 15, and 63. The table in **Figure 9b** also summarizes the polymerization results when setting the monomer/**1** ratio to 500. The molecular weight determined by SEC becomes smaller than the theoretical molecular weight as the number of branches increases, while the absolute molecular weight determined by the multi-angle laser light scattering (MALS) detector is close to the theoretical value. This is consistent with the fact that the hydrodynamic volume of the polymer is reduced due to the branched structure. Note that the dispersity ($Đ$) of the synthesized HBPs has a larger value than that of linear polymers. Recent simulations have shown that this is due to the distribution of the number of branches.[68] In addition, the controlled synthesis of hyperbranched polystyrene[50] and hyperbranched MMA[69] becomes possible by changing the structure of the vinyl telluride. We are currently working to apply this method to the fabrication of polymer materials, and we hope to introduce the results in the near future.

6. SUMMARY

TERP satisfies the required technical elements to create high-value-added polymer materials at a high level. In addition, the structure-controlled synthesis of HBPs presented in the last section opens up a new possibility for using HBPs to produce polymeric materials with improved and/or new properties. We hope that TERP will become more popular in the future and contribute to society by being used to create superior functional materials.

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