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SYNTHESIS OF NOVEL BLOCK COPOLYMERS THROUGH ELECTRON TRANSFER SYSTEM BY SmI_2

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Abstract: This paper summarizes our recent efforts to offer block copolymers through the transformation reactions of a cationic growing center into an anionic one by the utilization of divalent samarium complexes. Four types of transformation reactions are described, and their scope and limitations are discussed. Several applications of these transformation reactions are also presented.

Introduction

Synthesis of block copolymers is generally performed by the sequential addition process in chain polymerizations. Especially, recent tremendous strides in living polymerization have enabled precise synthesis of block copolymers. One can facilely obtain block copolymers with desired segment ratio, controlled chain length and well-defined stereostructure only by the addition of second monomers after the first monomer-polymerization. In spite of these remarkable developments, the kind of second monomers which can be copolymerized with first monomers is strictly limited; the polymerization mechanism of the second monomer should be identical to that of the first one, in principle. Therefore, there are many restrictions of the combination of monomers in block copolymerization.

One of the techniques which can solve these problems represents the mechanism-switching of propagation ends by the adequate reactions of growing centers (Ref. 1). Appropriate design of reactions of growing centers is possible to adapt them to distinct monomers with different polymerization mechanisms. The transformation of active centers, *i.e.*, polarity inversion, requires two-electron oxidation or reduction of propagation species to take place, theoretically (Scheme 1). Although many efforts have been made to switch the mechanism of polymerization so far, direct electron transfer of growing centers had not been achieved until the use of SmI_2 as a reducing agent in these laboratories (Ref. 2b). In this paper, we describe a

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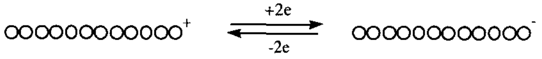
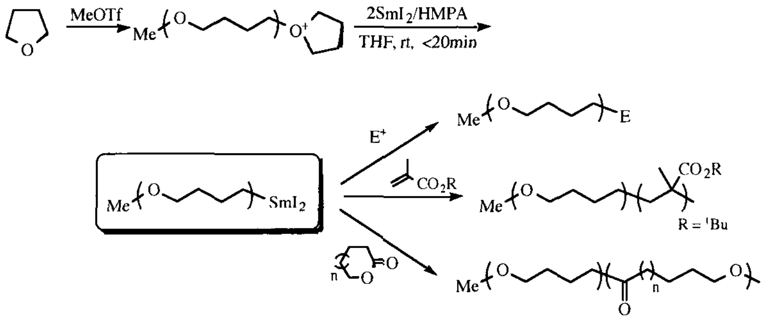
brief summary of our efforts to develop new transformation reactions of a cationic growing center into an anionic one by using divalent samariums.



(Scheme 1)

Results and Discussion

A. Direct Reduction by SmI_2. The first example for the direct reduction of the growing center of poly(THF) was achieved by using SmI_2/hexamethylphosphoramide (HMPA) system (Scheme 2) (Ref. 2b). The reaction can be easily carried out only by the addition of HMPA and then a solution of SmI_2 in THF into the solution of poly(THF). The reaction is facilely monitored by the color change of SmI_2 (Ref. 3), and the reaction completes within 20 min at room temperature. It is worthy of note that no isolation step of the prepolymer is required and that the reduction is quantitative without any serious side reactions.

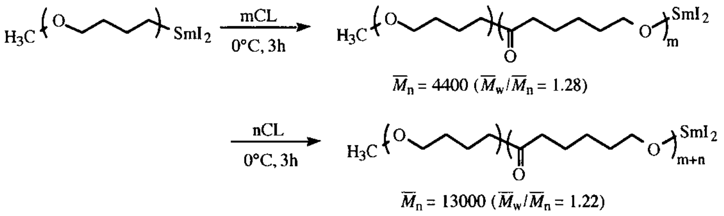


(Scheme 2)

The produced terminal alkylsamarium reacts with electrophiles including aliphatic and aromatic aldehydes and ketones. Quite high efficiency of the introduction of electrophiles is attainable. It means that the cationic polymerization is formally end-capped with electrophiles.

The terminal carbanion is also active for the polymerization of *tert*-butyl methacrylate (TBMA) giving a block copolymer of THF with TBMA (Ref. 4a, b). Of particular notes is that both the reduction of propagation center and initiation efficiency of the second monomer-polymerization are quantitative, consequently leading to the selective formation of block copolymer with narrow molecular weight distribution. Homopolymers of THF or TBMA are not detected. The polymerization of δ-valerolactone with the terminal carbanion also provides a quantitative block efficiency (Ref. 4d).

The transformation into a living anionic polymerization is also feasible. For example, the polymerization of ε-caprolactone (CL) by the terminal carbanion proceeds in a living fashion without back-biting and termination reactions (Ref. 4c). A post-polymerization experiment clearly indicated the living nature of the propagation end of the block copolymer (Scheme 3).

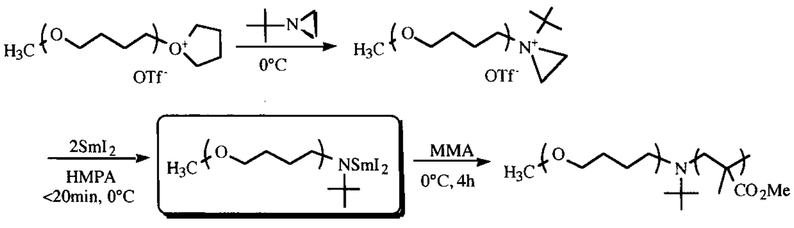


$\overline{M}_n = 4400$ ($\overline{M}_w/\overline{M}_n = 1.28$)

$\overline{M}_n = 13000$ ($\overline{M}_w/\overline{M}_n = 1.22$)

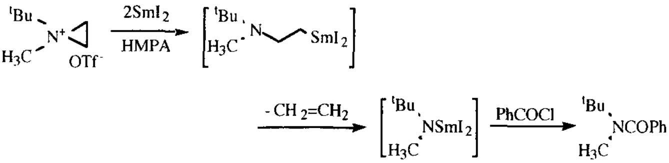
(Scheme 3)

B. Transformation into a Terminal Samarium Amide. It is unfortunate that the terminal carbanion obtained by the above-mentioned reaction cannot polymerize methacrylates except for TBMA with bulky ester groups. This limitation may render the transformation useless considering the facile modification of the nature of the polymers by varying ester functional groups of methacrylates. An alternative method, transformation into a terminal samarium amide, partly solved this problem (Ref. 5). This transformation was accomplished by the end-capping of living poly(THF) with *N*-*tert*-butylaziridine followed by the reduction under the SmI_2/HMPA system (Scheme 4).



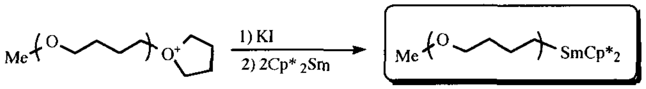
(Scheme 4)

Model reaction, *i.e.* the reduction of *N*-*tert*-butyl-*N*-methylaziridinium trifluoromethanesulfonate with SmI_2 clearly revealed that the reduction proceeds *via* the reductive cleavage of the carbon-nitrogen bond on the ring and spontaneous elimination of ethylene (Scheme 5). Although the efficiency of this transformation is not of satisfaction (within 20 %), even methyl methacrylate (MMA) undergoes the polymerization with the terminal samarium amide.



(Scheme 5)

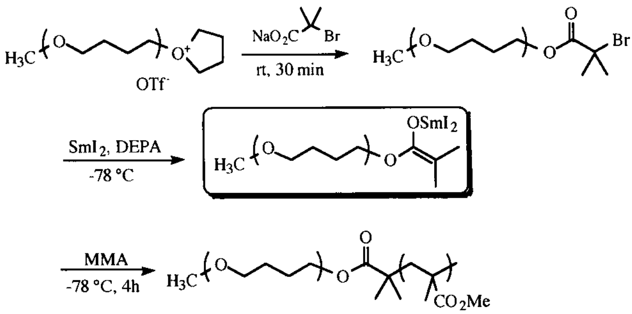
C. Transformation into a Terminal Carbanion with Bulky Counter Anion. Bis(pentamethylcyclopentadienyl)samarium ($Cp^*{}_2Sm$) serves as a reducing agent to promote some electron transfer reactions (Ref. 6). It is also well-known that trivalent lanthanide complexes with Cp* ligands exhibit high activity for the polymerization of a variety of polar monomers (Ref. 7). $Cp^*{}_2Sm$ was utilized with the motivation of expanding the availability of second monomers (Ref. 8). In contrast to the transformation induced by SmI_2, an attempt to reduce the cationic growing center of living poly(THF) with $Cp^*{}_2Sm$ resulted in a failure since the Cp*-ligand reacts with the polymer end. An end-capping of the living poly(THF) with potassium iodide before the reduction permits the formation of the desired macroinitiator (Scheme 6). Although the broadening of the molecular weight distribution after the reduction suggests the presence of coupling reaction of the macroanion with the prepolymer, ^1H NMR analyses of end groups revealed high reduction efficiency (62 %).



(Scheme 6)

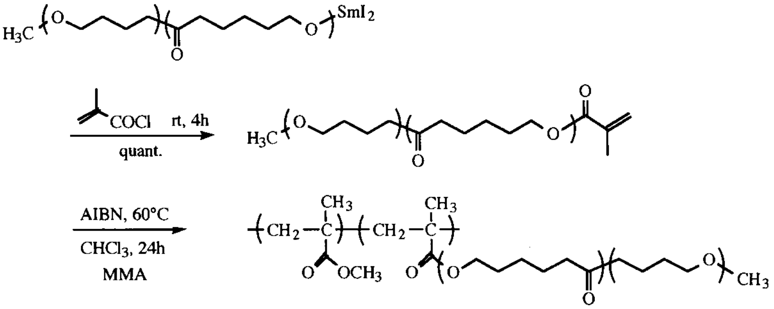
The utility of this transformation is realized by the availability of a wide range of second monomers, which is in contrast to that of the SmI_2-induced transformation. The macroanion has proven to be effective for the polymerization of MMA, ethyl, isopropyl, and benzyl methacrylates, ε-caprolactone, δ-valerolactone, and 2-oxo-1,3-dioxane. It is notable that the block copolymerization with cyclic carbonate successively proceeds whereas its polymerization with alkylsamarium ($RSmI_2$) affords a low-molecular weight polymer.

D. Transformation into a Terminal Samarium Enolate. The transformation into a terminal samarium enolate was touted as the alternative most effective method for the preparation of the block copolymer of THF with methacrylates (Ref. 9). For example, the end-capping of living poly(THF) with sodium 2-bromoisobutyrate followed by the reduction in the presence of MMA affords the block copolymer of THF with MMA in quantitative block efficiency (Scheme 7). Especially, the use of *N,N*-diethylpivalamide (DEPA) as an additive in place of HMPA provides extremely narrow molecular weight distribution. Performing this transformation offers two advantage; 1) prospects for the availability of various ring-opening polymerizable monomers as first monomers whose propagation ends cannot supply suitable active species by the reduction with divalent samarium salts and 2) the avoidance of the use of HMPA.



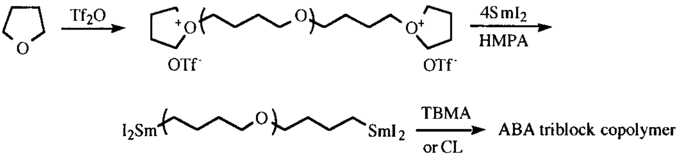
(Scheme 7)

E. Applications. The application of the SmI_2-induced transformation provides diverse unique polymer architectures. For example, the ability of the transformation to provide a living block copolymer allows the formation of a novel macromonomer which consists of two kinds of monomer with different polymerization mechanisms (Ref. 10). The radical copolymerization of the macromonomer with MMA leads to the good yield of the graft copolymer (Scheme 8).

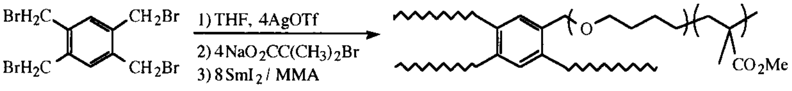


(Scheme 8)

ABA-type triblock copolymers are also facilely generated when the first-monomer polymerization is carried out with a difunctional initiator (Scheme 9). The kinetic study on the triblock copolymerization supported the formation of triblock copolymers where the observed polymerization rate was twice as large as that of the diblock copolymerization (Ref. 11a, b). In the similar way, the use of multi-functional initiator leads to star-block copolymers of THF with MMA (Scheme 10) (Ref. 11c).

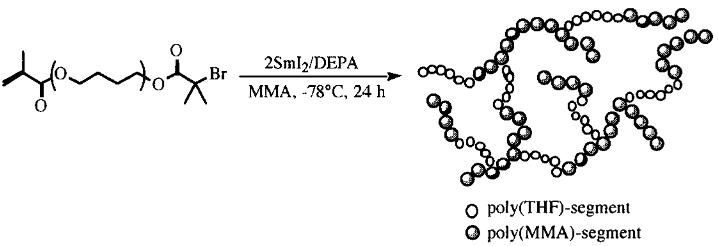


(Scheme 9)



(Scheme 10)

One of the interest applications of the transformation represents the synthesis of novel hyperbranched block copolymer. Hyperbranched or dendritic polymers have been of great interest due to their geometrically unique structure with characteristic properties in a solution and solid state (Ref. 12). All of the produced hyperbranched polymers, however, possess only one kind of polymer chain. Therefore, their properties are originated from only the geometrically unorthodox structure. The incorporation of alternative polymer segments would allow them to exhibit the properties as both hyperbranched and block copolymers. An attempt was made to synthesize this novel hyperbranched block copolymer by using the transformation technique (Ref. 13). That is, poly(THF)-macromonomer with methacryloyl group at one terminal and 2-bromoisobutyrate group at the other was synthesized, and the selective reduction of the carbon-bromine bond with SmI_2 formed poly(THF) having the polymerizable group at one polymer end and the initiation species at the other. The reduction of the macromonomer in the presence of MMA resulted in the formation of a novel hyperbranched block copolymer (Scheme 11).



(Scheme 11)

The success in the formation of the hyperbranched block copolymer is contributed by the adequate control of the reaction conditions. Methacryloyl group can undergo the reduction under the SmI_2/HMPA system (Ref. 2a), which may contribute to an irregular structure of the polymer. However, the reaction conditions employed (-78 °C, without HMPA) permits the selective reduction of carbon-bromine bond remaining the methacryloyl group intact. The tolerance of methacryloyl moiety enables it to provide regular structure of the hyperbranched block copolymer.

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