SmI_2 as a Reagent in Polymer Chemistry

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Abstract: The use of divalent samarium iodide (SmI_2) as a reducing agent has stimulated remarkable evolution in organic synthesis, which has been followed by the application of this chemistry to polymer science in the last ten years. Here, we briefly summarize the exciting developments in which SmI_2-induced electron transfer processes participate in key steps in polymerization reactions. We focus on the following systems: 1) transformation reaction from cationic to anionic growing centers by SmI_2, 2) formation of bimetallic initiator through the reductive coupling of electrophilic monomers by SmI_2, and 3) stepwise polymerization by the extension of carbon–carbon bond-forming reactions by SmI_2.

Keywords: copolymerizations · electron transfer · polymerizations · samarium · umpolung

Introduction

A recent development in organic synthesis is the application of divalent samarium iodide (SmI_2) as an excellent one-electron reducing agent.[1] The utility of this reagent is readily demonstrated by opening a few pages of a textbook on SmI_2 chemistry. There, one will find many kinds of unique reactions which are apparently inaccessible by the traditional methodologies. Nobody would doubt that these tremendous strides are due to the satisfactory but not extremely strong reducing ability of this reagent toward organic compounds ($Sm^{2+}/Sm^{3+} = -1.55$ V vs. SCE).[2] Furthermore, the reducing ability can be easily controlled by the simple addition of cosolvents such as alcohols and amides not only to accelerate the rate of reduction but to steer the reaction along specific pathways.[1] Thus active species with desired reactivity are available from the electron-transfer process of SmI_2; this provides an opportunity to establish numerous novel reactions with high selectivity and efficiency. It is also worth noting that SmI_2 is soluble in a variety of polar solvents, which is a remarkable contrast to the poor solubility of usual inorganic reducing agents. These characteristics, which are combined with facility in preparation and handling and high stability in an inert atmosphere, have led many chemists to the discovery of various SmI_2-mediated reactions in organic chemistry. These achievements, therefore, have been naturally followed by the application of SmI_2 chemistry to polymer synthesis.

One may be amazed at the fact that SmI_2 chemistry has evolved prodigiously in only these two decades; systematic study of the reactivity of SmI_2 started in just 1980![3] Reflecting this brief history, only ten years have passed since the first publication concerning the use of SmI_2 in polymer synthesis appeared in 1987.[4] Thus, the number of polymerization systems using SmI_2 is still limited. However, one can undoubtedly understand the great potential of this reagent in polymer chemistry by learning that the only access to some unique polymerizations is by the use of SmI_2. In this paper, the authors wish to briefly summarize these attractive studies on the new polymerization reactions where the electron transfer induced by SmI_2 serves as a key step.[5] SmI_2-promoted polymerizations are roughly classified into the following three types. One is the polarity inversion of a cationic growing center into an anionic one followed by polymerization of electrophilic monomers to produce block copolymers made of different types of monomers with different polymerization mechanisms. The second involves the bisinitiation of electrophilic vinyl monomers by electron transfer from SmI_2 to monomers. The last is the extension of carbon–carbon bond-forming reactions into stepwise polymerizations.

Discussion

Transformation reactions: What distinguishes electron-transfer reactions from normal ones is their ability to invert the polarity of reactants. For example, cationic and anionic species are theoretically changed in polarity by two-electron transfer into nucleophilic and electrophilic agents, respectively. This concept was applied to the polarity inversion of growing centers for chain polymerization. The strategy of

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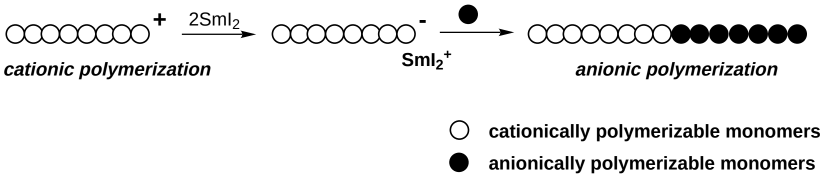
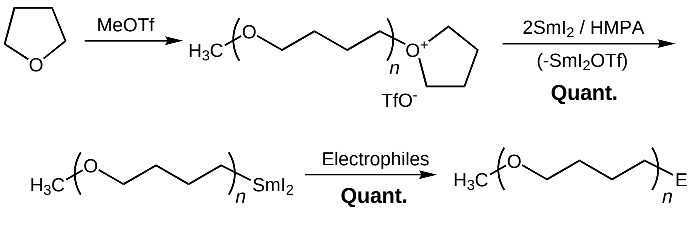
double-electron reduction of cationic growing centers by SmI_2 into terminal nucleophiles and subsequent polymerization of electrophilic monomers is schematically illustrated in Scheme 1.



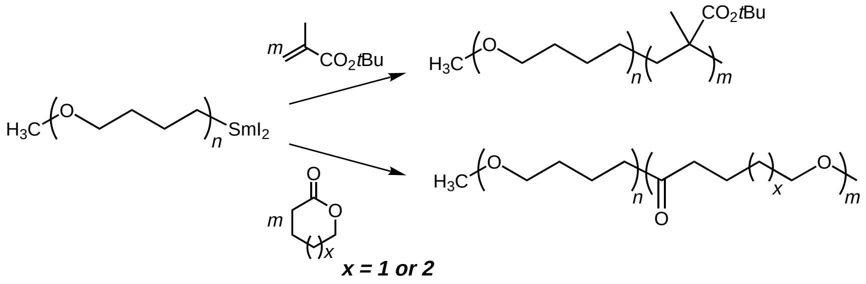
Scheme 1. Schematic representation of the SmI_2-induced transformation.

One may consider that this reaction is quite simple and readily achieved. However, the difficulty of accomplishing this reaction is demonstrated by the fact that there had been no examples for the direct reduction of growing centers until quite recently. This is not only because the stability of propagation ends of polymers is not always enough to undergo further reactions even in the case of living polymerization, but also because appropriate electron-transfer agents with mild reactivity, moderate solubility, and facility in usage have not been established. Only in 1994 was the direct double-electron reduction of the living cationic end of poly(THF) reported for the first time, utilizing SmI_2.[6] The growing center of living poly(THF) is smoothly and quantitatively reduced into a terminating carbanion by treating the living polymer with two equivalents of SmI_2 in the presence of hexamethylphosphoramide (HMPA) (Scheme 2). It should be noted that direct reduction of the cationic growing center is achieved in one pot, in contrast to the traditional methods, in which complicated multistep pathways are usually required.[7] Furthermore, the terminating carbanion reacts with typical electrophiles including aromatic and aliphatic aldehydes, aromatic ketones, and isocyanates quantitatively.[6] In other words, the SmI_2-induced transformation enables the cationic polymerization to be formally end-capped by electrophiles.



Electrophile = $PhCHO$, $PhCH_2CH_2CHO$, $PhCOCH_3$, p-$CH_3C_6H_4NCO$

Scheme 2. Double-electron reduction of the cationic living end of poly(THF) with SmI_2.



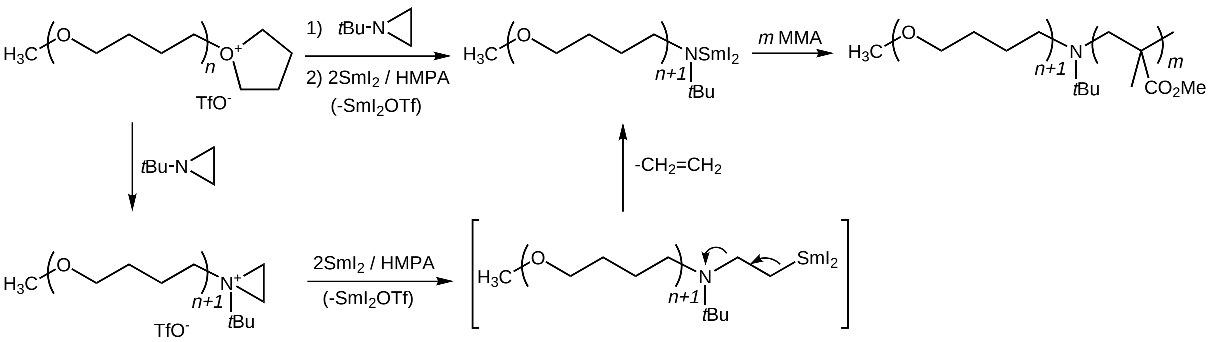
Scheme 3. Polymerization of TBMA, CL, and VL with poly(THF) macroanion.

The ability of alkylsamarium ($RSmI_2$) to initiate the polymerization of electrophilic monomers provides block copolymers of the cationic polymerizable monomer (THF) with anionic ones (Scheme 3). For example, polymerization of *tert*-butyl methacrylate (TBMA) by the poly(THF) macroanion gives the block copolymer of THF with TBMA.[8] It should be noted that the initiation efficiency of TBMA polymerization with the macroanion is quantitative. Thus, contamination with homopolymers of THF or TBMA is negligible, and the block copolymer is attainable with relatively narrow molecular weight distribution and controlled unit ratio. Block copolymers of THF with ε-caprolactone (CL)[9] or δ-valerolactone (VL)[10] are also selectively accessible by a similar procedure. Additionally, ABA-type triblock copolymers can be obtained simply by using trifluoromethanesulfonic anhydride as an initiator for the THF polymerization.[11]

The terminating carbanion generated by the above-mentioned reaction is not adequate for the polymerization of methacrylates other than TBMA because the attack of the terminal carbanion toward the carbonyl carbon of methacrylates dominates over the conjugated addition in the case of sterically undemanding methacrylates.[12] Therefore, it is necessary to control the reactivity of the terminal nucleophile to fit the second monomer. Again, the capability to generate various active species constitutes a salient feature of electron-transfer reactions. This concept was combined with recent

Abstract in Japanese:

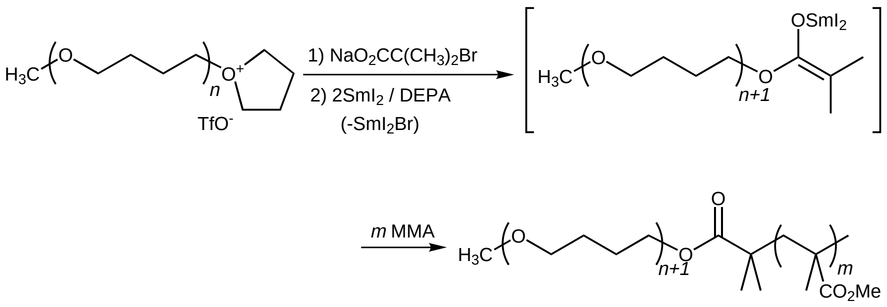
近年、二価のヨウ化サマリウムを用いる有機合成が顕著な発展を遂げた。これに伴い高分子合成においても、ヨウ化サマリウムを積極的に用いることで従来の手法では達成できない重合反応が数多く開発されるに至っている。本総説では、二価のヨウ化サマリウムによって開始される電子移動反応をキーステップとする新しい重合反応を以下の分類に従って紹介する。1) カチオン重合からアニオン重合への生長末端変換反応　2) 電子不足オレフィンの還元カップリングによる二官能性開始剤の生成　3) ヨウ化サマリウムによる炭素−炭素結合形成反応の逐次型重合への応用



Scheme 4. Transformation of the cationic growing center of living poly(THF) into a terminal samarium amide.

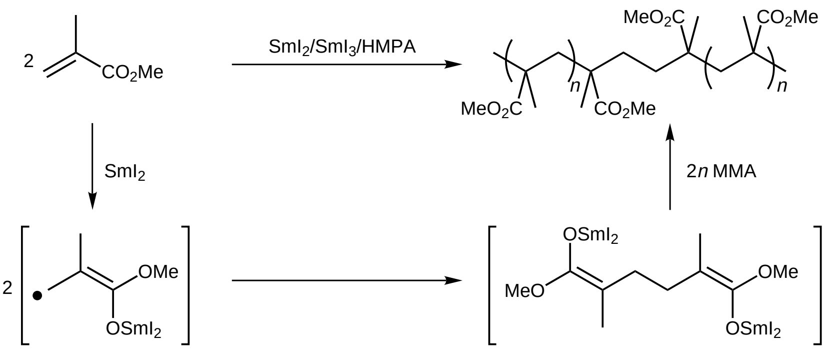
progress where, in the lanthanide-catalyzed polymerization, the appropriate choice of ligands or counterions of lanthanide metals greatly expands the availability of monomers.[13] Namely, a simple modification of the reduction enabled the creation of poly(THF) with samarium amide at the terminal, which is suitable for the polymerization of methyl methacrylate (MMA) (Scheme 4).[14] The formation of terminal samarium amide is achieved by treatment of living poly(THF) with *N-tert*-butylaziridine before the reduction with SmI_2. The reductive cleavage of the carbon–nitrogen bond of the terminal aziridinium moiety and the subsequent elimination of ethylene gives the samarium amide.

The diversity of active species generated by the electron-transfer process of SmI_2 also permits the living end of poly(THF) to be transformed into a stabilized carbanion, samarium enolate, which mimics the propagation group of poly(MMA) (Scheme 5).[15] This can be accomplished by the end-capping of living poly(THF) with sodium 2-bromoisobutyrate followed by the reduction of the carbon–bromine bond with SmI_2 in the presence of *N,N*-diethylpivalamide (DEPA). The initiation efficiency of MMA is quantitative; thus, a block copolymer of THF with MMA with quite narrow molecular weight distribution is selectively obtained without any formation of the homopolymer of THF or MMA. This reaction is the most effective method for the production of well-defined block copolymers of THF with methacrylates. The block copolymer of THF with 2-hydroxyethyl methacrylate, an amphiphilic block copolymer, is also readily available by the polymerization of 2-*tert*-butylsiloxyethyl methacrylate and acidic hydrolysis of the siloxy group.[16] Considering that cationic polymerizations, especially those of cyclic monomers, can be terminated with alkali metal carboxylates, this method will expand the range of applicability of the first monomers whose propagation ends cannot supply suitable active species by direct reduction with SmI_2. Furthermore, this reaction excludes the use of the hazardous additive, HMPA.



Scheme 5. Transformation of the cationic growing center of living poly(THF) into a terminal samarium enolate.

Bifunctional initiators: From the viewpoint of polymer synthesis, active species with plural initiation sites serve as multifunctional polymerization initiators. In spite of the long history of the concept of bifunctional initiators introduced by Szwarc,[17] metallic bisinitiators are relatively uncommon. A traditional route to bimetallic initiators is the use of highly reactive reducing agents such as sodium naphthalenide. Electron transfer between a metal naphthalenide and a monomer gives an anion radical, which dimerizes to a dianion. Although this kind of dianion works well for the bisinitiation of nonpolar monomers such as styrene and dienes, it cannot be applied to polar monomers. This is simply because the extremely high reactivity of reducing agent induces side reactions that inhibit the precise polymerization.[18] The mild and controllable reducing ability of SmI_2 very nicely circumvented these restrictions; some active species formed through the electron-transfer processes by SmI_2 have proven to be useful as new bifunctional initiators. A typical example was given by the bisinitiation of methacrylates under the SmI_2/HMPA system.[12] Poly(MMA) with propagation ends at both terminals is obtained in good yield. It is interesting that the addition of a small amount of SmI_3 as a common cationic salt drastically improves the living nature of the polymerization (Scheme 6). For example, the observed molecular weight of poly(MMA) becomes much higher than the calculated one when the polymerization is conducted without SmI_3.[12] In fact, in the presence of SmI_3, the quantitative formation of poly(MMA) with predicted molecular weight and low polydispersity is attainable.[19] An alternative divalent samarium salt, Cp^*_2Sm, is also known to serve as an excellent reducing agent which leads to the bisinitiation of methacrylates.[20, 21] However, in the case of Cp^*_2Sm, the isolation of the dianion and strict conditions with rigorous exclusion of air and water are required for the well-controlled formation of polymer because of the instability of the dianion. The advantage of



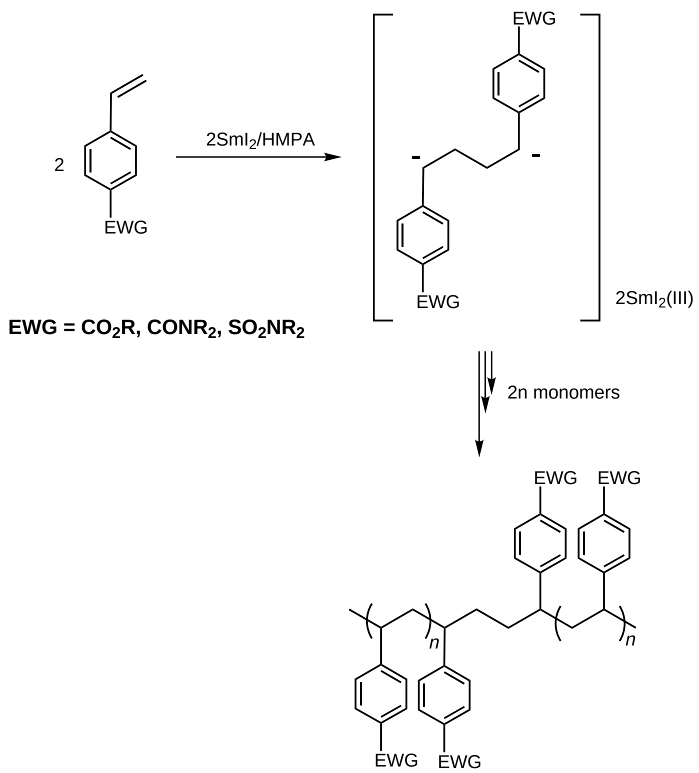
Scheme 6. Polymerization of methacrylates by the SmI_2/HMPA system.

SmI_2 is the convenient access to well-defined polymethacrylates by the simple Grignard technique.

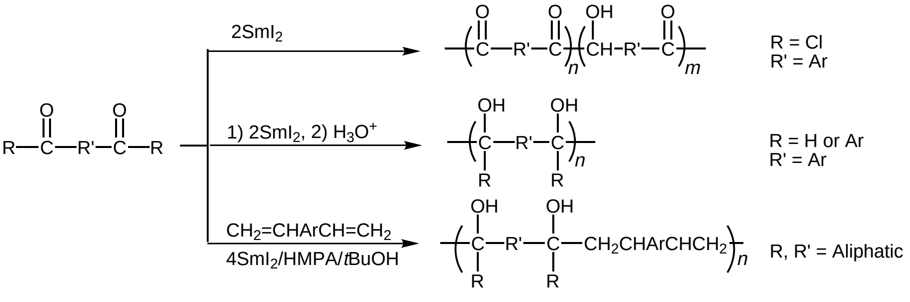
The reducing ability of the SmI_2/HMPA system also enables the reduction and consequential bisinitiation of styrene derivatives having electron-withdrawing groups such as amides,[22a] esters,[22b] and sulfonamide groups[22c] (Scheme 7). An example is the polymerization of *N*,*N*-dimethyl-4-ethenylbenzamide (EWG = $CONMe_2$) with SmI_2, giving a polymer with quite narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n = 1.04$) in quantitative yield.[22a] Isolation of the homocoupled products of *N*,*N*-diethyl-4-ethenylbenzamide (EWG = $CONEt_2$) is possible; this gives evidence of the in situ formation of bimetallic initiators. The effect of the addition of a common salt, SmI_3, is also observed on the polymerization of ester-substituted styrenes. For example, without SmI_3, quantitative consumption of *tert*-butyl 4-ethenylbenzoate is not attainable (up to 70%), and the polymer produced exhibits broad polydispersity ($\overline{M}_w/\overline{M}_n = 1.36$). In contrast, simply the addition of SmI_3 leads to the quantitative formation of the polymer with quite narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n = 1.05$).[22b]

Stepwise polymerizations: As described in the literature, the use of SmI_2 often gives unorthodox reaction patterns which cannot be achieved by conventional methods. The idea of extending these bond-forming reactions to polymer synthesis is a simple way to construct new materials with novel main chain structures.

Most of these stepwise polymerizations involve the C–C bond formation of active species which are generated through the reduction of carbonyl compounds with SmI_2 (Scheme 8). Brandukova et al. have demonstrated an example of the stepwise polymerization, which includes a reductive homocoupling polymerization of aromatic dicarboxylic acid chlorides to poly(1,2-diketone)s.[4, 23] The polymer produced contains both 1,2-diketone and 1-hydroxyketone units, and their ratio depends on the reaction conditions. In some cases, poly(1,2-diketone)s with high molecular weight ($\overline{M}_w = 25000$) are attainable. The relatively high solubility and thermal stability of the polymer provide a prospect of their utilization as heat-resistant materials. The presence of reactive groups in the polymer main chain, that is the 1,2-diketone unit, permits the polymer to be transformed into quinoxaline-containing polymers by reaction with *o*-diamines. The analogous homocoupling polymerization of aromatic dialdehydes produces poly(1,2-diol)s with moderate molecular weight.[24]



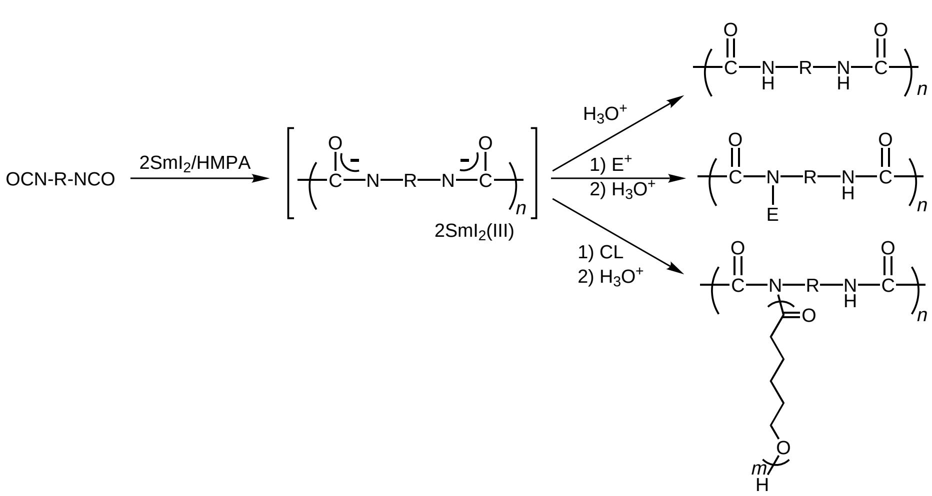
Scheme 7. Polymerization of substituted styrenes by the SmI_2/HMPA system.



Scheme 8. SmI_2-induced stepwise polymerizations of bifunctional carbonyl compounds.

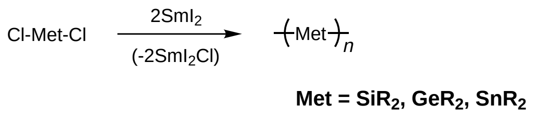
Poly(alcohol)s with a tertiary alcohol moiety in the main chain are accessible by the cross-coupling polymerization of diketones with bifunctional unsaturated compounds (Scheme 8).[25] The present polymerization also involves the reduction of the carbonyl group into a ketyl radical that attacks the olefinic carbon of diolefins. The interest of this polymerization lies in the formation of a tertiary alcohol segment in the main chain. In spite of the great utility of poly(alcohol)s, especially poly(vinyl alcohol)s as hydrophilic materials, the unavoidable oxidation of secondary alcohol units often causes serious problems in practical use. Furthermore, the 1,2-diol units present as contaminants in the main chain are subject to oxidation with eventual cleavage of the main chain. However, the polymers produced by this method are resistant to oxidative conditions;[25c] no changes in molecular weight of the polymer are found after the treatment with ceric ammonium nitrate (CAN), whereas a serious decrease in the molecular weight of poly(vinyl alcohol) is observed under similar conditions.

Of particular interest is the formation of a reactive polymer with anionic sites along the polymer main chain by the reductive coupling polymerization of aromatic diisocyanates. Treatment of aromatic diisocyanates with SmI_2 in the presence of HMPA affords a polymer with aromatic oxamide structure after protonation (Scheme 9).[26a] Without acidic work-up, novel reactive polymers with nucleophilic active sites on the polymer backbone are attainable. Subsequent reactions of this poly(anion) with electrophiles such as alkyl and allyl halides, aliphatic isocyanates, acid chlorides, and aldehydes are feasible, leading to substituted poly(oxamide)s in a one-pot procedure.[26b] In contrast to the poor solubility of the parent unsubstituted poly(oxamide)s, the substituted polymers exhibit excellent solubility in organic solvents, which offers opportunities for further reactions and processes. Synthesis of poly(oxamide)s soluble in water as well as having characteristic properties as polyelectrolytes is also possible by reaction with 1,3-propane sultone.[26c] Furthermore, the poly(anion) is available as a novel polymeric initiator; the polymerization of electrophilic monomers including CL, MMA, and TBMA provides the corresponding graft copolymers in one pot.[26d]



Scheme 9. Reductive homocoupling polymerization of diisocyanates.

Another example for the utilization of SmI_2 in stepwise polymerization is the preparation of polymers containing the Group 14 elements such as poly(silane)s, poly(stannane)s, and poly(germane)s (Scheme 10).[27] The utility of SmI_2 in the production of these materials lies in the fact that these polymerizations can be conducted under much milder conditions than those of traditional synthetic methods including the Wurtz-type condensation (Kipping method). Although the molecular weights of the polymers are not always high, the extremely mild conditions of the polymerization sugest that the method may supplant the Kipping method.



Scheme 10. Reductive homocoupling polymerization of Group 14 metal halides.

In this paper, we have described several examples for the applications of SmI_2 for polymer synthesis. SmI_2-catalyzed polymerizations that do not involve electron transfer and the use of other divalent samarium salts in polymer synthesis have not been discussed[28] although they are also nice approaches to new polymeric materials. The versatility of SmI_2 in making unique polymerization reactions accessible may lead many chemists to recognize the great potential of this reagent to provide novel methodologies in polymer chemistry as well as in organic synthesis. In addition, the recent success in the development of a catalytic cycle of SmI_2[29] promises to further expand its utility as a polymerization catalyst in stepwise polymerizations. In SmI_2, polymer chemists possess a new and powerful tool. The combination of fresh ideas and elegant use of this tool will allow access to a variety of unexpected polymer architectures.

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