

Manuscript version: Author's Accepted Manuscript

The version presented in WRAP is the author's accepted manuscript and may differ from the published version or Version of Record.

Persistent WRAP URL:

<http://wrap.warwick.ac.uk/113714>

How to cite:

Please refer to published version for the most recent bibliographic citation information. If a published version is known of, the repository item page linked to above, will contain details on accessing it.

Copyright and reuse:

The Warwick Research Archive Portal (WRAP) makes this work by researchers of the University of Warwick available open access under the following conditions.

Copyright © and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners. To the extent reasonable and practicable the material made available in WRAP has been checked for eligibility before being made available.

Copies of full items can be used for personal research or study, educational, or not-for-profit purposes without prior permission or charge. Provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.

Publisher's statement:

Please refer to the repository item page, publisher's statement section, for further information.

For more information, please contact the WRAP Team at: wrap@warwick.ac.uk.

End-functional polyolefins for block copolymer synthesis†

Paul D Goring^a, Colin Morton^b and Peter Scott^{a,*}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Polyolefins that contain polar functionalities are highly desired because they could extend the range of applications of these low production cost materials by modifying surface and other interfacial properties. Block copolymers containing polyolefin and polar segments are among the most sought-after architectures because of their ability to span the phase boundaries. This review focusses on the end-functionalisation of polyolefins by catalytic olefin polymerisation processes, almost invariably by metal-catalysed routes, followed by the growth polar blocks by various polymerisation techniques.

Introduction

Making up 50% of plastic production worldwide, polyolefins (PO) are by far the largest volume class of polymers.¹ Properties such as chemical stability, flexibility, mechanical strength, recyclability, processability and low production cost mean that these materials are used in a wide range of commercial applications.^{2–4} However their properties of low reactivity, poor adhesion and incompatibility with other polymers present technical challenges in e.g. recycling, printing, impact modification and composites manufacture.^{5,6,7}

The consequent demand for polymeric additives with which to modify the interfaces between polyolefins and other substances is currently addressed by statistical copolymers such as poly(ethylene-vinyl acetate) or e.g. polyolefins grafted with maleic anhydride. In the search for polymers that can more efficiently span the relevant phase boundary,^{8,9} block copolymers containing polyolefin and polar polymer segments have been sought. Several reviews reporting functional polyolefin synthesis based on final structure,⁴ end-group,¹⁰ synthetic strategy^{2,11} or of a more general nature⁵ have been published in recent decades.

One entry to block copolymers with reasonably polar segments is provided commercially by sequential anionic polymerization of e.g. dienes and styrene followed by hydrogenation, but few monomers are tolerated.^{12,13} As a generality, the differences in polarity and reactivity of these monomer classes lead to technical challenges; olefins are difficult to polymerise by radical methods^{14,15,16,17} and polar monomers tend to deactivate coordination polymerisation catalysts.^{7,18,19} The search for catalysts that could be used to make block copolymers *via* sequential monomer addition – i.e. living polymerisation – met with some early successes,^{20–26} but the current scope of this technology is limited by productivity, accessibility of the catalysts and monomer scope.

Another approach has been widely researched – the use of end-functionalised polyolefins as initiators or macromonomers in polar monomer polymerisations – and this is the subject of the current manuscript. The polyolefins are almost invariably synthesised from catalytic organometallic routes.

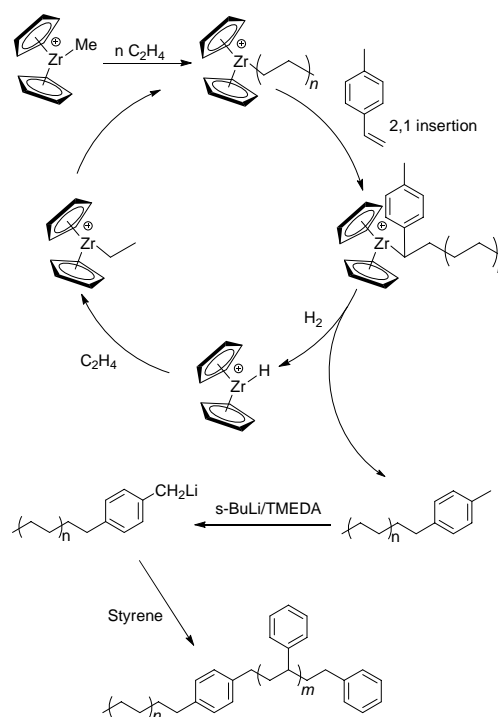


Figure 1: A copolymerisation of ethylene and *p*-methylstyrene (PMS) in presence of H₂ yields PE terminated by PMS. This is subject to metalation and reaction with styrene to give PE-*b*-PS *via* anionic polymerisation.^{27,28}

Polyolefin initiators for ionic polymerisation

A number of studies have followed a catalytic coordination polymerisation of an olefin e.g. ethylene or propylene with

^a Department of Chemistry, University of Warwick, Coventry, CV4 7AL

^b Infineum UK Ltd, Milton Hill, Abingdon OX13 6BB, U.K.

† Dedicated to Geoff Cloke – a fearless, inspiring scientist and loyal friend – on the occasion of his 65th birthday.

conversion to a macroinitiator for the ionic polymerisation to produce a block copolymer.

Although the second polymerisation mechanism in this area is almost always anionic, in 1983 a number of PP-*b*-P(THF) diblock copolymers were synthesised by Doi using coordination polymerisation followed by living cationic polymerisation.²⁹ Synthesis of iodine-terminated PP using a vanadium acetylacetonate (acac) catalyst was followed by conversion to a macroinitiator for cationic polymerisation of THF by reaction with AgClO₄.

Chung and co-workers found that metallocene catalysts activated by MAO could be used to incorporate terminal *para*-methylstyrene (PMS) units during ethylene or propylene polymerisation in the presence of hydrogen. These PMS end groups could be metallated in the presence of *s*-BuLi and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to convert the polyolefin into a macroinitiator for the living anionic polymerisation of styrene yielding PE-*b*-PS and PP-*b*-PS diblock copolymers (Figure 1).^{27, 28} It was found by Chung that polyolefins containing vinylbenzene functionalities could be used to prepare graft copolymers with styrene in a similar fashion,³⁰ though the synthesis of block copolymer was not reported.

The Chung group have also studied the synthesis and reactions of polyolefins containing 9-BBN end groups by a similar mechanism to that of Figure 2;³¹ see also seminal work in this area by Marks.³² As well as being able to initiate free-radical polymerisation (*vide infra*), oxidation of the 9-BBN groups followed by metalation converts the boranes into efficient initiators for the anionic polymerisation of ethylene oxide to yield block copolymers (Figure 2). A similar process was also used for the synthesis of PE-*b*-P(ϵ -caprolactone) and PS-*b*-P(ϵ -caprolactone) copolymers *via* anionic ring-opening polymerisation.³³

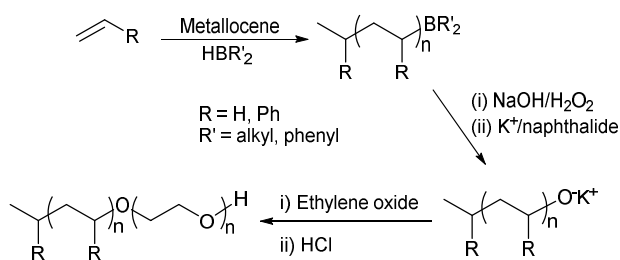


Figure 2: Synthesis of poly(ethylene oxide) block copolymers from borane-terminated polyolefins.³¹

Polyolefin initiators for radical polymerisation

9-Borabicyclononane oxidation

As well as being able to initiate anionic polymerisation from oxidised alkyl borane end groups, Chung and co-workers have demonstrated that exposure of 9-BBN-terminated polyolefins to oxygen produces a borane peroxide that can either be reduced by another alkyl borane or cleaved homolytically to generate a stable 9-BBN-O• radical, along with alkyl and alkoxy radicals capable of initiating radical polymerisation of various

polar monomers at ambient temperature.³⁴ The B-O• radical does not initiate the polymerisation itself, but can react reversibly with the growing radical, resulting in an equilibrium between dormant and active species. The group utilised the oxophilicity of alkyl boranes to develop two methods for the preparation of polyolefins bearing terminal 9-BBN functionalities.³⁵⁻³⁷ Following oxidation of the 9-BBN group, the polyolefins could be used as initiators for the free-radical polymerisation of methyl methacrylate to form PE-*b*-PMMA and PP-*b*-PMMA copolymers (Figure 3).

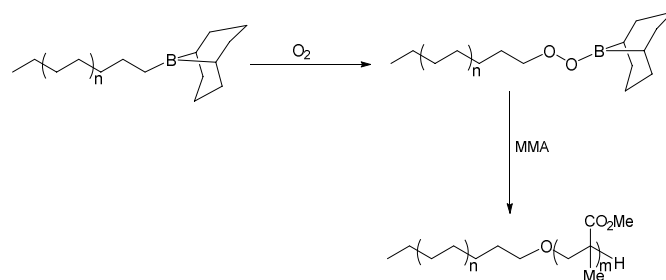
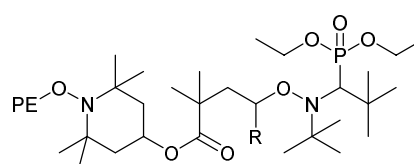
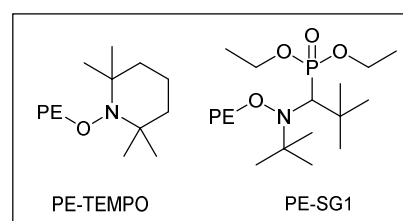
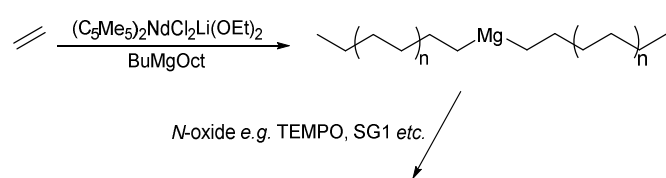


Figure 3: Oxidation of borane end group and subsequent radical polymerisation of methyl methacrylate.³⁵⁻³⁷



DD1: R = COBu
DD2: R = Ph

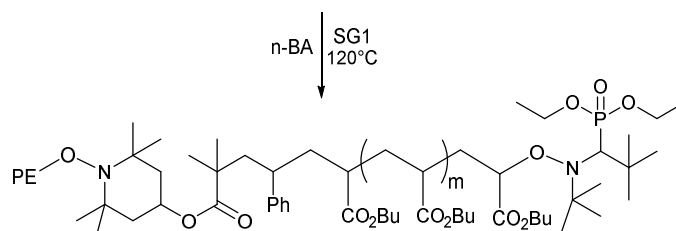


Figure 4: From catalytic chain transfer polymerisation for ethylene to block copolymer *via* NMP.³⁸⁻⁴²

Nitroxide-mediated radical polymerisation (NMP)

The transformation of polyolefins into macroalkoxyamines for nitroxide-mediated graft polymerisation of various polar monomers has been studied by several groups, but there are fewer reports of successful block copolymer synthesis.

A lanthanide-catalysed PE synthesis incorporating magnesium chain transfer³⁸ gave access to versatile MgPE₂ (Figure 4) which was used in the production of a range of end-functionalised PEs by various post-polymerisation reactions³⁹ to give alkoxyamine-functionalised PEs.⁴⁰⁻⁴² Of these the DD2 derivative required a substantially lower temperature (60°C) than either TEMPO or SG1 to cleave the C-ON bond and thus initiate nitroxide-mediated polymerisation to give e.g. *n*-butyl acrylate copolymers, albeit with modest end-group fidelity.⁴²

Atom transfer radical polymerisation (ATRP)

The conversion of functionalised polyolefins to macroinitiators for ATRP of polar monomers is by far the most-studied strategy to produce both polyolefin-polar block and graft copolymers.

Matyjaszewski and co-workers⁴³ described a hydrosilylation route (Figure 5) whereby terminal vinylidene groups or metallocene-derived PP give a 2-bromoisobutyrate suitable for the synthesis of PP-*b*-PMMA and PP-*b*-P(*n*-BA) copolymers with low dispersity and good conversion, though with long reaction times.

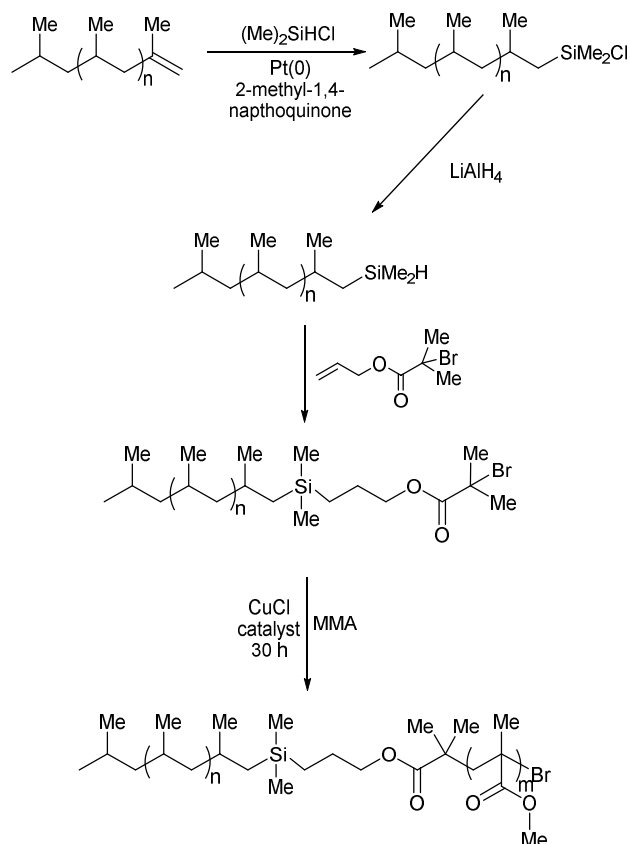


Figure 5: Conversion of vinyl-terminated PP to an ATRP initiator via hydrosilylation, followed by P(MMA) block copolymer synthesis.⁴³

A more straightforward synthesis was developed by the same group for PE block copolymers (Figure 6).⁴⁴ Vinyl-

terminated PE produced using a phenoxyimine zirconium catalyst was treated directly with 2-bromopropanoic acid in the presence of triflic acid to yield a 75% functionalised PE ATRP macroinitiator; PE-*b*-PMMA, PE-*b*-P(*n*-BA) and PE-*b*-PS copolymers of low dispersity were prepared.

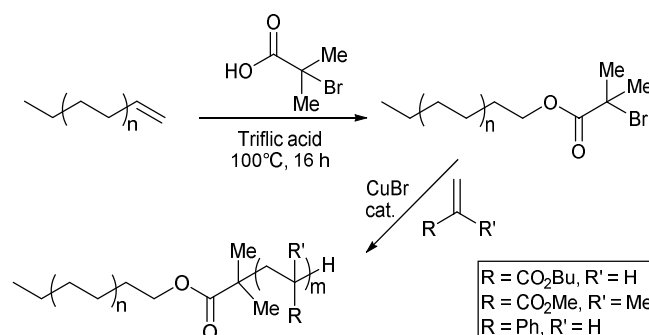


Figure 6: Direct synthesis of a PE-based macroinitiator and subsequent ATRP of MMA, *n*-BA and Styrene.⁴⁴

Matsugi and co-workers⁴⁵ described their preparation of vinyl-terminated PP from commercial PP by pyrolysis and its subsequent conversion to an allylic bromide by reaction with *N*-bromosuccinimide. This was used to initiate ATRP of styrene, MMA and *n*-BA respectively to yield block copolymers. The authors recently extended this technology substantially, reporting a range of different bromine-terminated polyolefins and their subsequent use in ATRP of polar monomers including MMA, *t*-butyl acrylate, ethyl acrylate and styrene to yield a great variety of polyolefin block copolymers.⁴⁶

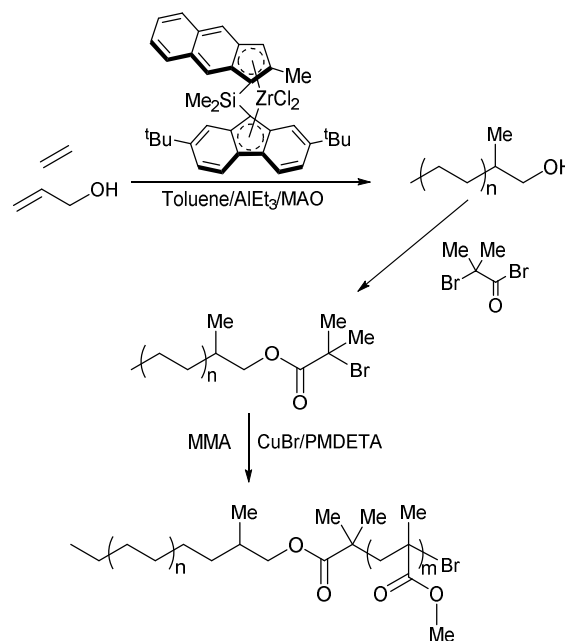


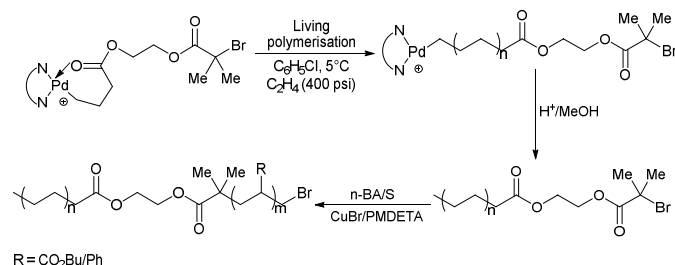
Figure 7: Copolymerisation of ethylene with allyl alcohol in the presence of a metallocene catalyst gives directly a hydroxyl-terminated PE, subsequently converted to an ATRP macroinitiator for the synthesis of PE-*b*-PMMA.^{47,48}

The above strategies involving modification of terminal vinyl groups requires several reaction steps and long polymerisation

times for the synthesis of the second block. Kashiwa and co-workers described the development of a one-pot synthesis of hydroxyl-capped PE using allyl alcohol as a comonomer and a bulky metallocene indenyl-fluorenyl catalyst in the presence of MAO. Selective end-incorporation of the allyl alcohol and chain transfer to aluminium allowed the synthesis of PE-OH by oxidative work-up (Figure 7).⁴⁷ The PE-OH was used to synthesise macroinitiators by reaction with α -bromoisobutyryl bromide in the presence of Et_3N , and block copolymerisation by ATRP of MMA was achieved.⁴⁸ The effective compatibilisation of PE and PMMA homopolymers by the block copolymer was also reported.

Matyjaszewski and co-workers⁴⁹ reported ATRP of *n*- or *t*-butyl acrylate from a PE ATRP macroinitiator prepared by chain transfer to zinc to afford PE block copolymers with substantially faster polar monomer conversion than that achieved by modification of vinyl-terminated polyolefins. See also related work utilising aluminatation.⁵⁰⁻⁵²

Also noteworthy are macromonomers based on PE bearing methacrylic end groups, achieved by Matyjaszewski and co-workers utilising Pd(II) α -diimine catalysts (Figure 8).⁵³ The functional PE was then able to copolymerise with *n*-BA under ATRP conditions. A novel functionalised Pd diimine catalyst containing a 2-bromoisobutyryl substituting group allowed Ye and co-workers⁵⁴ to directly synthesise 2-bromoisobutyryl-terminated PE. The terminal groups could then be used to initiate ATRP of styrene or *n*-BA to produce block copolymers in two steps, a significant achievement given the number of strategies described here that require more steps to achieve the same.



R = $\text{CO}_2\text{Bu/Ph}$

Figure 8: Tandem strategy for functionalised PE block copolymer synthesis.^{53, 54}

Other organometallic-mediated methods include a recent contribution by Yagci and co-workers,¹⁷ who demonstrated the use of $\text{Mn}_2(\text{CO})_{10}$ for the thermally-induced controlled radical polymerisation of styrene and MMA to produce block copolymers or relatively low dispersity from iodo-terminated PE (Figure 9). The PE macroinitiator was formed from catalysed chain growth on magnesium followed by reaction with iodine. The authors also report the synthesis of a triblock copolymer under the same conditions by polymerisation of styrene in the presence of the PE-*b*-PMMA-I species.

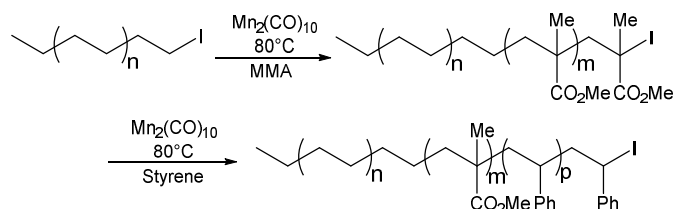


Figure 9: Synthesis of a diblock and a triblock copolymer by sequential thermally induced polymerisation with MMA and styrene.¹⁷

Detrembleur and co-workers⁵⁵ recently described the one-pot organometallic-mediated radical copolymerisation of ethylene with a variety of polar monomers where the transition metal complex reversibly traps the growing polymer chains (Figure 10). The authors report that by altering the ethylene feed pressure the synthesis of block-like copolymers (i.e. with ethylene-rich and polar monomer-rich segments) can be achieved.

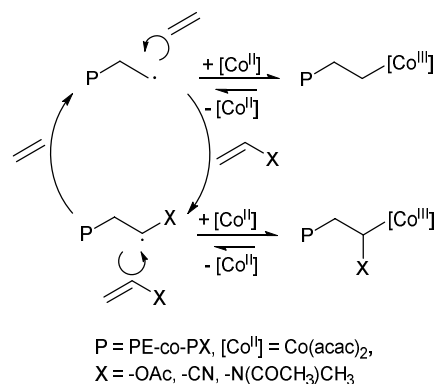


Figure 10: Organometallic-mediated polymerisation of ethylene with polar monomers to give block-like copolymers. $\text{Co}(\text{acac})_2$ traps the radical polymer chain formed by the addition of ethylene (top) or polar monomer (bottom) to give a $\text{Co}(\text{III})$ alkyl.⁵⁵

In related work a reversible shuttling process between catalytic insertion and radical polymerisation mechanisms at one metal centre, was proposed.^{56, 57}

Reversible addition-fragmentation chain transfer polymerisation (RAFT)

Polyolefin macro-RAFT agents are, like polyolefin macroalkoxyamines for NMP, scarce in literature. A macro-RAFT agent derived in two steps from the PE-OH of Figure 7 gave access to PE-PMMA [Figure 11(a)].⁵⁸ The conversion of $\text{Mg}(\text{PE})_2$ species to macro-RAFT agents was achieved by D'Agosto and co-workers (b)⁵⁹⁻⁶¹ and despite occasional low conversion and the presence of side reactions, subsequent RAFT polymerisations of *n*-BA provided a path to PE-based block copolymers. Wu and co-workers described the production of thermo- and pH-responsive PE-based di- and triblock copolymers with NIPAM and 2-vinylpyridine by RAFT polymerisation mediated by a RAFT agent made from hydroxyl-terminated PE.⁶²

While it does not involve catalytic coordination polymerisation, it is nonetheless noteworthy that Monteil, D'Agosto and co-workers¹⁶ have recently reported the first RAFT polymerisation of ethylene using xanthates as mediators.

They also report the copolymerisation of ethylene with small amounts of vinyl acetate mediated by xanthates under far milder conditions (70°C, 200 bar) than those required for free-radical ethylene polymerisation.

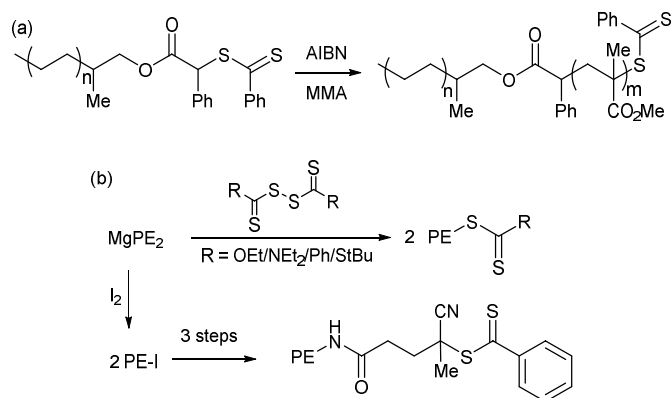


Figure 11: Selected PE macro-RAFT agent chemistry. ⁵⁸⁻⁶¹

Also noteworthy is the preparation of conjugated diene-containing block copolymers utilising RAFT polymerisation, as discussed in a recent review by Moad.⁶³ The synthesis of isoprene-containing block copolymers with various polar monomer segments has been reported using trithiocarbonates as RAFT agents.⁶⁴⁻⁶⁶ The synthesis of similar block copolymers containing butadiene blocks has also been reported.⁶⁷⁻⁷⁰

Polyolefin initiators for ring-opening polymerisation

Combining catalytic coordination polymerisation with ring-opening provides a useful route to copolymers with novel and controlled structures that are generally considered inaccessible by more conventional techniques.⁷¹ ROP can be accomplished thermally, ionically or by a transition metal catalyst and in order to achieve block and graft copolymers.

Access *via* hydroxyl group-bearing polyolefins is overwhelmingly the preferred method.^{11, 71} and generally involves *in situ* chain transfer to e.g. organoboranes,^{35, 36, 72, 73} alkyl aluminiums^{51, 74-78} and alkyl zincs^{49, 79-82} during catalytic olefin polymerisation, followed by oxidation. Chung and co-workers reported the synthesis of PE-*b*-PEO by anionic ROP of ethylene oxide following oxidation and metalation of borane-functionalised PE.³¹ The resulting block copolymers contained between 40 and 80 mol% ethylene oxide. Using a similar approach, the same authors also synthesised a series of PO-*b*-P(ϵ -caprolactone) copolymers which found use as polymeric compatibilisers.³³ Fujita and co-workers⁸³ reported the use of diol- and triol-terminated PE as initiators for ROP of ethylene oxide to yield PE/PEG hybrid materials (Figure 12).

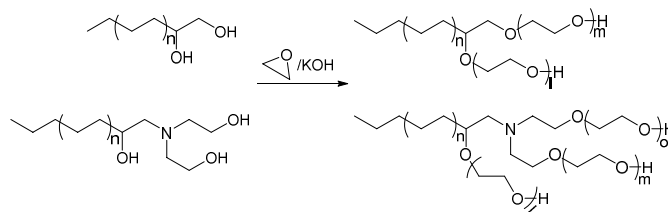


Figure 12: Synthesis of PE-PEG AB₂- and AB₃-type hybrid materials by ROP. ⁸³

Kim and co-workers⁸⁴ described the synthesis of PE-*b*-P(ϵ -caprolactone) *via* catalytic ring-opening polymerisation in the presence of OH-terminated PE using stannous octanoate as a catalyst. A similar approach was taken by Dubois, Mülhaupt and co-workers to prepare PE-*b*-P(lactide).⁸⁵ In both cases Zn-terminated PE^{75, 76} was converted to OH-terminated PE by exposure to air and was then used as a macroinitiator for the ROP of lactide in the presence of stannous octanoate (Figure 13).

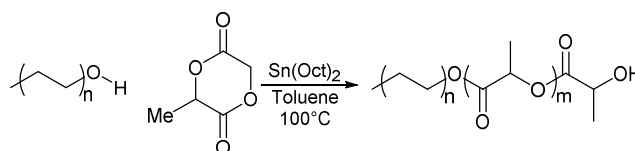


Figure 13: ROP of lactide initiated by PE-OH/Sn(oct)₂.⁸⁵

The iodine terminated PE of Figure 11(b) was converted in two steps to PE-SH⁸⁶ which initiated ROP of lactide.⁸⁷

Last year, Guironnet and co-workers⁸⁸ reported the tandem hydroformylation/hydrogenation of a vinyl-terminated PE to form a terminal hydroxyl group, from which ROP of ϵ -caprolactone was initiated using stannous octate as a catalyst to form a diblock copolymer.

ROMP polyolefins for radical polymerisation

To this point, the strategies covered for the synthesis of polyolefin-polar block copolymers have involved the use of catalytic coordination polymerisation for the synthesis of the polyolefin. Ring-opening metathesis polymerisation (ROMP) has also been utilised in certain examples, and has also been used to develop telechelic polymers which can be used for the synthesis of triblocks.^{89, 90}

ATRP

Matyjaszewski and co-workers⁹¹ described the production of ROMP-synthesised poly(norbornene) using a molybdenum imido/alkylidene metathesis catalyst, and the subsequent conversion to an ATRP macroinitiator by reaction with *p*-(bromomethyl)-benzaldehyde (Figure 14). The ATRP reactions of styrene and methyl acrylate were then described to yield block copolymers. The same method has also been used to make block copolymers using poly(dicyclopentadiene) as the hydrocarbon block.

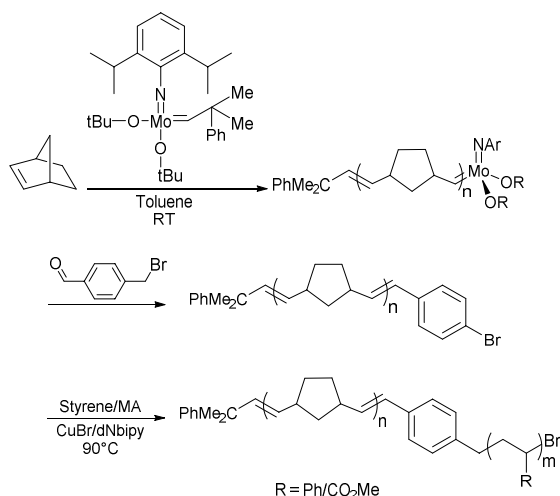


Figure 14: Successive living ROMP and ATRP to produce block copolymers.⁹¹

The use of a functional chain transfer agent (CTA) during the ROMP of 1,5-dicyclopentadiene in the presence of a ruthenium catalyst allowed Grubbs and co-workers⁹² to obtain telechelic polybutadiene bearing chlorine or 2-bromopropionyl ester end groups, from which ATRP or styrene or MMA could be efficiently conducted to yield poly(styrene-*b*-butadiene-*b*-styrene) and poly(MMA-*b*-butadiene-*b*-MMA) triblock copolymers with good control over the radical polymerisation.

Similar to the ATRP example mentioned above, Bates, Hillmyer and co-workers⁹³ conducted ROMP of 1,5-cyclooctadiene in the presence of another ruthenium catalyst and functional CTA (Figure 15). The double-end-functionalised polymer could then be used to mediate RAFT polymerisation of styrene and *t*-butyl acrylate respectively to yield triblock copolymers.

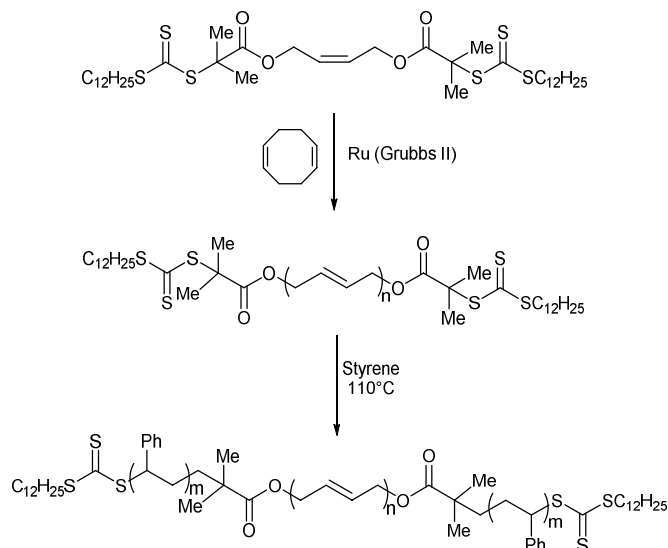


Figure 15: Tandem ROMP and RAFT strategy for triblock copolymer synthesis.⁹³

C1 polymerisation

C1 polymerisation (or polyhomologation) strategies have been used to build linear PE chains one carbon unit at a time with very narrow molecular weight distribution.^{94, 95}

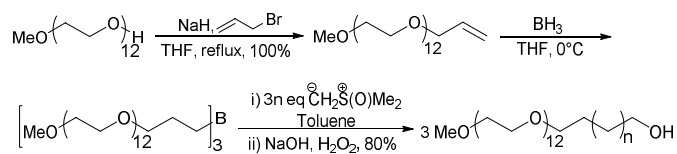


Figure 16: Synthesis of a poly(methylene-*b*-ethylene glycol) copolymer *via* hydroboration and polyhomologation.⁹⁶

Shea and co-workers⁹⁶ reported the synthesis of poly(methylene-*b*-ethylene glycol) diblocks by conversion of commercially available methoxy-terminated poly(ethylene glycol) to a trialkylborane initiator for the subsequent polyhomologation of dimethylsulfoxonium methylide, leading to well-defined, low dispersity diblock copolymers (Figure 16). In the same publication, the group also report the first example of a poly(methylene-*b*-dimethylsiloxane-*b*-methylene) triblock from α,ω -divinylpoly(dimethylsiloxane) using a similar strategy. The authors then looked into the possibility of combining polyhomologation with NMP in a sequential living polymerisation (Figure 17).⁹⁷ Starting from a specially prepared TEMPO PS initiator, which was hydrolysed to convert the benzoyloxy group, TEMPO-mediated polymerisation of styrene was conducted to produce the hydroxyl-terminated PS. From there a hydroboration reaction followed by polyhomologation using dimethylsulfoxonium methylide yielded the block copolymer in a six-step process.

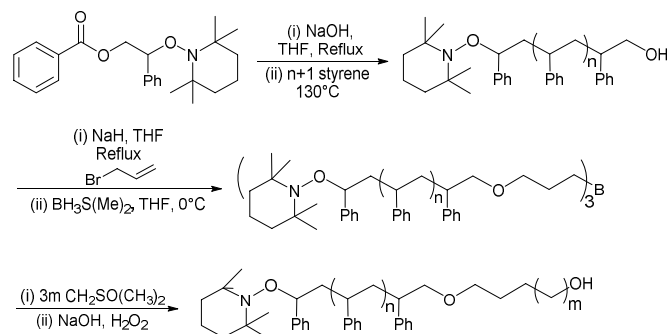


Figure 17: Synthesis of poly(methylene-*b*-styrene) *via* NMP and polyhomologation.⁹⁷

De Bruin and co-workers showed that functionalised and non-functionalised carbenes formed from either diazomethane or sulfoxonium ylides could be copolymerised using these rhodium catalysts, with the resulting copolymers exhibiting a blocky microstructure (Figure 18).^{98, 99} The composition and thus also the functional group content could be tuned by varying the monomer feed ratio over a large range.

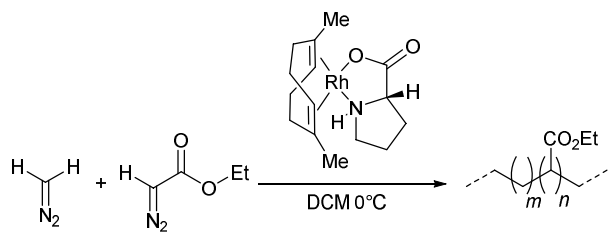


Figure 18: Copolymerisation of functionalised carbenes using rhodium catalysts.^{98, 99}

Ma and co-workers¹⁰⁰ described the preparation of a hydroxyl-terminated poly(methylene) *via* polyhomologation of dimethylsulfoxonium ylides and oxidation, and these and related polymers were employed in a similar manner to that shown in Figure 7 to make block polymers *via* ATRP,^{101, 102} or ring-opening polymers.¹⁰³

In the last few years, Hadjichristidis and co-workers¹⁰⁴ described the one-pot combination of polyhomologation and living anionic polymerisation to produce PE block copolymers. The process involves the synthesis of living macroanions of poly(butadiene) or poly(styrene), from which the trialkylborane macroinitiator is prepared by reaction with BF_3OEt_2 . The polyhomologation of dimethylsulfoxonium methylyde was then carried out *in situ* to produce PBD-*b*-PE and PS-*b*-PE copolymers.

Latest developments

Last year saw the publication of two new platforms which attempt to address the barriers to commercial application of PO-*b*-PX materials.

Guironnet and co-workers¹⁰⁵ reported a method that utilised cross-metathesis reactions to convert a range of vinyl-terminated polyolefins into macroinitiators for coordinative ROP of lactide, anionic ROP of ethylene oxide or ATRP of styrene to yield the corresponding block copolymers. We reported that an investigation of Chung's mechanism (Figure 1) led to the development of a highly productive, one-step metallocene-catalysed synthesis of the end-functionalised PE of Figure 19 – an α -methylstyrene derivative.¹⁰⁶ This macromonomer forms fairly low dispersity block copolymers directly with acrylates, methacrylates, vinyl esters and styrene under simple free-radical conditions. The materials are available on large scale and have demonstrated interface/interphase activity e.g. in the mediation of blending of immiscible polymers.

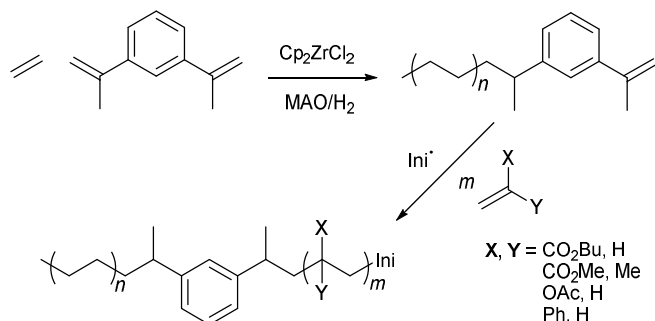


Figure 19: Synthesis of PE initiated by 1,3-diisopropenylbenzene and subsequent copolymerisation with polar monomers under free-radical conditions.¹⁰⁶

Conclusions

The importance of the field of polyolefins and the incentive for the development of efficient, commercially-viable functionalisation strategies is very much reflected in the level of interest it has received in recent decades. The modification of polyolefins through the synthesis of block copolymers, just one of many strategies in a vast area of research, has seen the development of a large variety of continuously improving methods for the production of some remarkable materials.

The biggest obstacle remains the large intrinsic reactivity differences between unfunctionalised olefins and polar vinyl monomers, with no single polymerisation mechanism currently capable of handling substantial quantities of both types of monomer. Sequential monomer addition during living olefin polymerisation allows block copolymer synthesis of olefins and polar monomers, but only under strict conditions and in the presence of specialised catalysts that are more tolerant of polar functional groups. This strategy may prove more applicable in the future as catalyst technologies develop and this may also improve the currently limited range of compatible polar monomers.

The majority of block copolymers containing olefins and polar monomers involve the synthesis of chain end-functionalised polyolefins, either by catalytic coordination polymerisation or ROMP, then conversion of the chain ends to specific functional groups to initiate a second polymerisation mechanism to generate the second block. The production of end-functionalised polyolefins of high end group fidelity has benefitted hugely from advances in chain transfer processes and reactive comonomers and they make excellent building blocks for block copolymers. The combination of distinct polymerisation mechanisms substantially increases the range of polymerisable monomers and also means that more readily available catalysts can be used to generate the first block. The main drawback is the requirement for multi-step procedures, particularly in order to convert the terminal functional groups for controlled radical or ionic polymerisation. The use of anionic polymerisation for growth of the second block also requires challenging reaction conditions and has a limited compatible monomer range. As with living olefin polymerisation, future advances in the development of late transition metal catalysts may yet allow block copolymers to be prepared using a coordination polymerisation mechanism.

Polyhomologation of functionalised carbenes is also a promising emerging method with which to produce functionalised polyolefins and block copolymers. Copolymers can be formed either in a single transition metal-catalysed step to overcome some of the previously mentioned challenges, or in combination with another polymerisation mechanism. Although reports of block copolymer synthesis are currently scarce, the ability to produce tuneable molecular weight, highly stereoregular polymers with very low dispersities and access to a large range of functionalities will push development in this area.

There are thus many routes to take from here, but if we have an eye on the practical purposes outlined in the introduction, it becomes rather clearer where to focus effort. In short, scalability is paramount. While there is certainly interest in any polyolefin-polar block copolymer, if the synthesis requires rarefied or inefficient catalysts, expensive reagents and/or multiple steps, then the work will remain in the laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

PS thanks EPSRC and Infineum UK Ltd for support and The Royal Society for an Industry Fellowship.

Notes and references

- H. D. Tabbá, Y. M. Hijji and A. S. Abu-Surrah, in *Polyolefin Compounds and Materials: Fundamentals and Industrial Applications*, eds. M. Al-Ali AlMa'adeed and I. Krupa, Springer International Publishing, Cham, 2016, DOI: 10.1007/978-3-319-25982-6_3, pp. 51-77.
- R. Godoy Lopez, F. D'Agosto and C. Boisson, *Prog. Polym. Sci.*, 2007, **32**, 419-454.
- N. Kashiwa, T. Matsugi, S.-I. Kojoh, H. Kaneko, N. Kawahara, S. Matsuo, T. Nobori and J.-I. Imuta, *J. Polym. Sci. A: Polym. Chem.*, 2003, **41**, 3657-3666.
- T. C. Chung, *Prog. Polym. Sci.*, 2002, **27**, 39-85.
- N. M. G. Franssen, J. N. H. Reek and B. de Bruin, *Chem. Soc. Rev.*, 2013, **42**, 5809-5832.
- T. C. M. Chung, *Macromolecules*, 2013, **46**, 6671-6698.
- L. S. Boffa and B. M. Novak, *Chem. Rev.*, 2000, **100**, 1479-1494.
- F. R., J. R. and T. Ph., *Journal of Polymer Science Part B: Polymer Physics*, 1989, **27**, 775-793.
- C. Koning, M. Van Duin, C. Pagnouille and R. Jerome, *Progress in Polymer Science*, 1998, **23**, 707-757.
- T. C. Chung and H. L. Lu, *J. Mol. Catal. A: Chem.*, 1997, **115**, 115-127.
- Y. Zhao, L. Wang, A. Xiao and H. Yu, *Prog. Polym. Sci.*, 2010, **35**, 1195-1216.
- P. S. Chum and K. W. Swogger, *Progress in Polymer Science*, 2008, **33**, 797-819.
- P. D. Hustad, *Science*, 2009, **325**, 704-707.
- M. Busch, M. Roth, M. H. Stenzel, T. P. Davis and C. Barner-Kowollik, *Australian Journal of Chemistry*, 2007, **60**, 788-793.
- C. Dommanget, C. Boisson, B. Charleux, F. D'Agosto, V. Monteil, F. Boisson, T. Junkers, C. Barner-Kowollik, Y. Guillaneuf and D. Gigmes, *Macromolecules*, 2013, **46**, 29-36.
- C. Dommanget, F. D'Agosto and V. Monteil, *Angew. Chem. Int. Ed.*, 2014, **53**, 6683-6686.
- M. Ciftci, S. Norsic, C. Boisson, F. D'Agosto and Y. Yagci, *Macromol. Chem. Phys.*, 2015, **216**, 958-963.
- A. Nakamura, S. Ito and K. Nozaki, *Chemical Reviews*, 2009, **109**, 5215-5244.
- B. P. Carrow and K. Nozaki, *Macromolecules*, 2014, **47**, 2541-2555.
- H. Yasuda, M. Furo, H. Yamamoto, A. Nakamura, S. Miyake and N. Kibino, *Macromolecules*, 1992, **25**, 5115-5116.
- G. Desurmont, Y. Li, H. Yasuda, T. Maruo, N. Kanehisa and Y. Kai, *Organometallics*, 2000, **19**, 1811-1813.
- G. Desurmont, M. Tanaka, Y. Li, H. Yasuda, T. Tokimitsu, S. Tone and A. Yanagase, *J. Polym. Sci. A: Polym. Chem.*, 2000, **38**, 4095-4109.
- G. Desurmont, T. Tokimitsu and H. Yasuda, *Macromolecules*, 2000, **33**, 7679-7681.
- H. Frauenrath, S. Balk, H. Keul and H. Höcker, *Macromol. Rapid Commun.*, 2001, **22**, 1147-1151.
- E. Ihara, M. Morimoto and H. Yasuda, *Macromolecules*, 1995, **28**, 7886-7892.
- H. Yasuda and E. Ihara, *Macromol. Chem. Phys.*, 1995, **196**, 2417-2441.
- T. C. Chung and J. Y. Dong, *J. Am. Chem. Soc.*, 2001, **123**, 4871-4876.
- J. Y. Dong and T. C. Chung, *Macromolecules*, 2002, **35**, 1622-1631.
- Y. Doi, Y. Watanabe, S. Ueki and K. Soga, *Makromol. Chem., Rapid Commun.*, 1983, **4**, 533-537.
- J. Y. Dong, H. Hong, T. C. Chung, H. C. Wang and S. Datta, *Macromolecules*, 2003, **36**, 6000-6009.
- Y. Lu, Y. Hu, Z. M. Wang, E. Manias and T. C. Chung, *J. Polym. Sci. A: Polym. Chem.*, 2002, **40**, 3416-3425.
- S. B. Amin and T. J. Marks, *Angew. Chem. Int. Ed.*, 2008, **47**, 2006-2025.
- Y. Lu, Y. Hu and T. C. M. Chung, *Polymer*, 2005, **46**, 10585-10591.
- T. C. Chung, W. Janvikul and H. L. Lu, *J. Am. Chem. Soc.*, 1996, **118**, 705-706.
- G. Xu and T. C. Chung, *J. Am. Chem. Soc.*, 1999, **121**, 6763-6764.
- T. C. Chung, G. Xu, Y. Lu and Y. Hu, *Macromolecules*, 2001, **34**, 8040-8050.
- T. C. Chung, H. L. Lu and W. Janvikul, *Polymer*, 1997, **38**, 1495-1502.
- J.-F. Pelletier, A. Mortreux, X. Olonde and K. Bujadoux, *Angew. Chem. Int. Ed.*, 1996, **35**, 1854-1856.
- J. Mazzolini, E. Espinosa, F. D'Agosto and C. Boisson, *Polymer Chemistry*, 2010, **1**, 793-800.
- R. G. Lopez, C. Boisson, F. D'Agosto, R. Spitz, F. Boisson, D. Bertin and P. Tordo, *Macromolecules*, 2004, **37**, 3540-3542.
- D. Benoit, V. Chaplinski, R. Braslau and C. J. Hawker, *J. Am. Chem. Soc.*, 1999, **121**, 3904-3920.
- R. Godoy Lopez, C. Boisson, F. D'Agosto, R. Spitz, F. Boisson, D. Gigmes and D. Bertin, *J. Polym. Sci. A: Polym. Chem.*, 2007, **45**, 2705-2718.
- K. Matyjaszewski, J. Saget, J. Pyun, M. Schlögl and B. Rieger, *J. Macromol. Sci. A*, 2002, **39**, 901-913.
- Y. Inoue and K. Matyjaszewski, *J. Polym. Sci. A: Polym. Chem.*, 2004, **42**, 496-504.
- H. Kaneko, J. Saito, N. Kawahara, S. Matsuo, T. Matsugi and N. Kashiwa, *J. Polym. Sci. A: Polym. Chem.*, 2009, **47**, 812-823.
- R. Sugimoto, H. Kaneko, J. Saito, N. Kawahara, S. Matsuo and T. Matsugi, *Polym. Bull.*, 2014, **71**, 1421-1431.
- J.-i. Imuta, N. Kashiwa and Y. Toda, *J. Am. Chem. Soc.*, 2002, **124**, 1176-1177.

48. T. Matsugi, S.-i. Kojoh, N. Kawahara, S. Matsuo, H. Kaneko and N. Kashiwa, *J. Polym. Sci. A: Polym. Chem.*, 2003, **41**, 3965-3973.
49. H. Kaneyoshi, Y. Inoue and K. Matyjaszewski, *Macromolecules*, 2005, **38**, 5425-5435.
50. H. Kaneyoshi and K. Matyjaszewski, *J. Appl. Polym. Sci.*, 2007, **105**, 3-13.
51. H. Kaneko, S.-i. Kojoh, N. Kawahara, S. Matsuo, T. Matsugi and N. Kashiwa, *J. Polym. Sci. A: Polym. Chem.*, 2005, **43**, 5103-5118.
52. H. Kaneko, S.-i. Kojoh, N. Kawahara, S. Matsuo, T. Matsugi and N. Kashiwa, *Macromol. Symp.*, 2004, **213**, 335-346.
53. S. C. Hong, S. Jia, M. Teodorescu, T. Kowalewski, K. Matyjaszewski, A. C. Gottfried and M. Brookhart, *J. Polym. Sci. A: Polym. Chem.*, 2002, **40**, 2736-2749.
54. K. Zhang, Z. Ye and R. Subramanian, *Macromolecules*, 2008, **41**, 640-649.
55. A. Kermagoret, A. Debuigne, C. Jérôme and C. Detrembleur, *Nat. Chem.*, 2014, **6**, 179-187.
56. A. Leblanc, E. Grau, J.-P. Broyer, C. Boisson, R. Spitz and V. Monteil, *Macromolecules*, 2011, **44**, 3293-3301.
57. A. Leblanc, J.-P. Broyer, C. Boisson, R. Spitz and V. Monteil, *Journal*, 2012, **84**, 2113.
58. N. Kawahara, S.-i. Kojoh, S. Matsuo, H. Kaneko, T. Matsugi, J. Saito and N. Kashiwa, *Polym. Bull.*, 2006, **57**, 805-812.
59. R. Godoy Lopez, C. Boisson, F. D'Agosto, R. Spitz, F. Boisson, D. Gignes and D. Bertin, *Macromol. Rapid Commun.*, 2006, **27**, 173-181.
60. F. D'Agosto and C. Boisson, *Aust. J. Chem.*, 2010, **63**, 1155-1158.
61. R. Briquel, J. Mazzolini, T. Le Bris, O. Boyron, F. Boisson, F. Delolme, F. D'Agosto, C. Boisson and R. Spitz, *Angew. Chem. Int. Ed.*, 2008, **47**, 9311-9313.
62. Y. Zhao, X. Shi, H. Gao, L. Zhang, F. Zhu and Q. Wu, *J. Mater. Chem.*, 2012, **22**, 5737-5745.
63. G. Moad, 2017, **66**, 26-41.
64. D. S. Germack and K. L. Wooley, 2007, **208**, 2481-2491.
65. J. W. Bartels, P. L. Billings, B. Ghosh, M. W. Urban, C. M. Greenlief and K. L. Wooley, *Langmuir*, 2009, **25**, 9535-9544.
66. J. W. Bartels, S. I. Cauët, P. L. Billings, L. Y. Lin, J. Zhu, C. Fidge, D. J. Pochan and K. L. Wooley, *Macromolecules*, 2010, **43**, 7128-7138.
67. G. Bar-Nes, R. Hall, V. Sharma, M. Gaborieau, D. Lucas, P. Castignolles and R. G. Gilbert, *European Polymer Journal*, 2009, **45**, 3149-3163.
68. R. Wei, Y. Luo and Z. Li, *Polymer*, 2010, **51**, 3879-3886.
69. R. Wei, Y. Luo and P. Xu, 2011, **49**, 2980-2989.
70. P. Froimowicz, B. van Heukelum, C. Scholten, K. Greiner, O. Araujo and K. Landfester, 2014, **52**, 883-889.
71. I. Cho, *Prog. Polym. Sci.*, 2000, **25**, 1043-1087.
72. T. C. Chung and D. Rhubright, *J. Polym. Sci. A: Polym. Chem.*, 1993, **31**, 2759-2763.
73. T. C. Chung, H. L. Lu and C. L. Li, *Macromolecules*, 1994, **27**, 7533-7537.
74. K. K. Kang, T. Shiono and T. Ikeda, *Macromolecules*, 1997, **30**, 1231-1233.
75. D.-J. Byun, D.-K. Shin and S. Y. Kim, *Macromol. Rapid Commun.*, 1999, **20**, 419-422.
76. D.-J. Byun and S. Y. Kim, *Macromolecules*, 2000, **33**, 1921-1923.
77. J. Saito, Y. Tohi, N. Matsukawa, M. Mitani and T. Fujita, *Macromolecules*, 2005, **38**, 4955-4957.
78. W. P. Kretschmer, T. Bauer, B. Hessen and R. Kempe, *Dalton Trans.*, 2010, **39**, 6847-6852.
79. G. J. P. Britovsek, S. A. Cohen, V. C. Gibson and M. van Meurs, *J. Am. Chem. Soc.*, 2004, **126**, 10701-10712.
80. G. J. P. Britovsek, S. A. Cohen, V. C. Gibson, P. J. Maddox and M. van Meurs, *Angew. Chem.*, 2002, **114**, 507-509.
81. M. van Meurs, G. J. P. Britovsek, V. C. Gibson and S. A. Cohen, *J. Am. Chem. Soc.*, 2005, **127**, 9913-9923.
82. L. R. Sita, *Angew. Chem. Int. Ed.*, 2009, **48**, 2464-2472.
83. K. Matoishi, S. Nakatsuka, K. Nakai, M. Isokawa, N. Nagai and T. Fujita, *Chem. Lett.*, 2010, **39**, 1028-1029.
84. C. J. Han, M. S. Lee, D.-J. Byun and S. Y. Kim, *Macromolecules*, 2002, **35**, 8923-8925.
85. J. O. Ring, R. Thomann, R. Mülhaupt, J.-M. Raquez, P. Degée and P. Dubois, *Macromol. Chem. Phys.*, 2007, **208**, 896-902.
86. J. Mazzolini, I. Mokthari, R. Briquel, O. Boyron, F. Delolme, V. Monteil, D. Bertin, D. Gignes, F. D'Agosto and C. Boisson, *Macromolecules*, 2010, **43**, 7495-7503.
87. C. Lefay, D. Glé, M. Rollet, J. Mazzolini, D. Bertin, S. Viel, C. Schmid, C. Boisson, F. D'Agosto, D. Gignes and C. Barner-Kowollik, *J. Polym. Sci. A: Polym. Chem.*, 2011, **49**, 803-813.
88. T. Yan, D. J. Walsh, C. Qiu and D. Guironnet, *Macromolecules*, 2018, **51**, 10167-10173.
89. T. C. Chung and M. Chasmawala, *Macromolecules*, 1992, **25**, 5137-5144.
90. T. C. Chung and M. Chasmawala, *Macromolecules*, 1991, **24**, 3718-3720.
91. S. Coca, H.-j. Paik and K. Matyjaszewski, *Macromolecules*, 1997, **30**, 6513-6516.
92. C. W. Bielawski, T. Morita and R. H. Grubbs, *Macromolecules*, 2000, **33**, 678-680.
93. M. K. Mahanthappa, F. S. Bates and M. A. Hillmyer, *Macromolecules*, 2005, **38**, 7890-7894.
94. K. J. Shea, J. W. Walker, H. Zhu, M. Paz and J. Greaves, *J. Am. Chem. Soc.*, 1997, **119**, 9049-9050.
95. K. J. Shea, B. B. Busch and M. M. Paz, *Angew. Chem. Int. Ed.*, 1998, **37**, 1391-1393.
96. K. J. Shea, C. L. Staiger and S. Y. Lee, *Macromolecules*, 1999, **32**, 3157-3158.
97. X.-Z. Zhou and K. J. Shea, *Macromolecules*, 2001, **34**, 3111-3114.
98. N. M. G. Franssen, K. Remerie, T. Macko, J. N. H. Reek and B. de Bruin, *Macromolecules*, 2012, **45**, 3711-3721.
99. A. I. O. Suarez, M. P. del Rio, K. Remerie, J. N. H. Reek and B. de Bruin, *ACS Catal.*, 2012, **2**, 2046-2059.
100. H.-C. Lu, Y. Xue, Q.-L. Zhao, J. Huang, S.-G. Xu, S.-K. Cao and Z. Ma, *J. Polym. Sci. A: Polym. Chem.*, 2012, **50**, 3641-3647.
101. J.-Z. Chen, K. Cui, S.-Y. Zhang, P. Xie, Q.-L. Zhao, J. Huang, L.-P. Shi, G.-Y. Li and Z. Ma, *Macromol. Rapid Commun.*, 2009, **30**, 532-538.
102. Y. Xue, H.-C. Lu, Q.-L. Zhao, J. Huang, S.-G. Xu, S.-K. Cao and Z. Ma, *Polym. Chem.*, 2013, **4**, 307-312.
103. C. Yuan, H.-C. Lu, Q.-Z. Li, S. Yang, Q.-L. Zhao, J. Huang, L.-H. Wei and Z. Ma, *J. Polym. Sci. A: Polym. Chem.*, 2012, **50**, 2398-2405.
104. H. Zhang, N. Alkayal, Y. Gnanou and N. Hadjichristidis, *Chem. Comm.*, 2013, **49**, 8952-8954.
105. D. J. Walsh, E. Su and D. Guironnet, *Chem. Sci.*, 2018, **9**, 4703-4707.
106. C. J. Kay, P. D. Goring, C. A. Burnett, B. Hornby, K. Lewtas, S. Morris, C. Morton, T. McNally, G. W. Theaker, C.

Waterson, P. M. Wright and P. Scott, *J. Am. Chem. Soc.*,
2018, **140**, 13921-13934.