The use of (metallo-)supramolecular initiators for living/controlled polymerization techniques

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The introduction of supramolecular interactions in synthetic polymers seems to be a promising approach towards novel 'smart' materials that combine both the (reversible) supramolecular interactions and the properties of the polymers. In this *tutorial review*, the use of (metallo-)supramolecular initiators for the preparation of end-functionalized (metallo-)supramolecular polymers will be discussed in detail. The different polymerization techniques that have been applied as well as the different ligands and metal complexes that were used to initiate these polymerizations will be discussed together with the resulting polymer properties.

1. Introduction

Inspired by the magnificent application of supramolecular interactions in Nature, the incorporation of (metallo-)supramolecular interactions in macromolecular systems has been introduced as a new concept in polymer science to improve the material properties and to create completely new architectures and functionalities.[1] The combination of supramolecular interactions[1] and polymer chains can lead to novel 'smart' materials[2] that exhibit both the reversible binding behavior of the supramolecular interactions and the properties of the polymeric materials. Moreover, the introduction of directional supramolecular interactions like hydrogen bonding[3] and metal coordination[4] into a polymer structure allows the construction of well-defined supramolecular polymeric assemblies. Nevertheless, the application of metal coordinating ligands, like bipyridine[5] or terpyridine,[6] into polymeric structures seems to be more promising, because of the easy variation of binding strength and optical properties that can be achieved by varying the metal ions. Moreover, metal coordinating units are compatible with various living/controlled polymerization techniques,[7] which allow the preparation of well-defined

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Richard Hoogenboom was born in 1978 in Rotterdam (The Netherlands). In 2001 he obtained his MSc degree in chemical engineering at the Eindhoven University of Technology, where his undergraduate research was performed in the group of Bert Meijer (Eindhoven, The Netherlands). During these studies, he performed an internship within the group of Andrew Holmes (Cambridge, United Kingdom). In 2005, he obtained his PhD under the supervision of Ulrich Schubert (Eindhoven, The Netherlands) focusing on supramolecular initiators for controlled polymerization techniques, automated parallel synthesis of well-defined polymers and microwave irradiation in polymer chemistry. Currently, he is working as project leader for the Dutch Polymer Institute (DPI) with a major focus on the use of high-throughput experimentation and microwave irradiation for living/controlled polymerization techniques.

Ulrich S. Schubert

Ulrich S. Schubert was born in Tübingen in 1969. He studied chemistry at the Universities of Frankfurt and Bayreuth (both Germany) and the Virginia Commonwealth University, Richmond (USA). His PhD work was performed under the supervision of Professor Eisenbach (Bayreuth, Germany) and Professor Newkome (Florida, USA). In 1995 he obtained his doctorate with Professor Eisenbach. After a postdoctoral training with Professor Lehn at the Université Strasbourg (France) he moved to the Technische Universität München (Germany) to obtain his habilitation in 1999 (with Professor Nuyken). From 1999 to Spring 2000 he held a temporal position as a professor at the Center for NanoScience at the Universität München (Germany). Since Summer 2000 he has been Full-Professor at the Eindhoven University of Technology (Chair for Macromolecular Chemistry and Nanoscience). His awards include the Bayerischen Habilitations-Förderpreis, the Habilitandenpreis of the GDCh (Makromolekulare Chemie), the Heisenberg-Stipendium of the DFG, the Dozenten-Stipendium of the Fonds der Chemischen Industrie and a VICI award of NWO. The major focus of the research interest of his relates to organic heterocyclic chemistry, supramolecular materials, combinatorial material research, nanoscience and tailor-made macromolecules.

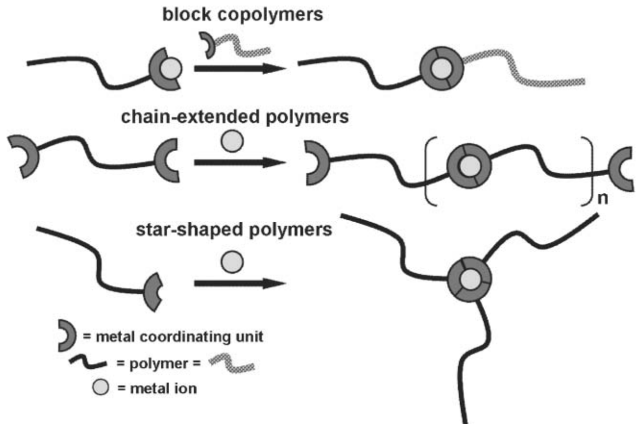

Fig. 1 Metal ion induced self-assembly of polymers with metal coordinating end-groups resulting in block copolymers, chain-extended polymers or star-shaped polymers.

structures using functional initiators, terminating agents or monomers. Polymers with metal coordinating end-groups can be (reversibly) assembled into, *e.g.*, block copolymers, star-shaped polymers or chain-extended polymers by the addition of metal ions as depicted in Fig. 1.

Chain-end functionalized polymers can be synthesized *via* end-group functionalization methods or *via* living/controlled polymerization techniques[7] utilizing (metallo-) supramolecular initiators. Both strategies are schematically depicted in Fig. 2. The end-group modification route has been applied for the synthesis of a variety of pyridine,[8] bipyridine[9–11] and terpyridine[12,13] functionalized polymers that were subsequently used for the construction of larger macromolecular structures *via* metal coordination. However, the (metallo-)supramolecular initiator approach seems favorable since all polymer chains contain a connected metal coordinating unit after simple purification of the polymer by precipitation. Furthermore, the nature of the resulting polymers can be fine-tuned by utilizing different (combinations of) monomers. By introducing more initiating groups onto the central metal complex or metal coordinating ligands, a wide variety of linear and star-shaped polymers is accessible.

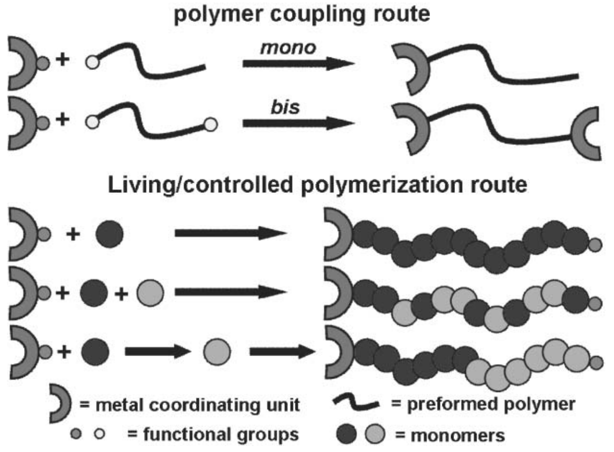

Fig. 2 Possible synthetic routes towards end-group functionalized metal coordinating polymers.

In this *tutorial review*, the use of metal coordinating ligands and metal complexes as initiators for living/controlled polymerization techniques will be introduced to the reader. Although the main focus of this review will be on the synthetic aspects, the novel polymer properties that result from the incorporation of the (switchable) supramolecular units into the polymer chains will be briefly addressed as well.

2. Cationic ring-opening polymerization of 2-oxazolines using (metallo-)supramolecular initiators

The first polymerization method that was explored utilizing (metallo-)supramolecular initiators was the cationic ring-opening polymerization of 2-oxazolines.[14] This living polymerization method can be initiated by electrophiles resulting in a cationic oxazolinium propagating species. The attack of the next monomers onto this cationic species results in the formation of ring-opened poly(2-oxazoline). When all monomer is consumed, a second monomer can be added to prepare block copolymers or a nucleophilic terminating agent can be added to introduce a functional group. A variety of bromomethyl functionalized bipyridines and terpyridines have been prepared to serve as initiator for the cationic ring-opening polymerization of 2-oxazolines. However, the direct polymerization of 2-oxazolines with these metal coordinating ligands cannot be performed since attack of the propagating species on the nitrogen atom of the pyridyls will result in loss of control over the polymerization. Therefore, metal complexes have to be applied as initiating species: the metal ions block the nitrogen atoms of the ligand and thus prevent chain termination reactions.

Fraser and coworkers reported the cationic ring-opening polymerization of 2-ethyl-2-oxazoline with di-, tetra- and hexa-(halomethyl)tris(bipyridine) iron(II)[15] and ruthenium(II)[15,16] complexes as initiators resulting in well-defined star-shaped polymers (Fig. 3, top). Decomplexation of these iron(II) centered metallo-supramolecular polymers was performed by reaction with potassium carbonate resulting in the free poly(2-ethyl-2-oxazoline) bipyridine macroligands. In addition, it was mentioned that decoloring of the polymer films was observed at 210 °C indicative of thermal decomplexation, whereby the violet color of the iron(II) complex returned upon cooling. Next to the polymerization of 2-ethyl-2-oxazoline, Fraser *et al.* demonstrated that these metallo-supramolecular initiators are also suitable for the polymerization of several other 2-oxazoline monomers including 2-methyl-, 2-phenyl- and 2-undecyl-2-oxazoline.[17] By the sequential addition of two different monomers to the polymerization mixture, an iron bipyridine centered six-arm star poly(2-ethyl-2-oxazoline-*b*-2-undecyl-2-oxazoline) was prepared that was decomplexed resulting in a bipyridine centered BAB triblock copolymer.[18] A cylindrical morphology was observed by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) for thin films of both the star-shaped metallo-supramolecular block copolymer and the metal-free macroligand.[19] Schubert and coworkers demonstrated the cationic ring-opening polymerization of 2-ethyl-2-oxazoline with bis(bromomethyl)bipyridine copper(I) initiators resulting in well-defined four-arm star

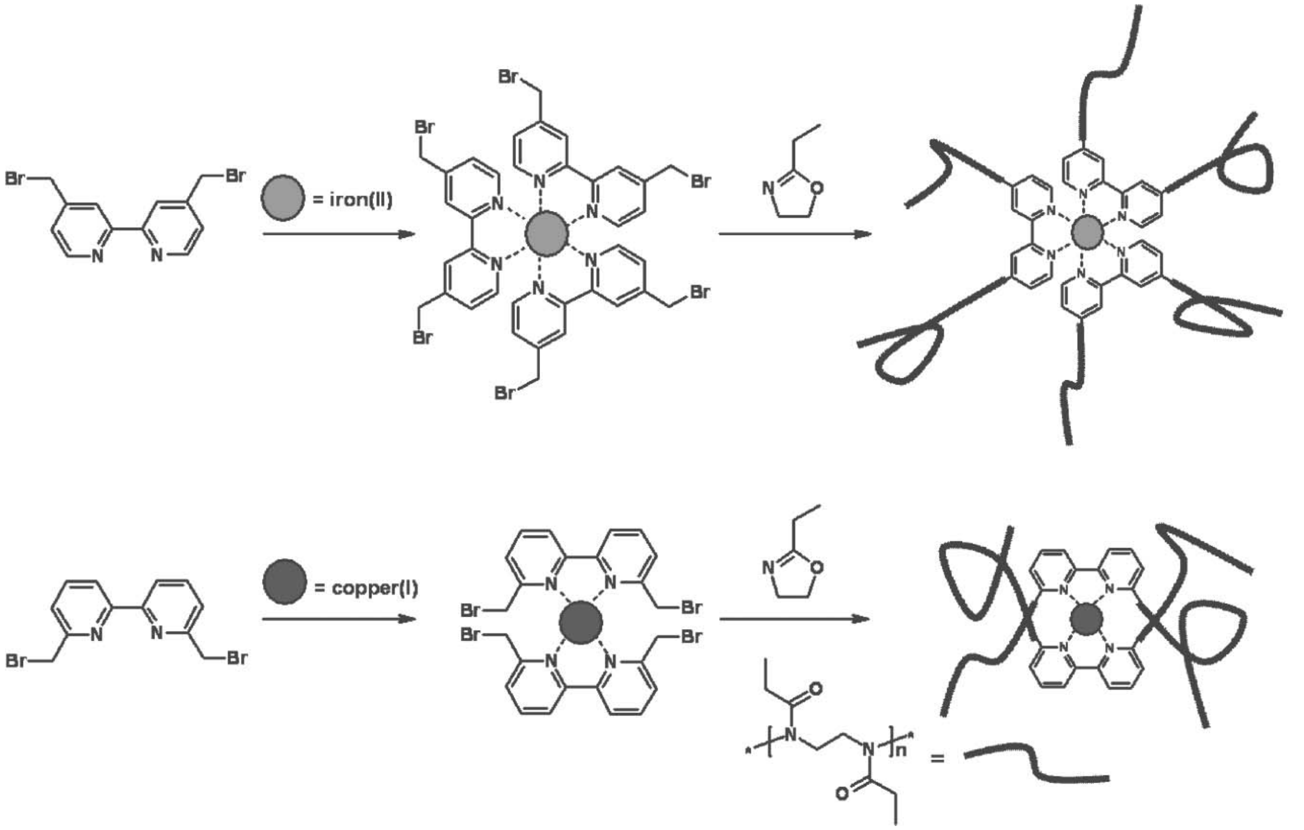

Fig. 3 Different approaches for the bipyridine initiated polymerization of 2-ethyl-2-oxazoline from Fraser[15] (top) and Schubert (bottom).[20]

poly(2-ethyl-2-oxazoline) (Fig. 3, bottom).[20] Additionally, a metallo-centered poly(2-ethyl-2-oxazoline-*b*-2-nonyl-2-oxazoline) was synthesized utilizing the same bis(bipyridine) copper(I) initiator.[21]

Iron(II) and cobalt(II) complexes of mono- and bis(bromomethyl)terpyridines were also applied as initiators for the cationic ring-opening polymerization of 2-ethyl-2-oxazoline by Schubert *et al.* resulting in two- or four-armed metallo-supramolecular polymers.[22–24] Decomplexation of both the iron(II) and cobalt(II) containing polymers was performed by refluxing the polymer with potassium carbonate in acetonitrile yielding the terpyridine functionalized poly(2-ethyl-2-oxazoline). Recomplexation of the macroligands with iron(II) ions was effective up to 94% according to UV-vis titration experiments. Moreover, an increase in viscosity was observed upon recomplexation due to the coupling of the polymer chains by the metal complexation.

3. Synthesis of (metallo-)supramolecular polyesters *via* controlled ring-opening polymerization of lactones and lactides

The controlled ring-opening polymerization of cyclic esters (*e.g.* ε-caprolactone, glycolide or DL-lactide) has often been applied for the synthesis of metallo-supramolecular polymers and macroligands. The controlled ring-opening polymerization techniques can be performed utilizing a hydroxyfunctional (co)initiator resulting in end-functionalized polymers.[25] The two most commonly used controlled ring-opening polymerization methods, namely stannous octoate and aluminium alkoxide catalyzed polymerizations, are compatible with metal coordinating ligands as well as metal complexes.

The stannous octoate-catalyzed ring-opening polymerization of ε-caprolactone and DL-lactide utilizing mono- and bis(hydroxyalkyl)bipyridines as initiator was reported by several groups.[26–28] Fraser and coworkers reported the preparation of a range of homo- and block copolymer macroligands based on a bis(hydroxymethyl)bipyridine initiator.[26] The resulting macroligands were assembled into star-shaped polymeric complexes by the addition of iron(II) ions and ruthenium(II) complexes were prepared bearing two or six polymer chains. Schubert and coworkers reported the application of a monohydroxyfunctional bipyridine initiator for the preparation of a poly(ε-caprolactone) bipyridine macroligand.[27] Metal complexes of this macroligand were synthesized utilizing both iridium(III) and ruthenium(II) precursors resulting in the corresponding polymeric metal complexes as was demonstrated by MALDI-TOF-MS analysis. In addition, it was confirmed that the polymer side-chain did not influence the optical and electrochemical properties of the metal complexes while it improved the solubility and provided film forming properties to the material. Farah and Pietro also reported the synthesis of bipyridine ligands with one poly(ε-caprolactone) side chain (Fig. 4).[28] These macroligands were used as building blocks for the preparation of ruthenium(II) complexes with one, two or three polymer side chains. The

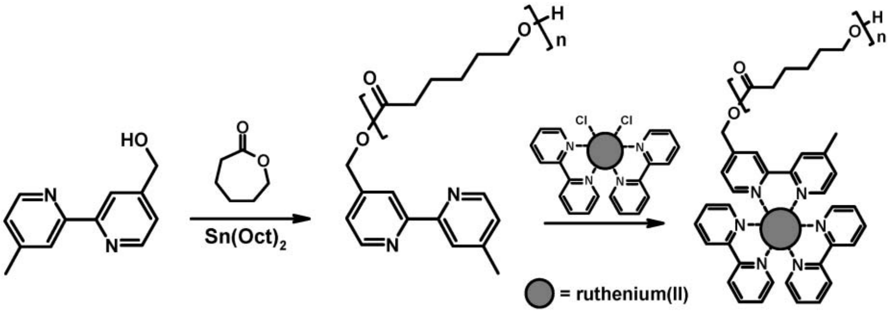

Fig. 4 Synthesis and complexation of a bipyridine poly(ε-caprolactone) macroligand using stannous octoate as catalyst.[28]

direct polymerization of ε-caprolactone utilizing a preformed ruthenium(II) bipyridine complex as initiator was described by these authors as well.[28] The resulting metallo-supramolecular polymers exhibited both the optical and electrochemical properties of the ruthenium(II) complex as well as the thermal properties of the polymers demonstrating the possibility of creating materials with a novel combination of properties *via* the (metallo-)supramolecular initiator approach.

A different type of (metallo-)supramolecular polymers was reported by Fraser and coworkers.[29] Mono- and bishydroxy-functionalized dibenzoylmethanes were synthesized and applied as initiator for the controlled ring-opening polymerization of ε-caprolactone. The resulting well-defined dibenzoylmethane macroligands were successfully complexed with europium(III), iron(III), nickel(II) and copper(II) ions. Moreover, a miktoarm metallo-supramolecular star-shaped copolymer was prepared consisting of an europium(III) complex bearing three poly(ε-caprolactone) dibenzoylmethane ligands and one poly(DL-lactide) bipyridine ligand.[30] This metallo-supramolecular polymer exhibited a lamellar morphology in thin films with the europium(II) ions on the phase boundary. Iron(II) complexes of the dibenzoylmethane ligand were very recently applied to simultaneously act as initiator, catalyst and activating group for the controlled ring-opening polymerization of DL-lactide as well.[31]

A hydroxypropylterpyridine was applied as initiator for polymerization of ε-caprolactone by Schubert and co-workers.[32] The mechanical properties of the resulting polymer were significantly improved upon the addition of iron(II) ions and only slightly improved upon complexation with zinc(II) ions (due to the lower binding strength) as was shown by rheometry. In addition, the observed mechanical polymer properties also changed by changing the counterions of the metal complexes. The terminal hydroxyl group of the α-terpyridine-ω-hydroxy-poly(ε-caprolactone) macroligand was coupled to an ureidopyrimidinone quadruple hydrogen bonding unit[33] resulting in a polymer with both metal-coordinating and hydrogen bonding end-groups (Fig. 5). The addition of iron(II) ions to this polymer resulted in the formation of high-molecular weight supramolecular polymers as shown by viscometry and rheometry. Moreover, the solution viscosity of this metallo-supramolecular polymer was strongly dependent on temperature due to the hydrogen bonding interactions. This example demonstrates that the (metallo-)supramolecular initiator approach provides further possibilities to introduce a second functional group at the polymer chain end.

Besides the stannous octoate catalyzed ring-opening polymerization of cyclic esters, the aluminium alkoxide mediated controlled ring-opening polymerization technique was also explored utilizing (metallo-)supramolecular initiators.[34–36] By reaction of a hydroxyl group and triethylaluminium, an aluminium alkoxide is generated which can be applied for the controlled ring-opening polymerization of cyclic esters. This synthetic route has been applied using mono- and bis(hydroxymethyl)bipyridines as well as the corresponding bipyridine copper(I) complexes for the polymerization of ε-caprolactone and DL-lactide.[34] Similarly, terpyridine functionalized poly(L-lactide)s were prepared.[35] These macroligands were successfully dimerized with iron(II) ions as demonstrated by GPC utilizing a photodiode array detector and by MALDI-TOF-MS. The resulting iron(II) metallo-supramolecular polymers could be decomplexed by changes in temperature or pH and by UV-irradiation, whereby the thermal decomplexation was found to be reversible. An analogous synthetic route was followed for the preparation of poly(L-lactide) functionalized 3,6-di(2-pyridyl)pyridazines. The resulting macroligands self-assembled into polymeric [2 × 2] grids[37] upon the addition of copper(I) ions as was demonstrated by UV-Vis titration experiments (Fig. 6).[36] These experiments could be successfully performed in dichloromethane demonstrating that both the properties of the ligands (complexation) and the polymers (solubility) could be combined in one material. With short polymer side-chains, the macroligands revealed strong cooperativity in the grid formation, whereas the larger macroligands formed polymeric [2 × 2] copper(I) grids without cooperativity.[38]

4. Controlled radical polymerizations using (metallo-)supramolecular initiators

Another promising route towards well-defined (metallo-)supramolecular polymers is the utilization of controlled radical polymerization techniques that allow the polymerization of a wide variety of styrenic and (meth)acrylate monomers and thus expand the scope of accessible polymers.[39] Moreover, controlled radical polymerization methods are very robust and insensitive to many functional groups including hydroxyls, ketones, amines and pyridyls, which are often present in metal coordinating ligands. The three most common controlled polymerization techniques [atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer polymerization (RAFT) and nitroxide mediated

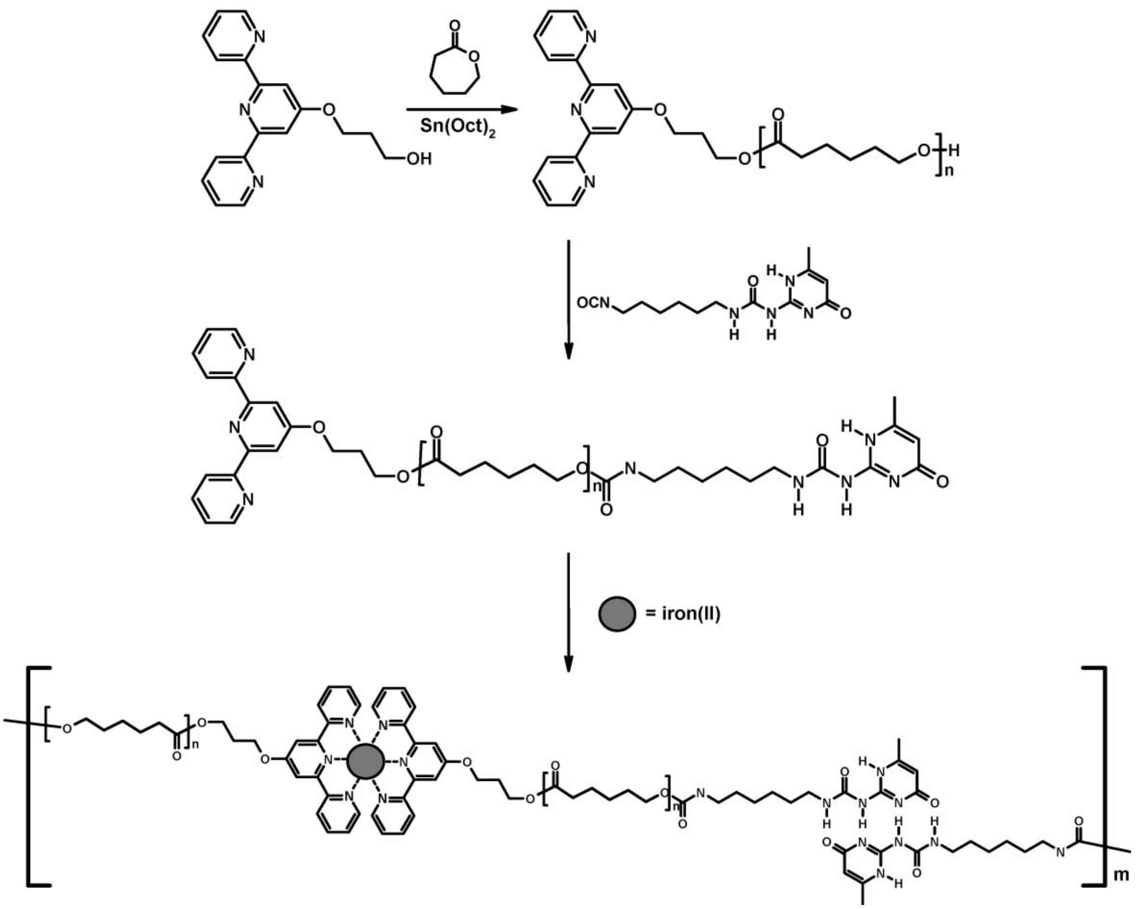

Fig. 5 Synthesis of a metallo-supramolecular poly(ε-caprolactone) with both terpyridine metal complexes and ureidopyrimidinone quadruple hydrogen bonding units in the main chain.[32]

polymerization (NMP)] have been applied for the synthesis of metallo-supramolecular polymers.

ATRP is the most commonly used controlled radical polymerization technique for the synthesis of metallo-supramolecular polymers. Fraser and coworkers have performed most of the pioneering work in this direction. Already in 1998, the ATRP of styrene was reported utilizing bis(chloromethyl)-bipyridine and the corresponding di-, tetra- and hexachloro-functionalized ruthenium(II) complexes, as initiators.[40] Well-defined polystyrene metallo-supramolecular polymers were obtained demonstrating the compatibility of the ATRP process with the cationic ruthenium initiators. In addition, the ATRP of methyl (meth)acrylate was performed utilizing a ruthenium bipyridine complex bearing six α-bromoester initiating groups resulting in well-defined polymers.[41] The ATRP of methyl methacrylate utilizing tris(dialkylaminostyryl-bipyridine) iron(II) and zinc(II) metallo-initiators was reported by Haddleton and Le Bozec (Fig. 7).[42] Both metal complexes

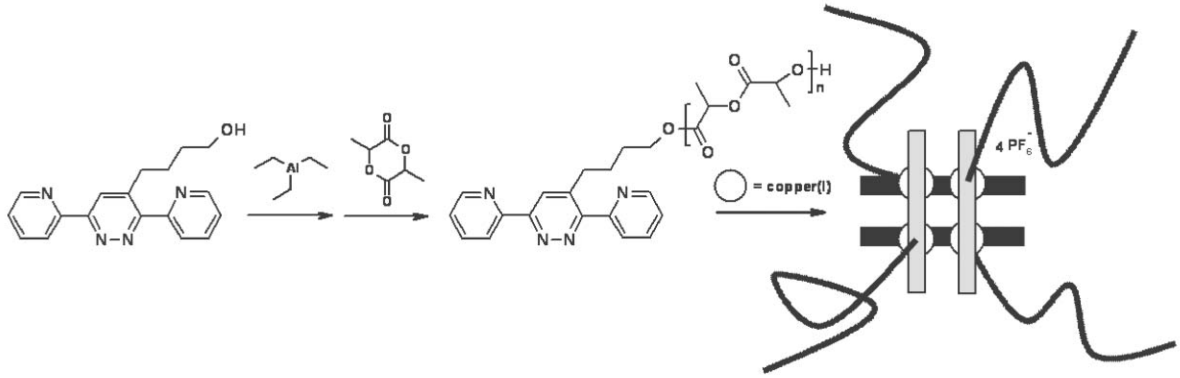

Fig. 6 Schematic representation of the synthesis of a poly(L-lactide) 3,6-di(2-pyridyl)pyridazine macroligand and the subsequent self-assembly into [2 × 2] grid-like complexes with copper(I) ions.

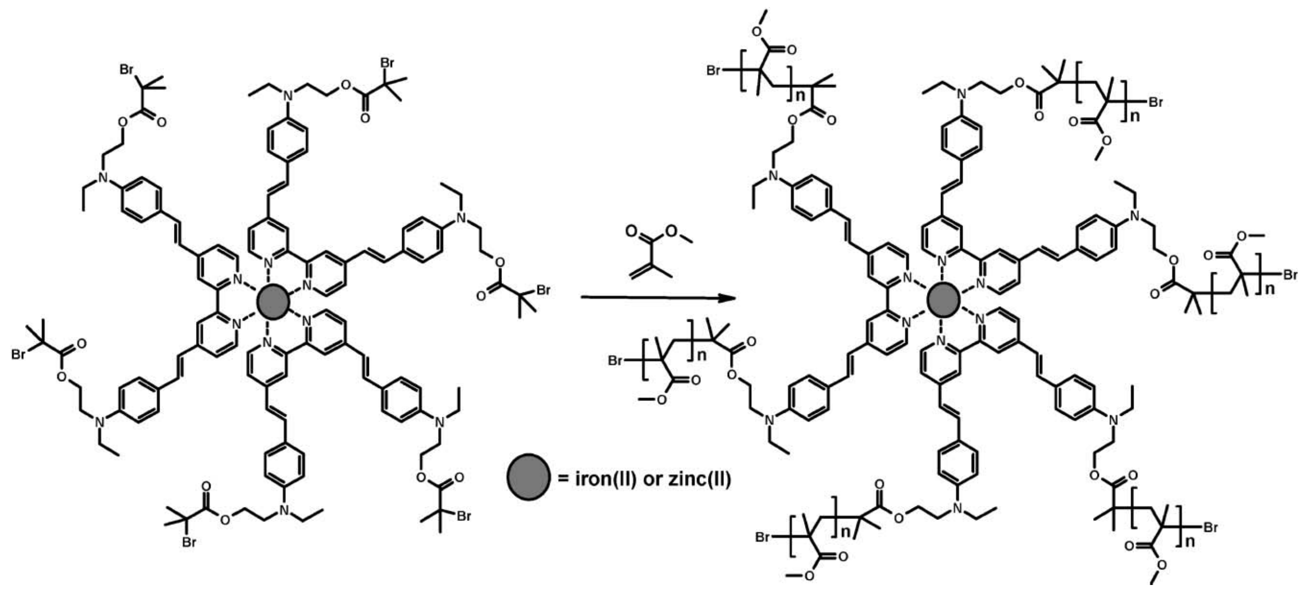

Fig. 7 Schematic representation of the synthesis of star-shaped metallo-supramolecular poly(methyl methacrylate)s.[42]

with six α-bromoesters were successfully applied for the controlled polymerization of methyl methacrylate. The good film-forming properties of the resulting polymers were illustrated by scanning electron microscopy images. The film formation together with the UV-spectra of the polymer film clearly revealed that both the properties of the polymer and the metal complexes were combined in the novel materials.

Sequential ATRP of styrene and methyl methacrylate was performed by Fraser to synthesize a bipyridine ligand bearing both a polystyrene and a poly(methyl methacrylate) polymer side chain.[43] First ATRP of styrene was performed using a bipyridine initiator bearing both hydroxy- and chloromethyl-groups. Subsequently, the resulting halide chain-end of the polystyrene was removed and the hydroxyl group was converted into an α-bromoester group. This α-bromoester was applied as initiator for the ATRP of MMA resulting in the mixed polymer bipyridine macroligand. The same bifunctional bipyridine initiator was applied as dual initiator for sequential ATRP of styrene and controlled ring-opening polymerization of ε-caprolactone.[44] The resulting two-armed bipyridine was used for the complexation with a bisbipyridine ruthenium(II) precursor, iron(II) or platinum(II) salts. The complexation with platinum(II) ions led to the formation of bipyridine platinum(II) monocomplexes that might be used in the formation of mixed ligand metal complexes. To be able to further combine all the prepared bipyridine ligands in supramolecular miktoarm star (block)copolymers, a stepwise ruthenium complexation method was developed by Fraser *et al.* as depicted in Fig. 8.[45] Ruthenium(II) precursors with two polymeric bipyridines were successfully prepared using elevated reaction temperatures and elongated reaction times to overcome the steric hindrance of the polymer chains. In a next step, the polymeric ruthenium(II) bipyridine precursors were coupled to a third polymeric bipyridine ligand resulting in ruthenium(II) complexes with two identical and one different bipyridine ligands.

Metal-complexes based on an α-bromoester functionalized diimine ligand were applied as initiator for ATRP by Chan and coworkers.[46] Both rhenium(I) tricarbonyl diimine and bis(bipyridine) ruthenium(II) diimine complexes resulted in the controlled polymerization of styrene and methyl methacrylate as demonstrated by linear first order kinetics and a linear

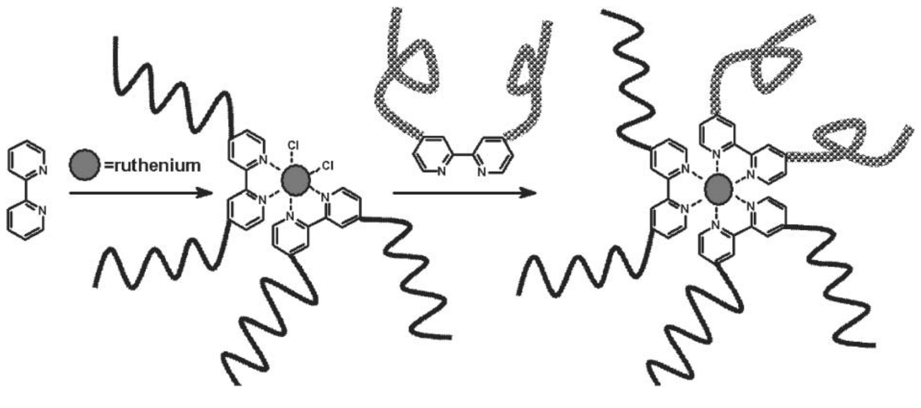

Fig. 8 Synthesis of hetero-arm metallo-supramolecular polymers from bipyridine ligands.[45]

increase of the molecular weight with conversion. The photoconducting properties of the resulting polymers were studied demonstrating that the metal complexes mainly act as photosensitizers and not as charge carriers. Although many examples of bipyridine (and diimine) initiated ATRP have been reported, the application of terpyridine initiators for ATRP is still completely unexplored.

The previous part of this section dealt with ATRP utilizing metallo-supramolecular initiators. However, ATRP is catalyzed by metal salts and thus the used metal salts might also be complexed by free ligand initiators. Therefore, the utilization of other metal-free controlled radical polymerization techniques seems to be more promising for the synthesis of metallo-supramolecular polymers. Nevertheless, only in the last few years some examples of RAFT and NMP utilizing metallo-supramolecular RAFT agents or NMP initiators have been reported. The slower introduction of RAFT and NMP for the synthesis of metallo-supramolecular polymers might be due to the higher (synthetic) complexity of the RAFT agents and the NMP initiators compared to ATRP initiators.

RAFT-agents coupled to bipyridine ligands were first reported by Ghiggino and coworkers.[47] A bis(hydroxymethyl)-bipyridine and corresponding di-, tetra- and hexahydroxy-functional ruthenium(II) complexes were coupled to a preformed acid functionalized RAFT agent using dicyclohexylcarbodiimide as coupling agent. These synthesized RAFT-agents were successfully applied for the controlled polymerization of a styrene functionalized coumarin monomer. The resulting metallo-supramolecular poly(styrene-coumarin)s exhibited energy transfer efficiencies up to 60% between the light-absorbing coumarin chromophores and the ruthenium bipyridine complexes. Zhou and Harruna synthesized a bipyridine ligand bearing two RAFT-agents directly attached to the 5,5′ positions of the bipyridine (Fig. 9).[48] This novel bipyridine RAFT-agent proved to be a good control agent for the polymerization of styrene resulting in linear first order kinetics and a linear increase of molecular weight with conversion. The resulting bipyridines with two polystyrene chains were successfully complexed with a bisbipyridine ruthenium(II) precursor to form the corresponding metallo-supramolecular polymers.

A similar synthetic procedure was applied by Zhou and Harruna for the synthesis of a terpyridine with one RAFT-agent connected.[49] It was demonstrated that this RAFT-agent can be used for the controlled polymerization of styrene and *n*-isopropylacrylamide resulting in terpyridine end-functionalized polymers. The terpyridine functionalized polystyrene was treated with ruthenium(III) trichloride to form a ruthenium(III) monocomplex. This monocomplex was further reacted with both the terpyridine functionalized polystyrene and poly(*n*-isopropyl-acrylamide) to yield the dimerized polystyrene and the poly(styrene-*b*-(*n*-isopropyl-acrylamide)) metallo-supramolecular polymers.

A terpyridine functionalized initiator for NMP has been reported by Lohmeijer and Schubert.[50] A preformed benzyl chloride functionalized initiator was coupled to 2,6-di(2-pyridyl)-4-pyridone in the presence of potassium carbonate. This initiator was successfully applied for the controlled bulk polymerization of styrene resulting in the formation of a polystyrene macroligand. Moreover, the remaining nitroxide group at the end of the polystyrene could be successfully substituted by a terpyridine modified maleimide resulting in bisterpyridine telechelic polystyrene as was demonstrated by MALDI-TOF-MS.

5. Conclusions

The design and preparation of novel materials that combine the reversible and optical properties of metal complexes and the processability and mechanical properties of polymers are flourishing fields in polymer science. In this *tutorial review*, the utilization of metallo-supramolecular initiators for living/controlled polymerization techniques resulting in end-functionalized polymers is described in detail. Up to this moment, only three different types of polymerization methods were performed with (metallo-)supramolecular initiators, namely living cationic ring-opening polymerization of 2-oxazolines, controlled ring-opening polymerization of cyclic esters and controlled radical polymerizations. Moreover, the mostly used metal coordinating ligands are bipyridines and terpyridines that can be assembled into metal complexes with two or three ligands.

Therefore, the current opportunities in the field of metallo-supramolecular initiators can be divided into three parts: (1) the expansion of living/controlled polymerization methods that can be performed with (metallo-)supramolecular initiators; (2) the application of other metal coordinating units that can (self-)assemble into larger structures and (3) the development of novel 'smart' materials based on the reversible assembly of the metal complexes. Moreover, the combination of different supramolecular units into one polymer chain might open a completely new field of materials with unique

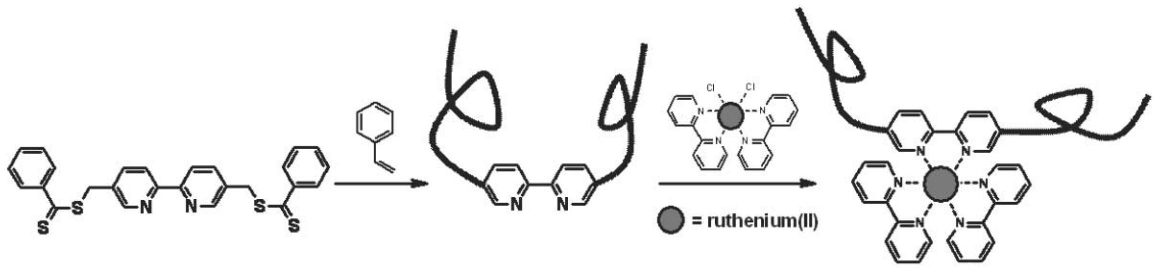

Fig. 9 RAFT polymerization of styrene utilizing a bipyridine unit with two coupled RAFT-agents and the subsequent formation of the metallo-supramolecular polymer.[48]

properties, although the dream of mimicking Nature will probably not be met in the near future.

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References

1 J.-M. Lehn, *Supramolecular Chemistry*, Wiley VCH, Weinheim, 1996.
2 I. Roy and M. N. Gupta, *Chem. Biol.*, 2003, **10**, 1161–1171.
3 L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071–4097.
4 U. S. Schubert and C. Eschbaumer, *Angew. Chem.*, 2002, **114**, 3016–3050, *Angew. Chem. Int. Ed.*, 2002, **41**, 2892–2962.
5 R. Ziessel, *Coord. Chem. Rev.*, 2001, **216–217**, 195–223.
6 A. M. W. Cargill Thompson, *Coord. Chem. Rev.*, 1997, **160**, 1–52.
7 For a review on living/controlled polymerization techniques, see: K. Matyjaszewski, *Macromol. Symp.*, 2001, **174**, 51–67.
8 K. Naka, A. Kobayashi and Y. Chujo, *Macromol. Rapid Commun.*, 1997, **18**, 1025–1032.
9 M. E. Williams, H. Masui, J. W. Long, J. Malik and R. W. Murray, *J. Am. Chem. Soc.*, 1997, **119**, 1997–2005.
10 C. L. Fraser and A. P. Smith, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 4704–4716.
11 V. Marin, E. Holder, M. A. R. Meier, R. Hoogenboom and U. S. Schubert, *Macromol. Rapid Commun.*, 2004, **25**, 793–798.
12 B. G. G. Lohmeijer and U. S. Schubert, *Angew. Chem.*, 2002, **114**, 3980–3984, *Angew. Chem. Int. Ed.*, 2002, **41**, 3825–3829.
13 J. B. Beck, J. M. Ineman and S. J. Rowan, *Macromolecules*, 2005, **38**, 5060–5068.
14 For a review on poly(2-oxazoline)s, see: K. Aoi and M. Okada, *Progr. Polym. Sci.*, 1996, **21**, 151–208.
15 J. J. S. Lamba and C. L. Fraser, *J. Am. Chem. Soc.*, 1997, **119**, 1801–1802.
16 J. E. McAlvin and C. L. Fraser, *Macromolecules*, 1999, **32**, 6925–6932.
17 J. E. McAlvin, S. B. Scott and C. L. Fraser, *Macromolecules*, 2000, **33**, 6953–6964.
18 J. E. McAlvin and C. L. Fraser, *Macromolecules*, 1999, **32**, 1341–1347.
19 C. Park, J. E. McAlvin, C. L. Fraser and E. L. Thomas, *Chem. Mater.*, 2002, **14**, 1225–1230.
20 G. Hochwimmer, O. Nuyken and U. S. Schubert, *Macromol. Rapid Commun.*, 1998, **19**, 309–313.
21 U. S. Schubert, O. Nuyken and G. Hochwimmer, *Design. Monom. Polym.*, 2000, **3**, 245–253.
22 U. S. Schubert, C. Eschbaumer, O. Nuyken and G. Hochwimmer, *J. Incl. Phenom.*, 1999, **35**, 23–34.
23 U. S. Schubert, G. Hochwimmer and M. Heller, *ACS Symp. Ser.*, 2002, **812**, 163–176.
24 M. Heller and U. S. Schubert, *Macromol. Symp.*, 2002, **177**, 87–96.
25 For a review on different controlled ring-opening polymerization techniques for lactide, see: O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147–6176.
26 P. S. Corbin, M. P. Webb, J. E. McAlvin and C. L. Fraser, *Biomacromolecules*, 2001, **2**, 223–232.
27 V. Marin, E. Holder, R. Hoogenboom and U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 4153–4160.
28 A. A. Farah and W. J. Pietro, *Can. J. Chem.*, 2004, **82**, 595–607.
29 J. L. Bender, Q.-D. Shen and C. L. Fraser, *Tetrahedron*, 2004, **60**, 7277–7285.
30 J. L. Bender, P. S. Corbin, C. L. Fraser, D. H. Metcalf, F. S. Richardson, E. L. Thomas and A. M. Urbas, *J. Am. Chem. Soc.*, 2002, **124**, 8526–8527.
31 J. L. Gorczynski, J. Chen and C. L. Fraser, *J. Am. Chem. Soc.*, 2005, **127**, 14956–14957.
32 H. Hofmeier, R. Hoogenboom, M. E. L. Wouters and U. S. Schubert, *J. Am. Chem. Soc.*, 2005, **127**, 2913–2921.
33 R. P. Sijbesma, F. H. Beier, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe and E. W. Meijer, *Science*, 1997, **278**, 1601–1604.
34 U. S. Schubert and G. Hochwimmer, *Macromol. Rapid Commun.*, 2001, **22**, 274–280.
35 M. Heller and U. S. Schubert, *Macromol. Rapid Commun.*, 2001, **22**, 1362–1367.
36 R. Hoogenboom, D. Wouters and U. S. Schubert, *Macromolecules*, 2003, **36**, 4743–4749.
37 For a review on grid-like metal complexes, see: M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine and J.-M. Lehn, *Angew. Chem.*, 2004, **116**, 3728–3747, *Angew. Chem. Int. Ed.*, 2004, **43**, 3644–3662.
38 R. Hoogenboom, J. Huskens and U. S. Schubert, *ACS Symp. Ser.*, 2005, **928**, 62–71.
39 For a review on controlled radical polymerization techniques, see: K. A. Davis and K. Matyjaszewski, *Adv. Polym. Sci.*, 2002, **159**, 1–169.
40 J. E. Collins and C. L. Fraser, *Macromolecules*, 1998, **31**, 6715–6717.
41 R. M. Johnson, P. S. Corbin, C. Ng and C. L. Fraser, *Macromolecules*, 2000, **33**, 7404–7412.
42 L. Viau, M. Even, O. Maury, D. M. Haddleton and H. Le Bozec, *Macromol. Rapid Commun.*, 2003, **24**, 630–635.
43 A. P. Smith and C. L. Fraser, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 4250–4255.
44 A. P. Smith and C. L. Fraser, *Macromolecules*, 2002, **35**, 594–596.
45 A. P. Smith and C. L. Fraser, *Macromolecules*, 2003, **36**, 5520–5525.
46 S. H. Chan, L. S. M. Lam, C. W. Tse, K. Y. K. Man, W. T. Wong, A. B. Djurisic and W. K. Chan, *Macromolecules*, 2003, **36**, 5482–5490.
47 M. Chen, K. P. Ghiggino, A. Launikonis, A. W. H. Mau, E. Rizzardo, W. H. F. Sasse, S. H. Thang and G. J. Wilson, *J. Mater. Chem.*, 2003, **13**, 2696–2700.
48 G. Zhou and I. I. Harruna, *Macromolecules*, 2004, **37**, 7132–7139.
49 G. Zhou and I. I. Harruna, *Macromolecules*, 2005, **38**, 4114–4123.
50 B. G. G. Lohmeijer and U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 4016–4027.