

Diiodosamarium based polymerisations †

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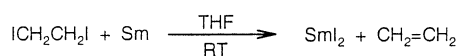
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1 Introduction

In recent years the utilisation of organometallic lanthanide complexes, which contain metals in low oxidation states, for polymer synthesis has gained a lot of attention.^{1–4} Out of all lanthanide metals, only Eu, Yb, and Sm have readily accessible divalent states under ambient reaction conditions. Sm(II) is the most reactive of these divalent lanthanides because of its reduction potential (Sm(III) + e → Sm(II); –1.5 V vs. normal hydrogen electrode (NHE))⁵ and its large size which makes it difficult to stabilise by steric saturation. One of the Sm(II) compounds, diiodosamarium (SmI₂), has rapidly become one of the most popular reducing agents in organic synthesis due to its facile synthesis,⁶ its good solubility in many organic solvents and its ability to reduce a wide range of functional groups. A 0.1 M solution (dark blue) of SmI₂ can be easily synthesised by the slow addition of diiodoalkanes to Sm metal in tetrahydrofuran (THF), as reported by Girard *et al.*⁶ (Scheme 1). Previous



Scheme 1

methods for the preparation of SmI₂ were tedious, requiring the reduction of trivalent lanthanide halides by hydrogen or by thermal dissociation.⁷ The role of SmI₂ as an excellent one-electron reducing agent in organic synthesis is well reviewed in the literature.^{8–12} Tailoring these reactions for high selectivity and efficiency is possible by simply changing the solvent or solvent system. Motivated by the versatility of SmI₂ chemistry for low molecular weight compounds, polymer chemists have tried to expand its horizon by utilising its unique properties for the synthesis of high molecular weight polymers. The range of

polymer reactions involving SmI₂ is continuously increasing since its first use in polymer synthesis by Korshak *et al.*¹³ SmI₂ can be used either as a catalyst or as a reagent in the synthesis of polymers, and these polymers cover a wide range of classes including functionalised poly(*p*-xylylene)s, polyamides, polyesters, vinyl polymers *etc.* Many polymer syntheses, which are inaccessible/difficult by conventional routes, can be easily carried out using SmI₂ under mild reaction conditions further emphasising the great potential of this reagent in providing unique methods of synthesis in polymer chemistry. In general, electron transfer reactions based on SmI₂ require more than stoichiometric amounts of this reagent (except the Meerwein–Ponndorf reduction and the Tishchenko reaction) thus limiting, to some extent, the synthetic value of this reaction. But recently the establishment of a catalytic cycle involving SmI₂ has increased the prospects of its use in polymer synthesis and it is expected to make these reactions economically attractive as well. Based on the literature available till now, SmI₂ based polymer reactions can be categorised as follows (Scheme 2):

- A) SmI₂ as a reagent:
 - 1) Reductive coupling polymerisations
- B) SmI₂ as a catalyst:
 - 1) Oxidative addition reactions
 - 2) Vinyl polymerisations
 - 3) Ring-opening polymerisation of cyclic esters and carbonates
- C) SmI₂ induced transformations

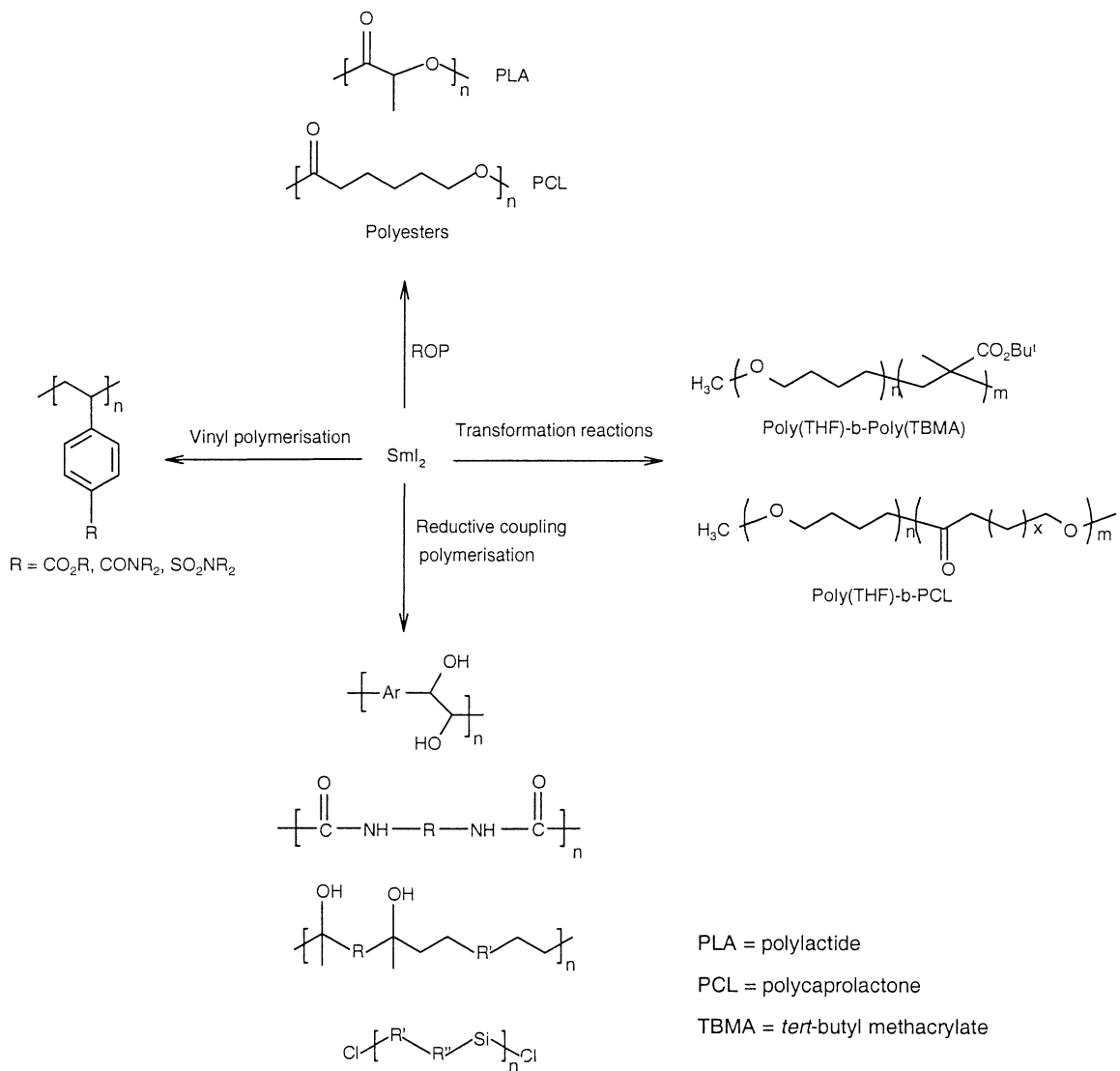
This article reviews the use of SmI₂ both as a catalyst and as a reagent in polymer synthesis.

2 Reductive coupling polymerisations

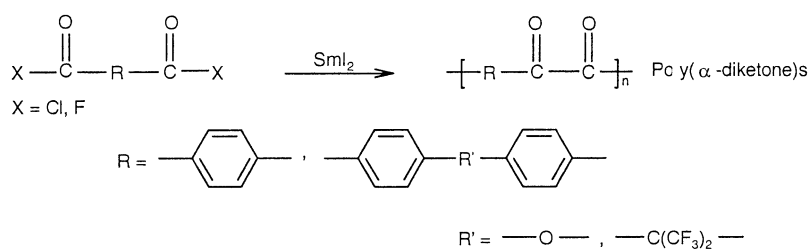
2.1 Poly- α -diketones

Sm(II) compounds have been established as useful reagents in organic synthesis for promoting reductive coupling reactions to generate C–C bonds because of their good selectivity, high yields, and mild reaction conditions.^{11,14–15} Interestingly, these electron transfer reactions are radical-anionic in nature. The ability to produce high molecular weight poly- α -diketones, by reacting SmI₂ with acid dihalides, was accomplished for the first time by Brandukova *et al.*^{16–17} (Scheme 3). The resulting polymers were amorphous with high glass transition temperatures (250–290 °C). These polymerisation reactions were based on the formation of the corresponding α -diketones by reaction of SmI₂ with acid monohalides. In these reactions, the intermediate radical anion, formed by the reaction of SmI₂ with acid halides, decomposes to an acyl radical, which can either combine with another acyl radical to form α -diketones (route 1, Scheme 4) or can undergo further reduction by SmI₂ to yield the corresponding anion. The anion can then, in turn, react with a second molecule of acid halide to produce the α -diketone (route 2, Scheme 4). By detailed studies designed to probe the reaction

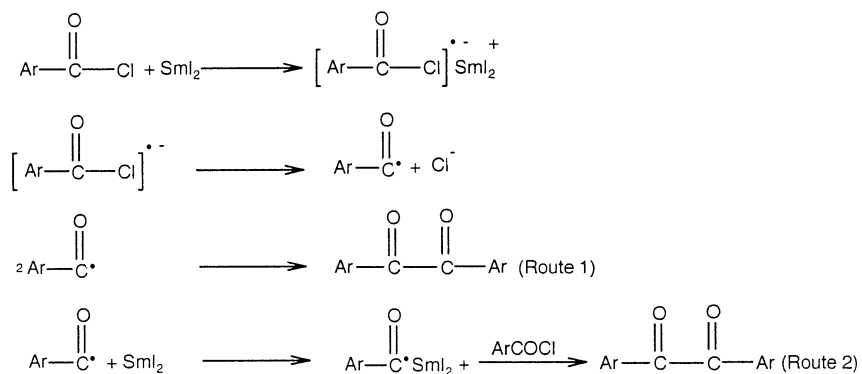
† Dedicated to Professor Walter Heitz on the occasion of his 70th birthday.



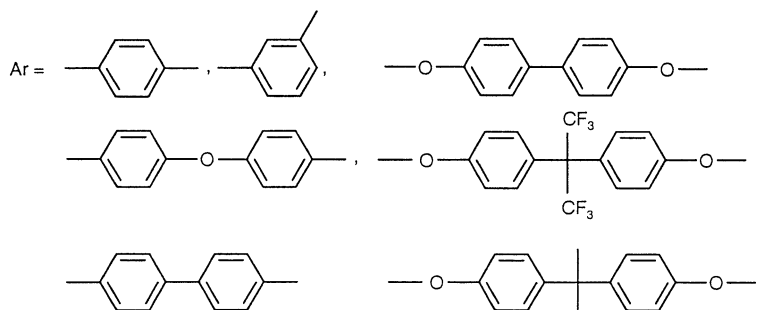
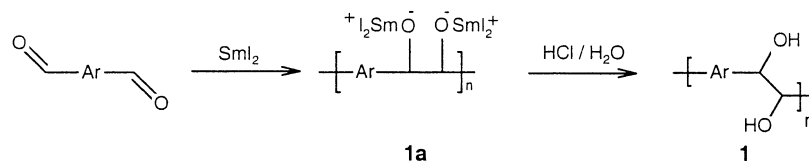
Scheme 2



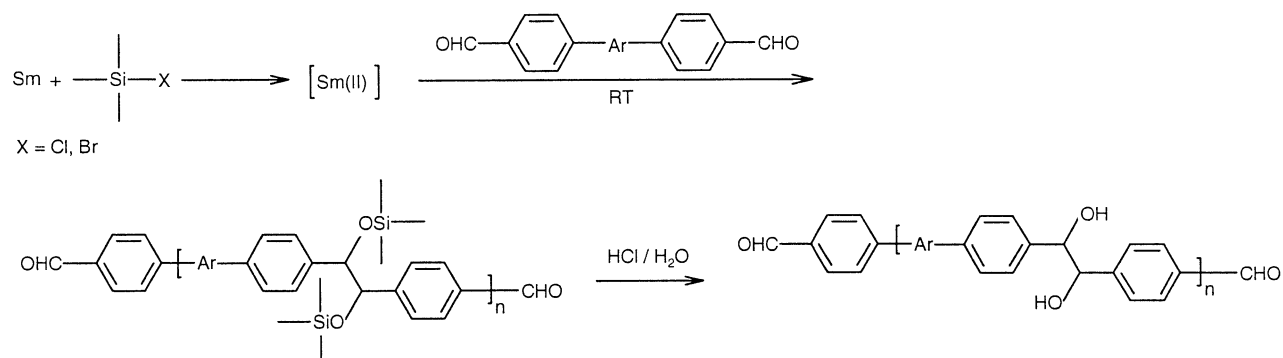
Scheme 3



Scheme 4



Scheme 5



Scheme 6

mechanism, Souppe *et al.*¹⁵ determined that the 2nd route (Scheme 4) is the major reaction pathway for low molecular weight compounds and therefore, it is assumed to be the means by which poly- α -diketones were produced by Brandukova *et al.*

2.2 Poly alcohols

2.2.1 OH-functionalised poly(*p*-xylylene)s

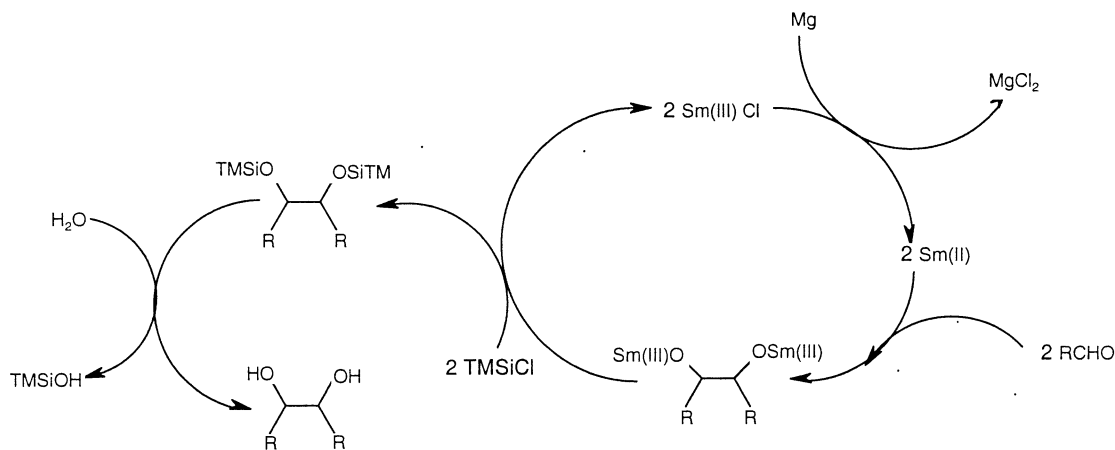
Pinacol (1,2-dihydroxy compounds) formation is one of the synthetically important C–C bond formation reactions^{18a} and is receiving renewed attention because of the availability of mild and selective reducing agents.^{18b} Among these, SmI₂ has been utilised successfully in the synthesis of several natural and nonnatural products. In polymer chemistry, this reaction has been utilised by the reductive coupling of dicarbonyl compounds for the synthesis of OH-functionalised poly(*p*-xylylene)s (PPXs) **1**. These telechelic PPXs are important because a large number of polymers with new and tailored properties can be produced *via* modifications to the hydroxy groups. A particular target for these polymers is the immobilisation of natural products such as enzymes, which can be used for various applications. Also, this coupling of natural products to the polymer support could lead to improvements in the biocompatibility of PPXs.

Since the preparation of 1,2-dihydroxy substituted PPXs by reductive coupling of terephthalaldehyde with the usual reducing systems, Cr₂(SO₄)₃–Zn or TiCl₄–Zn, lead to materials with low molecular weights and undesirable properties (the coupling of terephthalaldehyde to produce 1,2-dihydroxy substituted PPXs using Cr₂(SO₄)₃–Zn led to a material with very low inherent viscosity¹⁹ and the use of TiCl₄–Zn gave *M_n* values between 1000 and 2000 g mol⁻¹²⁰), there was a need to develop a polymerisation reaction in which the reducing agent allows the synthesis of high molecular weight PPXs. The high reducing

power of Sm(II), using its stoichiometric amounts for the synthesis of 1,2-dihydroxy substituted PPXs has been demonstrated by our group²¹ and by Brandukova *et al.*²² to produce high molecular weight polymers. The key step is the reductive coupling of carbonyl compounds with Sm(II) forming Sm(III) alkoxy complexes. The reaction most likely proceeds by the formation of a Sm(III) alkoxy radical anion, subsequent coupling by radical combination then gives OH-functionalisation of the PPXs. The limitation of this synthetic approach for the synthesis of OH-PPXs is that precipitation of intermediate products in the initial stage of the reaction, presumably because of the formation of polymer-alkoxy-Sm(III) compounds, limits the final molecular weight of the polymers obtained to 12000.²² This quasi crosslinking by a Sm(III) mediated macro-complex formation *via* alkoxy functionalities is attributed to the usage of large amounts of SmI₂ in this synthetic approach or to the stiff polymer backbone. In an attempt to prevent the formation of precipitates during the reaction, we have tried to structurally modify the starting monomer (dialdehydes) (Scheme 5) and to protect the OH groups (Scheme 6).^{23–24} Polymers of high molecular weight (*M_w* = 30 000) were obtained by incorporation of flexible ether linkages in the backbone.²³

In the second approach, we protected the OH groups with halotrimethylsilane (TMSiX; X = Cl, Br), which forms intermediate siloxy ethers (Scheme 6), to solve the problem of precipitation during polymerisation.^{23–24} This approach was successful in giving high molecular weight polymers (*M_w* = 50 000), but at the expense of a moderate yield.

Also, the intermediate Sm(III) polyalkoxides **1a** were used as polymeric initiators for further ring opening polymerisation of caprolactone (CL) and L-lactide (LA), generating a new class of biodegradable graft copolymers poly(PPX-*graft*-PCL/PLA) (PCL = polycaprolactone; PLA = polylactide) with graft efficiency of 14% and 28% for CL and LA, respectively.²⁵



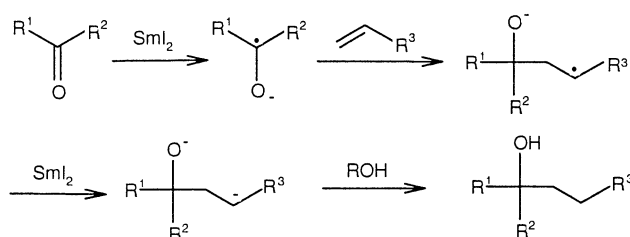
Scheme 7

Another drawback of this synthetic strategy, of making OH-functionalised PPXs by reductive coupling polymerisation of dialdehydes, requires for complete conversion the use of stoichiometric amounts of SmI_2 relative to carbonyl groups. The use of less than 1 equiv. of SmI_2 leads to the formation of defect structures like benzoin, benzyl benzoate, (4-formylphenyl)phenylmethanol *etc.*, and is therefore economically also not very attractive. The feasibility of a catalytic cycle for regeneration of Sm(II) in reductive coupling polymerisation reaction of dialdehydes was the focus of our recent work.²⁶ A catalytic cycle for the reductive coupling polymerisation of aromatic dialdehydes is established with 12 mol% of SmI_2 and excess of Mg or Mg/Hg in the presence of TMSiCl in THF. The plausible reaction pathway involves the reduction of a carbonyl compound by SmI_2 to give Sm(III) alcoholate, which is followed by silylation of the alkoxide by TMSiCl (trimethylchlorosilane) providing the corresponding silyl ether and liberating SmI_2Cl . From this, Sm(II) can be regenerated *in situ* by electron transfer from another electropositive metal like Mg, which acts as co-reductant (Scheme 7). Yields and molecular weights of polymers produced under these catalytic conditions were in the range of yields and molecular weights when SmI_2 was used in stoichiometric conditions. This can be considered a promising and significant step towards an easy and economically viable synthetic approach for the synthesis of functionalised polymers.

This reductive coupling of dicarbonyl compounds using SmI_2 has been utilised by Forster *et al.* for the synthesis of highly fluorescent ethylene-bridged poly(*p*-phenylene) ladder polymers.²⁷ These polymers were synthesised in two steps: 1) synthesis of single-stranded, 2,5-benzoyl-substituted poly(*p*-phenylene) precursors, and 2) their polymer-analogous cyclisation (pinacolisation) with SmI_2 . This is the first application of Sm reagents in the synthesis of ladder polymers.

2.2.2 Aliphatic poly(alcohol)s

Aliphatic poly(alcohol)s are important as coatings, adhesives and polymeric reagents. In spite of their useful applications, general synthetic methods for the preparation of polymers having hydroxy groups attached to the main chain are limited. For low molecular weight compounds, the reductive cross-coupling of ketones with various olefins in the presence of SmI_2 has been reported to give aliphatic alcohols in excellent yield and mild reaction conditions.²⁸ This reaction is initiated by electron transfer from SmI_2 to ketones forming ketyl radicals. The radical attacks double bonds to afford anion-radical species which are further reduced by SmI_2 and protonated by a coexisting alcohol (Scheme 8). As an application of these reactions, reductive cross coupling of diketones with diolefins (distyryls or diacetylenes), accomplished by the addition of 4 equiv. of SmI_2 , HMPA and a proton source, was reported by Endo *et al.*^{29,30} (Scheme 9) to proceed quantitatively under mild reaction condi-

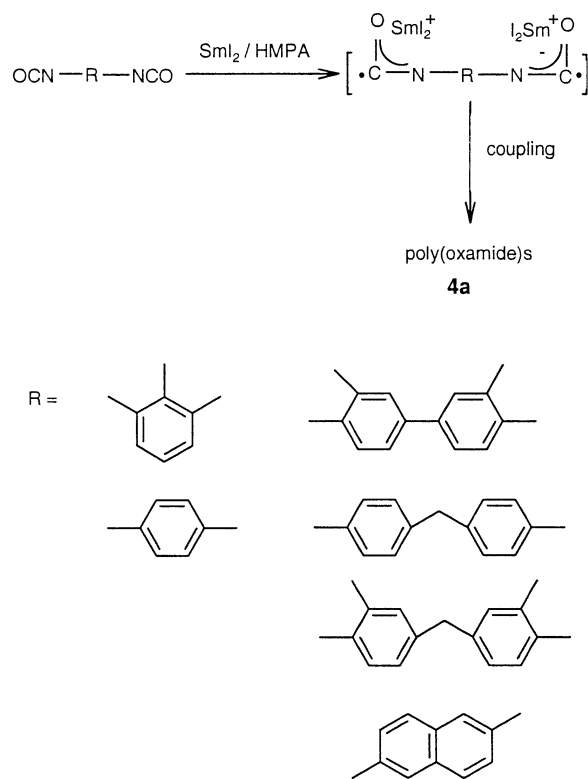


Scheme 8

tions to generate low molecular weight poly(alcohol)s **2** and **3**. The molecular weights of the obtained polymers were relatively low ($M_n = 2800\text{--}9000$), which indicates the existence of termination reactions. The possible termination reaction could be simple reduction of the carbonyl group resulting from hydrogen abstraction of the ketyl radical and/or further reduction of the ketyl radical to the corresponding anion. The pinacol coupling, the most probable side reaction, was found to be absent in this polymerisation. This step-polymerisation was applied to various distyryl compounds (**2b–2e**) having various functional groups like ether, ester and internal double bonds. The polymerisation proceeded without attack of the ketyl radical on the internal double bond or hydrolysis and/or reduction (by SmI_2) of ester groups. Therefore, this polymerisation method, *via* an electron transfer process, proposes a new synthetic strategy for multifunctional poly(alcohol)s with various functional groups like esters, ethers and alkenes in the main chain.

2.3 Poly(oxamide)s

Aromatic polyamides are high performance polymers with high thermal stability, mechanical strength and chemical resistance but have low solubility and poor processability. *N*-Substitution of the amide groups in the polymer chain leads to improved solubility and processability. However deprotonation to generate the anions necessary for the substitution reaction often results in cleavage of the polymer backbone. In contrast to this conventional method, reductive coupling polymerisation of diisocyanates, *via* the SmI_2 promoted single electron transfer, provides a new synthetic strategy for the synthesis of *N*-substituted poly(oxamide), in an one pot synthesis. Reductive coupling of different aromatic diisocyanates using SmI_2 –HMPA for the synthesis of aromatic poly(oxamide)s and its derivatives **4a–4c** was carried out successfully and details are given by Wang *et al.*³¹ (Scheme 10). The different diisocyanates used in this study are shown in Scheme 11. The selective homocoupling polymerisation of these aromatic diisocyanates *via* one electron transfer promoted by SmI_2 in the presence of hexamethylphosphoramide (HMPA) produced the corresponding poly(oxamide)s **4a** nearly quantitatively. HMPA was found to be an important factor for these reactions, and both the yield



Scheme 11

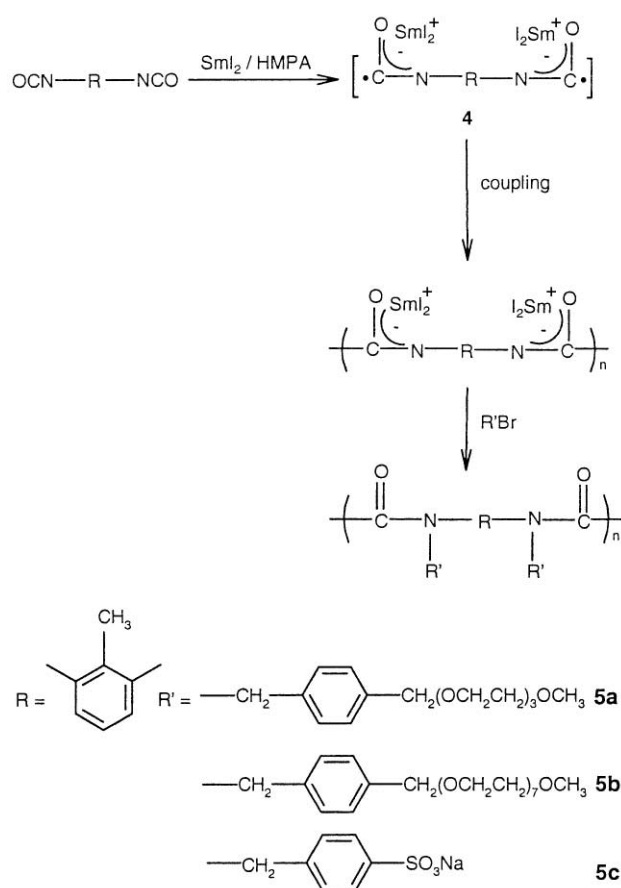
($M_n = 44500$; $M_w/M_n = 1.47$) in one-pot. The graft copolymer of poly(oxamide) from tolylene 2,6-diisocyanate (TDI) and methyl methacrylate (MMA) was reported to have M_n of 137 200 and a polydispersity index of 1.07.³³

N-Substituted poly(oxamide)s have improved solubility as compared to unsubstituted poly(oxamide)s in common organic solvents. The extent of substitution by low molecular weight electrophiles was 6–81% depending on the nature of the electrophile and on the reaction conditions. In general, the poor solubility of polyanion **4** and the large excess of HMPA, which occupies the available coordination sites of Sm(III), sterically hinder the access of electrophiles to the anionic reactive sites, possibly contributing to the low molecular weights and the low degree of substitution of the poly(oxamide)s that were obtained. These pendant groups (although in low degree of substitution) can provide the opportunity for further modification of the polymer by subsequent polymer analogous reactions.

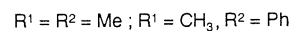
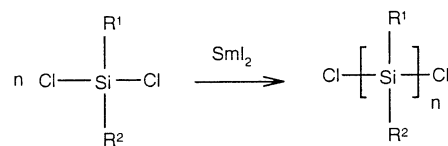
In another attempt, the *in situ* generated polyanion **4** (Scheme 12) was used for the synthesis of poly(oxamide) based water soluble polymers³⁴ having rigid skeletons and moderate molecular weights ($M_n = 6500$ –10 900). Two kinds of water-soluble polymers were made by introducing the designed hydrophilic substituents onto the poly(oxamide) polyanion. The nonionic poly(oxamide) bearing oligo(ethylene oxide) pendants **5a** and **5b** (Scheme 12), exhibited high solubilities in both common organic solvents and aqueous system. The poly(oxamide) based polyelectrolyte containing either alkyl or arenesulfonate side chain **5c** showed high solubilities in acidic and basic water.

2.4 Oligosilanes and germynes

SmI_2 has been also utilised in reductive coupling of metals like Si and Ge. Reaction of diorganodichlorosilanes with SmI_2 gives oligosilanes according to the reaction Scheme 13.³⁵ Branched oligogermynes are also reported by Mochida *et al.* by the reaction of alkyltrichlorogermynes with SmI_2 .³⁶ SmI_2 has the obvious advantage of mild reaction conditions over the traditional reaction (Wurtz–Fittig reaction) for their synthesis.



Scheme 12

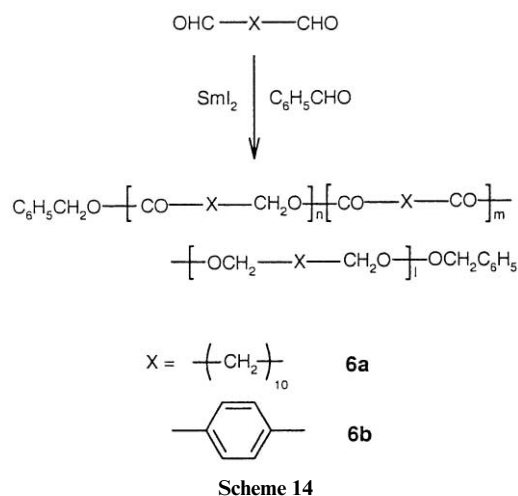


Scheme 13

3 SmI_2 catalysed polyreactions

3.1 Polyaddition of dialdehydes

One of the recent developments in polymer synthesis is the application of lanthanide compounds as initiators/catalysts.³⁷ A major characteristic of lanthanide based catalysts is their high ability to initiate and control the polymerisation of a wide range of monomers in polyaddition reactions. Polyaddition of dialdehydes utilising a SmI_2 catalysed Tishchenko reaction³⁸ is a new preparation method of polyesters, which have conventionally been obtained from polycondensation or ring-opening polymerisation reactions (ROP) (Scheme 14). The Tishchenko-type polymerisation seems to have many advantages over the conventional condensation or ring opening polymerisation methods, for the synthesis of polyesters. For example, this method is applicable to the synthesis of polyesters with long alkyl chains that are difficult to obtain by the ROP method. Also, the use of a single substrate (dialdehydes) in the polymerisation seems to be another advantage, because optimisation of the ratio between dicarboxylic acid derivatives and diols (in condensation polymerisation) is not required. Yamaguchi *et al.*³⁸ have reported the polyaddition of dodecane-1,12-diol in the presence of 10 mol% of SmI_2 (followed by addition of benzaldehyde) giving polyester **6a** (Scheme 14) containing three structural units, $[-\text{OCH}_2-(\text{CH}_2)_{10}-\text{CH}_2\text{O}-]$,



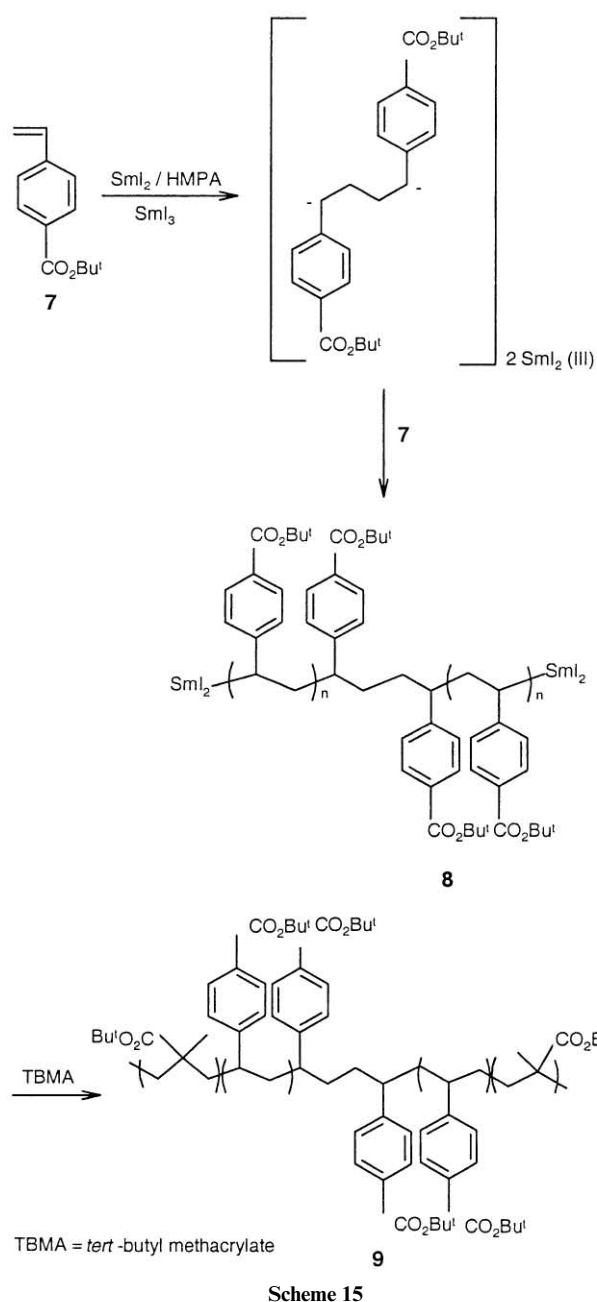
$[-\text{OCH}_2-(\text{CH}_2)_{10}-\text{C}(\text{O})-]$ and $[-\text{C}(\text{O})-(\text{CH}_2)_{10}-\text{C}(\text{O})-]$ in the main chain and an $-\text{OCH}_2\text{Ph}$ group capping the end. Only low molecular weight polyesters were obtained by this method ($M_n = 5500$). SmI_2 also catalyses the polyaddition of terephthalaldehyde to give the corresponding polyester with $M_n = 1.7 \times 10^3$ and $M_w = 3.7 \times 10^3$. It is worth noting that, SmI_2 promotes the reduction of stoichiometric amounts of dialdehyde into polypinacol as reported,^{23–24} however the polyesters obtained by using a catalytic amount of SmI_2 with respect to carbonyl groups do not show the formation of polypinacol as side product.

3.2 Vinyl polymerisations

Although lanthanide based catalysts have the ability to initiate and control the polymerisation of a number of monomers, the precise polymerisation of styrene and its derivatives could not be achieved for long. The first example for the living polymerisation of *tert*-butyl 4-vinylbenzoate **7**, a styrene derivative, was accomplished by Goshō *et al.*^{39a} using SmI_2 in catalytic amounts as an electron transfer agent in the presence of HMPA and SmI_3 (Scheme 15). SmI_2 – SmI_3 acted as bisinitiator for the vinyl polymerisation of **7**. The addition of a common salt, SmI_3 , remarkably enhanced the living nature of the polymerisation to provide living poly(*tert*-butyl 4-vinylbenzoate) **8** with narrow molecular weight distribution ($M_w/M_n = 1.05$). This may be due to the reduced reactivity of the propagation centers, depressing the nucleophilic attack of the growing center on the carbonyl carbon and hence making the system living. This ability to induce living polymerisation also provided later on the opportunity to make high molecular weight block copolymers **9** (Scheme 15) ($M_n = 196,000$; $M_w/M_n = 1.12$) with *tert*-butyl methacrylate (TBMA).

SmI_2 – SmI_3 also provided the living homo-polymerisation of MMA and TBMA under optimised reaction conditions (Scheme 16).^{39b} The number average molecular weight (M_n) of poly(MMA) was very close to the calculated value ($M_{n,\text{GPC}} = 2160$; $M_{n,\text{calc}} = 2200$). Also, the addition of MMA to the solution of living poly(TBMA) provided a defined triblock copolymer with narrow molecular weight distribution ($M_n = 7300$, $M_w/M_n = 1.13$).

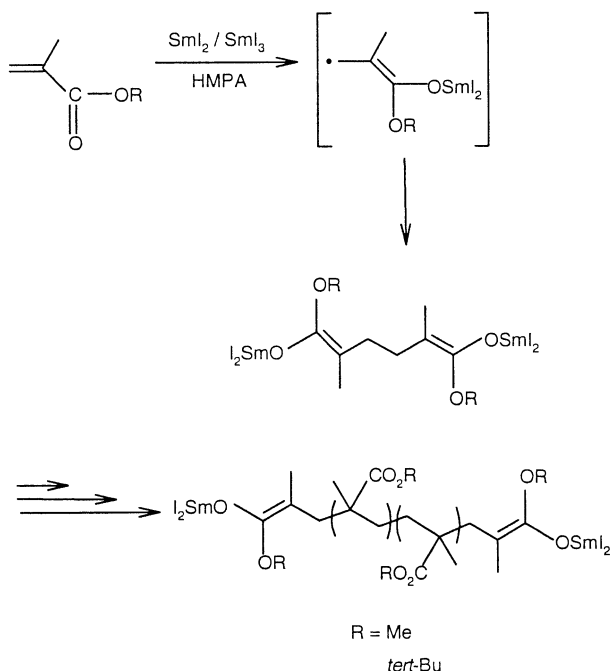
The samarium enolate, formed *in situ* by the reduction of 2-bromoisobutyric esters with SmI_2 could initiate the polymerisation of MMA in quantitative initiation efficiency to give polymers with narrow molecular weight distribution (Scheme 17).^{40a} This method provides the initiation species without isolation and an easy method of making star shaped polymers just by proper designing of the starting 2-bromoisobutyric esters. For example, the samarium enolate, prepared *in situ* by the reduction of 1,3,5-tris(2-bromoisobutyryloxymethyl)benzene **10** with SmI_2 , was used to synthesise star shaped poly(MMA) by Narita *et al.*^{40b} (Scheme 18).



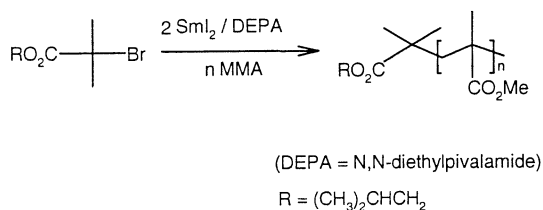
3.3 Ring-opening polymerisations

The ring-opening polymerisation of lactones is a convenient method for the synthesis of biodegradable polyesters, which have great potential for applications in biomaterials. These polymerisation reactions can be achieved using a variety of metal catalysts, among which the lanthanide catalysts are currently receiving the most interest due to their high reactivity and capability to produce narrow polydispersity polymers. The large size of metallic Sm and its high electropositive character allows (with Sm-X , Sm-O , Sm-N , Sm-R) rapid ligand exchange and insertion reactions thus making it a suitable initiator for ROP reactions.⁴¹ A mixture of SmI_2 – Sm ⁴² allowed room temperature ROP of caprolactone (CL) and valerolactone (VL), an enhanced reactivity as compared to the ROP initiation ability of SmI_2 by itself, which requires refluxing.⁴³ The mechanism of polymerisation was found to be initiation by alkyl-O cleavage resulting in product **11** (Scheme 19), which then reacts in a chain propagation step with another molecule of lactone *via* acyl-O cleavage. The polymerisation further proceeds by rapid chain growth through acyl-O cleavage. The observed side reactions are: C–C bond formation and the reduction of terminal CH_2I groups. Under reflux conditions,

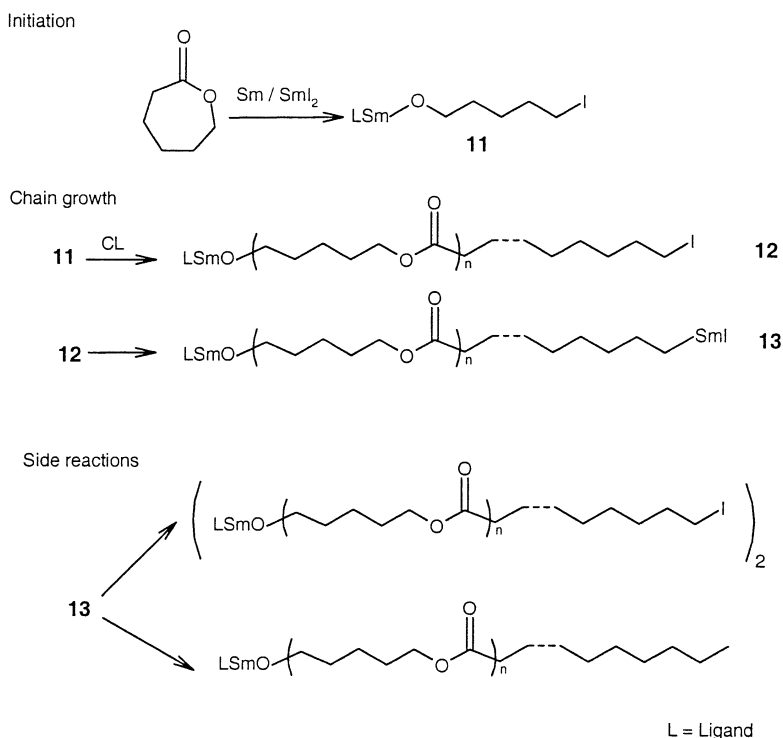
Evans *et al.* reported the SmI_2 catalysed copolymerisation of ethylene carbonate (EC) and caprolactone (CL) (EC : CL : Sm = 100 : 100 : 1 mole ratio).⁴⁴ Very low molecular weight ($M_n = 6000$) copolymers with 6 mol% of EC are obtained by this method.



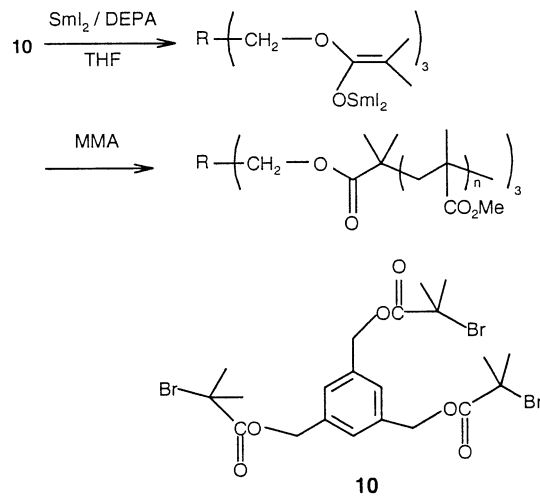
Scheme 16



Scheme 17



Scheme 19



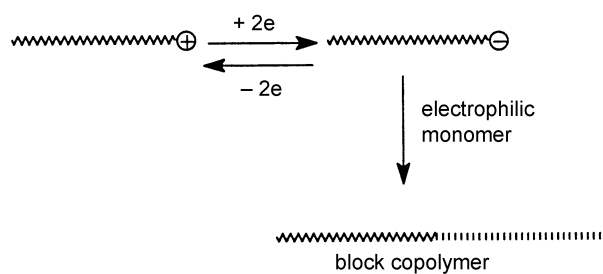
Scheme 18

A combination of Sm– SmI_2 facilitates ROP of L-lactide at 50 °C, leading to the synthesis of a semicrystalline, optically active poly(L-lactide) (PLA) retaining about 95% of its optical activity.⁴⁵

4 Polarity inversion reactions

One of the major advances in polymer synthesis has been the development of new polymerisation methods and techniques for the synthesis of various architectures like block, graft, hyperbranched structures *etc.* One of the most convenient methods for the synthesis of block copolymers is sequential addition of the monomers using anionic, cationic or living radical polymerisation methods but this limits the number of monomers which can be copolymerised. This restriction can be reduced by the transformation of the mechanism after polymerisation of the first monomer to one suitable for the polymerisation of the second monomer. For example, the transformation of the growing center of cationic polymerisation into an anionic one or anionic terminal chain ends into cationic ones (polarity inversion) is expected to increase the choice of monomers for the formation of block copolymers for any desired

application. The transformation of active centers, requires two-electron oxidation or reduction to take place during the transformations. The general scheme for polarity inversion in a growing polymer chain is given in Scheme 20. This quantitative double electron reduction of the cationic propagation end of poly(tetrahydrofuran) poly(THF) into a terminal nucleophile was achieved by Nomura *et al.* for the first time by using SmI₂ in the presence of HMPA^{46a} without any side reactions like dimerisation or termination. This method provides a new venue for polymer architecture and has led to the synthesis of well defined AB and ABA type block copolymers of THF with *tert*-butyl methacrylate^{46b,46c} (poly(THF)-*block*-poly(TBMA)), MMA^{46d,47} (poly(THF)-*block*-PMMA), CL⁴⁸ (poly(THF)-*block*-PCL), and VL⁴⁹ (poly(THF)-*block*-PVL).



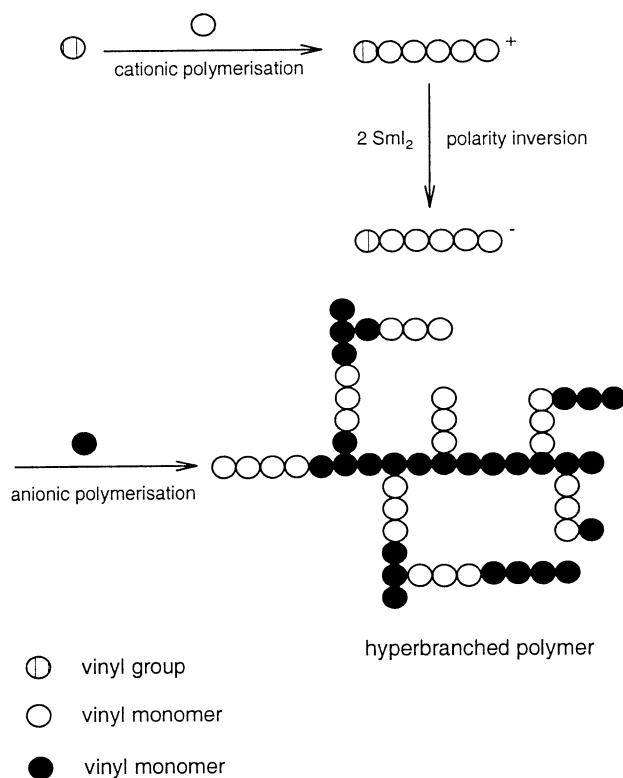
Scheme 20

As mentioned before, samarium enolates, obtained by reduction of 2-bromoisobutyric esters with SmI₂ work as useful initiators for the living polymerisation of MMA (Scheme 17).⁴⁰ This polymerisation system is also applied to the transformation from cationic to anionic polymerisation.⁵⁰ The cationic growing center of the living poly(THF) can be quantitatively transformed into a terminal samarium enolate by the end-capping of the living end with sodium 2-bromoisobutyrate followed by reduction with SmI₂. The sequential polymerisation of MMA with the terminal samarium enolate gives block copolymers of THF and MMA with controlled structures. Star shaped block copolymers can also be easily made by starting from star shaped living poly(THF) using this method.

Hyperbranched polymers are highly branched macromolecules in a three-dimensional architecture. They have large potential utility as advanced functional materials. The combination of the self-condensable monomer method and SmI₂-induced transformation (polarity inversion) can provide a hyperbranched block copolymer consisting of many types of polymer segments in the dendritic part. This would allow the formation of a variety of new hyperbranched polymers that can not be prepared by conventional techniques. The approach includes 1) the preparation of a macromonomer having α -vinyl groups. By the cationic polymerisation, 2) the transformation of the cationic growing center into a terminating nucleophile which is active for the polymerisation of α -vinyl group and 3) the copolymerisation of the corresponding vinyl monomers with the α -vinyl group by the generated nucleophile (Scheme 21).⁵¹

5 Conclusion

Although the use of SmI₂ in polymer chemistry is still limited, there is a steady increase in its use since its first application in polymer science in 1987. The strong single electron donor capability, ease of synthesis and facile ligand exchange makes SmI₂ a powerful tool in the synthesis of different polymer architectures and in carrying out many unique polymer reactions. Unfortunately, most of the electron transfer reactions require more than stoichiometric amounts of SmI₂, which limits the synthetic value when considering large or industrial scale reactions. With the development of a catalytic cycle, this problem is solved to some extent and one can now envision economically



Scheme 21

viable reactions that utilise the reductive ability of SmI₂. The available literature till now clearly highlights SmI₂ as an important and versatile reagent/catalyst in polymer synthesis. However, the field is still wide open for the full exploration of its properties and for the utilisation of these properties in the synthesis of new polymeric structures.

6 References

- 1 Y. Zhang, Z. Hou and Y. Wakatsuki, *Macromolecules*, 1999, **32**, 939.
- 2 J. Wang, R. Nomura and T. Endo, *Chem. Lett.*, 1996, **10**, 909.
- 3 W. J. Evans and H. Katsumata, *Macromolecules*, 1994, **27(14)**, 4011.
- 4 F. G. Yuan and Q. Shen, *Chem. Lett.*, 1997, **8(7)**, 639.
- 5 L. R. Morss, *Chem. Rev.*, 1976, **76**, 827.
- 6 P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. Soc.*, 1980, **102**, 2693.
- 7 G. Jantsh, N. Skalla and H. Jawurek, *Z. Anorg. Allg. Chem.*, 1931, **201**, 207.
- 8 N. E. Brandukova, Ya. S. Vygodskii and S. V. Vinogradova, *Russ. Chem. Rev.*, 1994, **63(4)**, 345.
- 9 G. R. Molander and C. R. Harris, *Chem. Rev.*, 1996, **96**, 307.
- 10 H. B. Kagan and J. L. Namy, *Handbook on the physics and chemistry of rare earths*, ed. K. A. Gschneider Jr. and L. Eyring, Elsevier Science, Amsterdam, 1984, vol. 6, 525–565.
- 11 H. B. Kagan and J. L. Namy, *Tetrahedron*, 1996, **42**, 6573.
- 12 N. Akane, Y. Kanagawa, Y. Nishiyama and Y. Ishii, *Chem. Lett.*, 1994, 2431.
- 13 V. V. Korshak, S. V. Vinogradova, Y. S. Vygodski, N. A. Churochkina and N. E. Brandukova, *Vysokomol. Soedin. Ser. A*, 1987, **29**, 1480.
- 14 G. R. Molander and C. R. Harris, *Chem. Rev.*, 1992, **92**, 29.
- 15 J. Souppe, J. L. Namy and H. B. Kagan, *Tetrahedron Lett.*, 1984, **25**, 2869.
- 16 N. E. Brandukova, Ya. S. Vygodskii, S. V. Vinogradova and H. Raubach, *Acta Polym.*, 1991, **42**, 82.
- 17 N. E. Brandukova and Ya. S. Vygodskii, *Macromol. Rep.*, 1995, **A32**, 941.
- 18 (a) J. L. Namy, J. Souppe and H. B. Kagan, *Tetrahedron Lett.*, 1983, **24**, 765; (b) G. M. Robertson, *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 3, 563.
- 19 J. M. Hoyt and K. Koch, *US Pat. 3 509 097*, National Distillers and Chemical Corporation, USA, 1970.
- 20 A. W. Cooke and K. B. Wagener, *Macromolecules*, 1991, **24**, 1404.
- 21 V. U. Wege and A. Greiner, *Acta Polym.*, 1995, **46**, 391.

- 22 N. E. Brandukova, Ya. S. Vygodskii and T. V. Strelkova, *Vysokomol. Soedin. Ser. A*, 1996, **38**, 1803.
- 23 N. E. Brandukova, S. Agarwal and A. Greiner, *Acta Polym.*, 1999, **50**, 35.
- 24 N. E. Brandukova, S. Agarwal and A. Greiner, *Polym. Prep. (Am. Chem. Soc. Div. Polym. Chem.)*, 1998, **39(2)**, 394.
- 25 (a) S. Agarwal, N. E. Brandukova and A. Greiner, *Polym. Adv. Technol.*, 1999, **10**, 528; (b) A. Greiner, S. Agarwal and N. E. Brandukova, *Polym. Prep. (Am. Chem. Soc. Div. Polym. Chem.)*, 1999, **40(2)**, 163.
- 26 N. E. Brandukova and A. Greiner, *Acta Polym.*, 1999, **50**, 141.
- 27 M. Forster and U. Scherf, *Macromol. Rapid Commun.*, 2000, **21**, 810.
- 28 O. Ujikawa, J. Inanaga and M. Yamaguchi, *Tetrahedron Lett.*, 1989, **30**, 2837.
- 29 R. Nomura and T. Endo, *Macromolecules*, 1994, **27**, 617.
- 30 R. Nomura and T. Endo, *Macromolecules*, 1994, **27**, 1286.
- 31 J. Wang, R. Nomura and T. Endo, *J. Polym. Sci., Polym. Chem. Ed.*, 1995, **33**, 869; J. Wang, R. Nomura and T. Endo, *J. Polym. Sci., Polym. Chem. Ed.*, 1995, **33**, 2901.
- 32 J. Wang, R. Nomura and T. Endo, *Polym. Bull.*, 1996, **37**, 281.
- 33 (a) J. Wang, R. Nomura and T. Endo, *J. Polym. Sci., Polym. Chem. Ed.*, 1995, **35**, 1381; (b) J. Wang, R. Nomura and T. Endo, *Macromolecules*, 1995, **29**, 2707.
- 34 J. Wang, R. Nomura and T. Endo, *Polym. Bull.*, 1997, **38**, 125.
- 35 B. G. Zavin, A. I. Chernyavskii, Y. S. Vygodskii and N. E. Brandukova, *Dokl. Chem. (Transl. of Dokl. Akad. Nauk.)*, 1994, **336**, 97.
- 36 K. Mochida, T. Ohkawa, H. Kawata, A. Watanabe, O. Ito and M. Matsuda, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2993.
- 37 H. Yasuda, *Catalysis in precision polymerisation*, ed. S. Kobayashi, John Wiley & Sons: Chichester, England, 1997 vol. 6, ch. 4, 189; and the references cited therein.
- 38 (a) I. Yamaguchi, T. Kimishima, K. Osakada and T. Yamamoto, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 2821; (b) I. Yamaguchi, T. Kimishima, K. Osakada and T. Yamamoto, *J. Polym. Sci.: Part A: Polym. Chem.*, 1997, **35**, 1265.
- 39 (a) A. Gosho, R. Nomura, I. Tomita and T. Endo, *Macromolecules*, 1998, **31(10)**, 3388; (b) A. Gosho, R. Nomura, I. Tomita and T. Endo, *Macromol. Chem. Phys.*, 2001, **202**, 1614.
- 40 (a) M. Narita, R. Nomura, I. Tomita and T. Endo, *Macromolecules*, 1998, **31(10)**, 3388; (b) M. Narita, R. Nomura, I. Tomita and T. Endo, *Polym. Bull.*, 2000, **45**, 231.
- 41 S. Agarwal, C. Mast, K. Dehnicke and A. Greiner, *Macromol. Rapid Commun.*, 2000, **21(5)**, 195.
- 42 S. Agarwal, N. E. Brandukova-Szmikowski and A. Greiner, *Macromol. Rapid Commun.*, 1999, **20**, 274.
- 43 W. J. Evans and H. Katsumata, *Macromolecules*, 1994, **27**, 2330.
- 44 W. J. Evans and H. Katsumata, *Macromolecules*, 1994, **27**, 4011.
- 45 S. Agarwal, M. Karl, K. Dehnicke and A. Greiner, *e-Polym.*, 2001, 12.
- 46 (a) R. Nomura and T. Endo, *Macromolecules*, 1994, **27(20)**, 5523; (b) R. Nomura, M. Narita and T. Endo, *Macromolecules*, 1994, **27(24)**, 7011; (c) R. Nomura, M. Narita and T. Endo, *Macromolecules*, 1995, **28(1)**, 86; (d) M. Narita, R. Nomura and T. Endo, *Macromolecules*, 1998, **31(9)**, 2774.
- 47 R. Nomura and T. Endo, *The Polymeric Materials Encyclopedia: Synthesis, properties and applications*, ed. S. Kodayashi, CRC, Florida, 1996, vol. 3, 2016.
- 48 R. Nomura and T. Endo, *Macromolecules*, 1995, **28**, 5372.
- 49 R. Nomura, Y. Shibasaki and T. Endo, *Polym. Bull.*, 1996, **37**, 597.
- 50 M. Narita, R. Nomura, K. Tomita and T. Endo, *Macromolecules*, 2000, **33**, 4979.
- 51 R. Nomura, T. Matsuno and T. Endo, *Polym. Bull.*, 1999, **42**, 251.