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Synthesis of functional 'polyolefins': state of the art and remaining challenges

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Functional polyolefins (*i.e.*, polyethene or polypropene bearing functional groups) are highly desired materials, due to their beneficial surface properties. Many different pathways exist for the synthesis of these materials, each with its own advantages and drawbacks. This review focuses on those synthetic pathways that build up a polymer chain from ethene/propene and functionalised polar vinyl monomers. Despite many recent advances in the various fields of olefin polymerisation, it still remains a challenge to synthesise high molecular-weight copolymers with tuneable amounts of functional groups, preferably with consecutive insertions of polar monomers occurring in a stereoselective way. To overcome some of these challenges, polymerisation of alternative functionalised monomers is explored as well.

1 Functional polymers

Polymers bearing polar functionalised side groups are highly desired materials, due to their unique and rapidly expanding range of material properties. Compared to their non-functionalised analogues they exhibit beneficial properties with respect to adhesion, toughness, print/paintability, miscibility and rheological properties.[1] The wide variety of existing polar monomers and their ability to be copolymerised in various ratios with non-functionalised monomers such as ethene and propene allows the synthesis of a nearly infinite amount of different polymer formulations, each with completely different material properties. Nowadays, most functional polymers are synthesised *on demand*, *i.e.* the polymer composition and microstructure are tuned in such a way that they match the desired material properties for specialty applications (Fig. 1).[2]

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Nicole Franssen (1985) studied chemistry at the Utrecht University, where she did an internship with Prof. Klein Gebbink followed by an internship with Prof. Vollhardt at the University of California, Berkeley (USA). After obtaining her MSc degree in 2008, she moved to the University of Amsterdam (UvA, The Netherlands) where she did her PhD research under the supervision of Prof. Reek and Prof. de Bruin. Her research focused on exploring the scope of homogeneously catalysed carbene polymerisation reactions and she obtained her PhD degree in 2012.

Joost N. H. Reek

Joost Reek (1967) did his PhD in Nijmegen (Prof. Nolte). After a postdoctoral fellowship in Sydney, Australia, with Prof. Crossley, he joined the group of Prof. van Leeuwen at the University of Amsterdam (UvA, The Netherlands) as an assistant professor (1998), with research activities focusing on transition metal catalysis. In 2006 he became a full professor. His current research activities include transition metal catalysis, supramolecular catalysis and catalysis for green energy applications. He further started a spin-off company (InCatT) to explore the commercial potential of new supramolecular strategies for combinatorial approaches in (asymmetric) catalysis.

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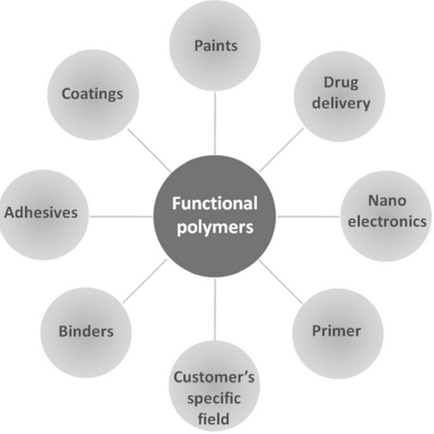


Fig. 1 Examples of application areas of functional polymers.

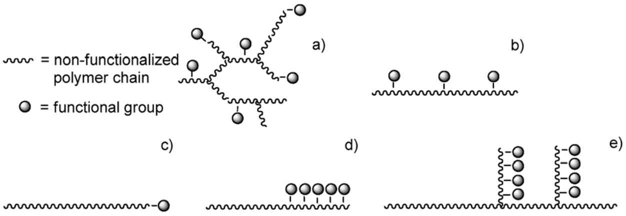


Fig. 2 Functionalised polyolefins divided into 4 classes based on structural differences: randomly functionalised copolymers (a and b), chain-end functionalised polymers (c), block copolymers (d), and graft copolymers (e).

2 Functionalised polyolefins

Due to the outstanding material properties of non-functionalised polyolefins (*i.e.* polyethene and polypropene), obtaining functional polymers based on polyolefins is of growing interest.[3] Introducing small amounts of polar functionalities into either polyethene or polypropene has a tremendous effect on the surface properties of the polymer.[2,4] In this way it is possible for polyolefins to enter a completely new area of applications, in which the material properties of polyolefins are combined with new beneficial surface properties imposed by the polar functionalities of the functionalised monomers.

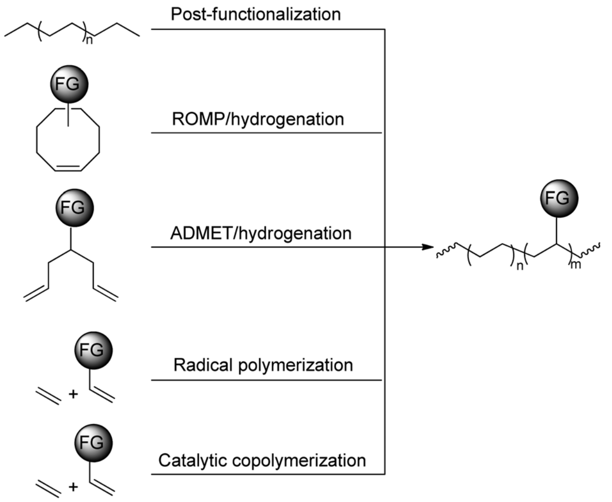
Functionalised polyolefins can be classified into four categories, based on their structures (Fig. 2): randomly functionalised copolymers that exist as either branched (a) or linear structures (b), end-functionalised copolymers (c), block copolymers (d), and graft copolymers (e).[3,5] In the following sections, each class of functional polyolefins will be discussed separately. Although many polar comonomers have been used, giving rise to polymers with a wide range of different properties, we focus on copolymers of polyolefins and polar vinyl monomers (*i.e.* monomers in which the C=C double bond is directly substituted by the polar functionality), thereby excluding copolymers based on *e.g.* polyetheneglycol and poly-tetrahydrofuran (poly-THF). Most of the emphasis will lie on copolymers of acrylates, although some attention is given to co-monomers bearing other functionalities. Amounts of polar monomers incorporated will be listed in mol% if available, unless stated otherwise. These types of copolymers have been widely covered in the patent literature of the last few decades. However, since we want many readers to have access to the examples covered in this review, we mainly focused on articles published in scientific journals. Where appropriate, a reference to the corresponding patent literature is given as suggestion for further reading. Scientific publications that appeared in the literature in the last decade are the main focus of this review, although appropriate older examples are mentioned as well to give a complete overview.

Bas de Bruin

Bas de Bruin (1971) did his PhD research at the RUN in Nijmegen (Prof. A. W. Gal, 1999). He did his postdoc at the MPI für Bio-Anorganische Chemie in Mülheim a/d Ruhr (Prof. K. Wieghardt), after which he returned to the RUN as an assistant professor. In 2005 he moved to the University of Amsterdam (UvA, The Netherlands), where he was promoted to full professor in 2013. He is involved in various research activities, including radical organometallic chemistry, EPR spectroscopy, olefin oxygenation, polymer synthesis, mechanistic studies and computational catalysis, with a focus on the development of new (bio-inspired) catalytic transformations.

3 Randomly functionalised copolymers

Randomly functionalised polyolefins (Fig. 2a and b) offer a way to drastically alter the properties of the corresponding homo-polyolefins by applying a minimum of changes. The beneficial effect of randomly placed polar functionalities stems from breaking-up the crystal packing of the otherwise non-functionalised polyolefins, thereby broadening their application window. The resulting copolymers exhibit completely different properties compared to more ordered structures (Fig. 2c–e) due to the random distribution of monomers along the backbone. Randomly functionalised polyolefins exist in many variations, differing not only in the type of functional groups but also in the amount of functionalisation and the polymer microstructure, *i.e.* the placement of functionalities along the non-functionalised chain (*cf.* Fig. 2a *vs.* b). Minor changes in the polymer structure often lead to major changes in the copolymer properties, making this class of copolymers an excellent starting point for the development of new materials. Functionalised polyolefins exhibiting linear structures as depicted in Fig. 2b are of particular interest since they can be regarded as a functionalised form of HDPE, thus benefiting from the highly developed HDPE chemistry, including properties and applications.[5,6]

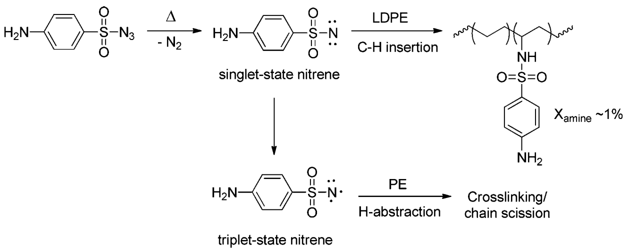


Scheme 1 Different synthesis pathways for the synthesis of randomly functionalised copolymers.

Random copolymers can be synthesised in a variety of ways as depicted in Scheme 1, and each pathway will be discussed separately in the following sections.

3.1 Polymer post-functionalisation

Polymer post-functionalisation is currently the most-used approach for the commercial synthesis of functionalised polyolefins, since this technique benefits most from the well-developed synthesis of non-functionalised polyolefins (for a review on the most recent advances in catalytic polyolefin synthesis, see Guan[7] and Qiao[8]). Polymer post-functionalisation of existing polymeric structures can be carried out in the bulk as well as on the surface, thereby offering ample opportunities for obtaining desired material properties.[2] The amount of functionalisation can be tuned by changes in stoichiometry and in principle any modification that can be carried out on a small molecule is useful for polymer modifications.[9] One of the most utilized approaches comprises reaction of free radicals with the C–H bonds of the polymer backbone, leading to H abstraction and the formation of a polymeric radical. These free radicals can be generated in various ways, with peroxide initiation being most common. In most cases maleic anhydride is added to this polymeric radical, giving rise to anhydride-functionalised polymer chains. These anhydride functionalities can in turn be converted to several other groups upon reaction with nucleophiles such as amines. A different post-functionalisation approach deals with insertions of carbenes or nitrenes into the C–H bonds of the polymer backbone (Scheme 2). This method allows for somewhat more selectivity and control over the reaction in contrast to the above-described free radical approach. From an industrial perspective, surface modification techniques based on plasma, corona and flame treatment are relevant as well.[6] However, since non-functionalised polyolefins contain no reactive groups, chemical modifications of the inert C–H bonds generally require harsh conditions (for an example, see Scheme 2).[6,9] Many undesirable side reactions (*e.g.* cross-linking or chain scission; for more details see ref. 6 or 9) may occur under these conditions, thereby severely altering the properties of the polymer, also in an undesired manner.[10] Aside from this, polymer post-functionalisation is often hampered by solubility problems and cumbersome purification steps. Although catalytic methodologies are being developed, this technique is still far from ideal due to the above-mentioned drawbacks.[9]

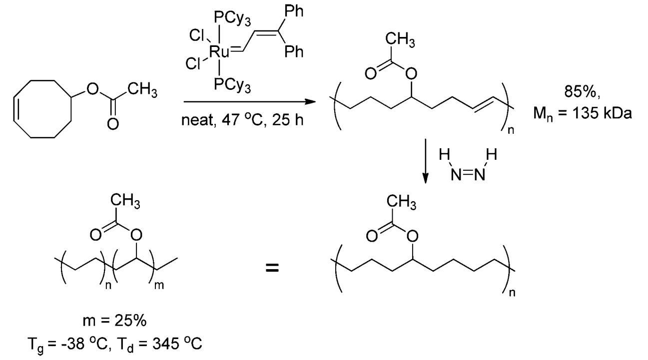


Scheme 2 Functionalisation of polyethene *via* post-functionalisation: C–H insertion of a nitrene generated from a tosylazide. The bottom pathway emphasises the undesirable side reactions.

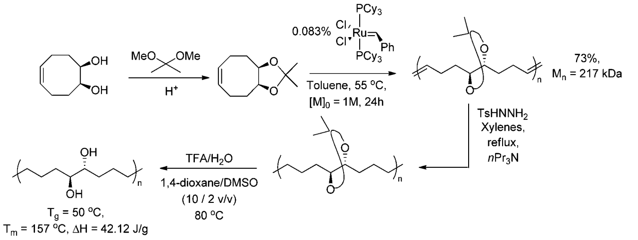
3.2 Ring-opening metathesis polymerisation

Ring-opening metathesis polymerisation (ROMP) of functionalised cyclic alkenes and subsequent hydrogenation of the resulting polyalkenamers is a viable alternative for obtaining functionalised polyolefins, although this technique requires specific monomers and occurs in a multi-step fashion. The production of linear, acyclic, functionalised polyolefins by homopolymerisation of functionalised cyclooctenes (Scheme 1) is of particular interest. However, the number of reports describing ROMP of cyclooctenes followed by hydrogenation is rather limited, since they exhibit lower ring-strain and are therefore more reluctant towards polymerisation than *e.g.* norbornene analogues. The presence of functional groups in cyclooctenes also hinders polymerisation.[11] Due to the development of more efficient and polar-tolerant catalysts (mainly based on ruthenium)[12,13] the field is rapidly emerging and polymerisations of (functionalised) cyclooctenes are of growing importance.

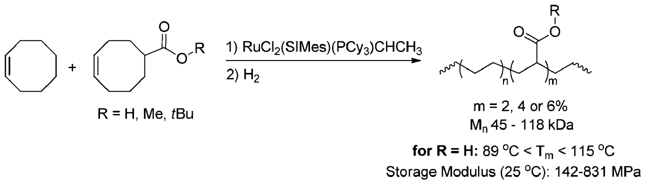
Homopolymerisation of cyclooctenes functionalised in the 5-position gave rise to polymers that resemble copolymers of non-functionalised and functionalised olefins, theoretically containing 25% of the corresponding polar vinyl monomers separated by either 6, 7 or 8 methylene units.[14–21] In this way, functional polyolefins bearing acrylate and ketone functionalities have been prepared (Scheme 3). Similar strategies have been applied to the synthesis of copolymers with highly regio- and stereoregular alcohol and amine functionalities (Scheme 4).[22–27] Due to their way of synthesis, these copolymers have precise sequence distributions that have a major effect on polymer crystallinity and physical properties.[28] More randomly distributed copolymers with lower contents of polar monomers (<10%) are accessible *via* ROMP copolymerisation of functionalised and non-functionalised cyclic monomers (Scheme 5).[11,28] The whole field of ROMP has recently been reviewed and summarised by Buchmeiser[29] and Slugovc.[30]



Scheme 3 Synthesis of functionalised polymers resembling copolymers of ethene and vinyl acetate *via* ROMP followed by hydrogenation.



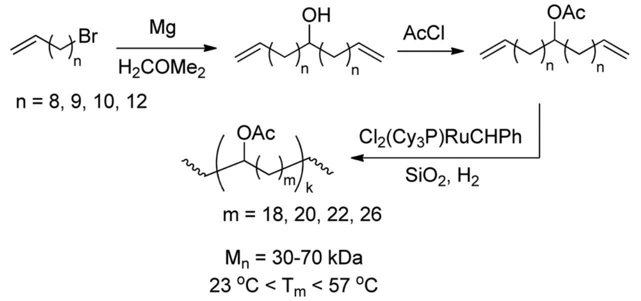
Scheme 4 Highly stereo- and regioregular analogues of hydroxy-functionalised PE obtained by ROMP of protected dihydroxy-functionalised cyclooctene.



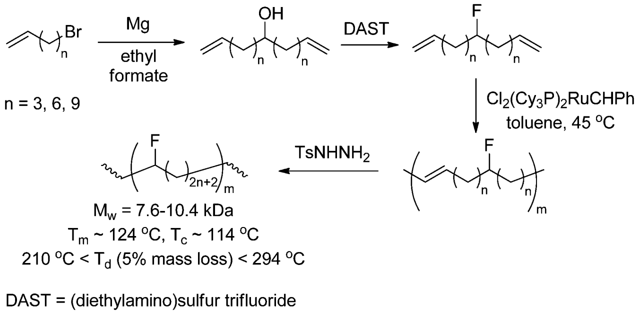
Scheme 5 Synthesis of analogues of ethene-acrylate copolymers obtained by ROMP copolymerisation of functionalised and non-functionalised cyclooctenes containing theoretically 2, 4 or 6% incorporation of polar vinyl monomers.

3.3 Acyclic diene metathesis polycondensation

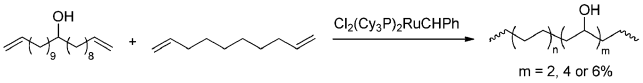
Acyclic diene metathesis polycondensation (ADMET), which is in fact based on the same elemental reaction as ROMP, followed by hydrogenation, is also a suitable approach for the synthesis of linear functional polyolefins, albeit with similar drawbacks as discussed above for ROMP. Instead of cyclic monomers, ADMET requires the synthesis of special symmetrically functionalised α,ω-diene monomers. The presence of polar functionalities in these monomers can lead to catalyst poisoning and often protection of the functional group prior to polymerisation is required (for examples see *e.g.* Wagener *et al.*[31–33]). However, recent advances in the field of catalyst development have led to the discovery of certain metal complexes that do allow the synthesis of high-M_w polymers with polar functionalities. By applying these catalysts a wide variety of functional polymers was obtained, including those with alcohol,[34] acetate (Scheme 6),[35] ether,[36,37] ester,[28,38,39] amine/amide,[40] and halide (Scheme 7)[38,41–43] side groups. ADMET allows precise control over the polymer microstructure and as such this technique is used for the synthesis of model systems to study the effect of both the nature of the functionality and its distribution along the polymer backbone on the general material properties. The resulting structures are perfectly linear and therefore ADMET can function as a complementary technique to radical polymerisation, which may yield similar copolymers but often with a high degree of branching.[44] More random distribution of the polar functionalities along the chain can be achieved by copolymerisation of functionalised and non-functionalised α,ω-diene monomers, similar to ROMP (Scheme 8).[28] By carefully choosing the comonomers and tuning their relative rate of polymerisation, alternating AB copolymers can be obtained with a degree of alternation between 90 and 99% (*i.e.* alternating diene metathesis polycondensation, ALTMET). The whole field of ADMET has recently been reviewed by Meier[44] and Wagener.[45]



Scheme 6 Synthesis of acetate-functionalised monomers and subsequent ADMET polymerisation.



Scheme 7 Fluorinated polyethene obtained *via* ADMET polymerisation of fluor-containing monomers.



Scheme 8 Synthesis of analogues of ethene-vinyl alcohol copolymers containing theoretically 2, 4 or 6% incorporation of polar vinyl monomers obtained by ADMET copolymerisation of functionalised monomers and 1,9-decadiene.

3.4 Direct copolymerisation of polar and non-polar vinyl monomers

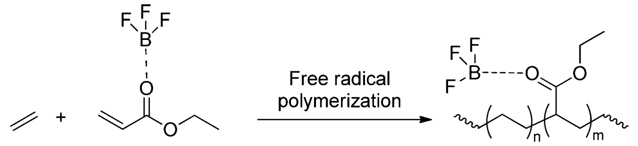
Despite some advantages of the above-mentioned techniques for obtaining functionalised polyolefins, direct copolymerisation of polar vinyl monomers and non-polar olefins remains of particular interest.[46] Obviously, direct copolymerisation circumvents the need for functionalisation *via* often cumbersome polymer post-functionalisation steps. By tuning the insertion efficiency of the functionalised monomer *vs.* the non-polar olefin, direct copolymerisation allows quantitative control over the amount of functionalisation. This difference in insertion efficiency, in combination with changes in the feed ratio of both monomers, also allows variations in copolymer architecture (*i.e.*, changing the arrangement of the monomers along the chain).[1] These features offer a broad window for tuning the copolymer properties, making direct copolymerisation a powerful method for the development of a wide variety of new materials. However, despite being the most logical approach, direct copolymerisation of polar and non-polar olefins is not that easy to achieve in a controlled way as is illustrated by the examples below. The two main copolymerisation pathways to obtain such copolymers are based on radical polymerisation or involve chain growth *via* catalytic processes, and each method will be discussed separately in the following sections.

3.4.1 Radical pathways. Radical polymerisation of olefins and polar vinyl monomers (*e.g.* acrylates, vinyl acetate and acrylic acid) is widely applied on a commercial scale, and the resulting copolymers find many applications in daily life.[47] The incorporated acetate or acid functionalities can be converted into their respective salts, giving rise to the formation of cross-linked ionomers, which find applications in areas that require extreme toughness (*e.g.* golf ball coatings) or enhanced sealing properties (*e.g.* bacon packaging).[48]

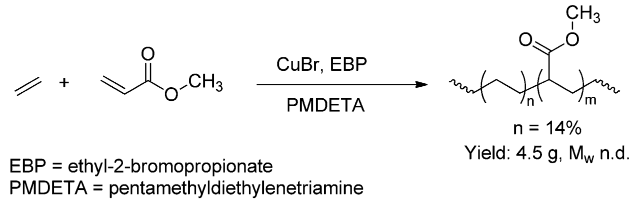
However, radical polymerisation of non-polar olefins and polar vinyl monomers is not easily achieved, since non-polar olefins are poorly reactive monomers in radical polymerisation. Due to the lack of stabilizing conjugation in non-polar olefins the stability of the generated radicals is too low to allow smooth polymerisation, and to be successful quite harsh polymerisation conditions (high temperatures and pressures) are required, resulting in the formation of highly branched polyolefins.[47,49] Since the reactivity of polar vinyl monomers towards radical polymerisation is much higher, the resulting copolymers contain large amounts of polar functionalities.[5] Reports dealing with the synthesis of such copolymers under milder and more controlled conditions are rather scarce.

Earlier attempts deal with the use of boron-protected polar vinyl monomers, leading to the formation of highly electron-deficient monomers. In this way, alternating copolymers of ethene/propene and ethyl acrylate could be obtained by free-radical polymerisations under relatively mild conditions (25–50 °C, 6–20 atm. ethene), with considerable amounts of tacticity (Scheme 9).[50–52] At low ethene/propene pressures the acrylate content in the copolymers is higher than 50%.

Copolymerisations using non-protected polar vinyl monomers have been developed as well, based on atom-transfer radical polymerisation (ATRP) catalysed by copper complexes (Scheme 10).[49,53] Copolymers of both ethene and propene with methyl acrylate were obtained containing up to 14 and 21% of non-functionalised olefin respectively (PDI < 1.5). Similar results were obtained in copolymerisations initiated by 2,2-azobis(isobutyronitrile) (AIBN), although those copolymers exhibited much broader molecular-weight distributions (PDI = 9 for ethene).[54] Consecutive insertions of non-polar olefins were not observed, due to the reactivity difference between both monomers. The incorporation of olefin could be slightly tuned by varying the feed ratio of both monomers. A drawback of this metal-catalysed process is that the copolymers often contain traces of metal impurities and are therefore colored.[54] Metal-free routes towards these copolymers have been developed based on nitroxide-mediated radical polymerisation (NMRP).[55] This allowed the synthesis of copolymers of methyl acrylate and ethene/propene containing ∼15% of non-functionalised olefin.



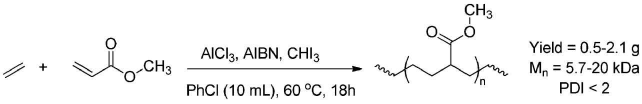
Scheme 9 Synthesis of alternating ethene-ethyl acrylate copolymers *via* free radical polymerisation of ethene and boron-protected ethyl acrylate.



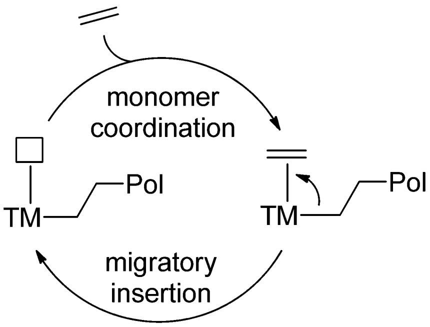
Scheme 10 Ethene-acrylate copolymers prepared *via* ATRP.

Reversible addition-fragmentation chain-transfer polymerisation (RAFT) or degenerative-transfer (DT) polymerisation of ethene and methylacrylate yields fully alternating copolymers, with a relatively narrow molecular-weight distribution (Scheme 11).[56]

3.4.2 Catalytic routes. Transition-metal (TM) catalysed routes towards random copolymers with a linear structure are highly desired, and potentially allow the synthesis of functionalised copolymers with control over the amount of polar functionalities and their distribution along the polymer backbone. In that respect, TM catalysed processes are advantageous over radical polymerisation reactions.[57] However, despite many years of research and recent advances in the field of coordination/insertion polymerisation (*i.e.* migratory insertion of an olefin into a metal–alkyl bond) (Scheme 12), direct copolymerisation of olefins with polar vinyl monomers still



Scheme 11 Synthesis of alternating ethene-methyl acrylate copolymers *via* degenerative transfer polymerisation.

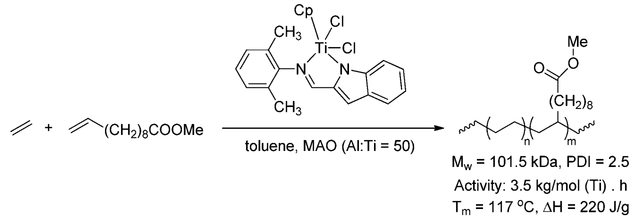


Scheme 12 Schematic representation of TM-catalysed coordination/insertion polymerisation.

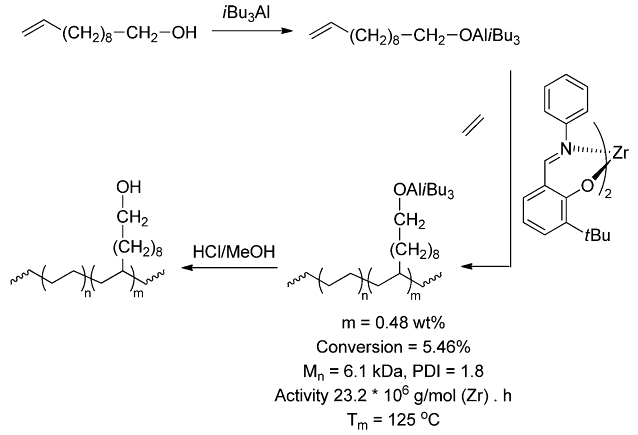
remains a challenge. In fact, achieving control over polymer composition and architecture, and development of catalysts that allow incorporation of a variety of functionalities during olefin polymerisation are two of the main goals set by the Council for Chemical Research (CCR) to be achieved in 2020, driven by the future technology needs of the chemical industry in the area of catalysis.[54] Early transition-metal (ETM) catalysts are most active in the homopolymerisation of ethene and propene, but they are easily poisoned by the functional groups in the co-monomers due to their high oxophilicity, and thus electronic or steric protecting strategies are required to prevent coordination to the metal center.[1,5] Recently, direct copolymerisation has been successfully achieved by applying late transition-metal (LTM) catalysts (mainly based on palladium), since they are more tolerant to the presence of functional groups and allow their incorporation without the need for protection. However, due to the presence of the electron-withdrawing or -donating functionalities directly attached to the double bond, the electronic environment around the reactive C–C bonds is drastically changed compared to the non-functionalised analogues. This has a major effect on the relative rates of incorporation of both monomers, often leading to the formation of copolymers containing only a few per cent of polar monomers.[5] In principle, the effect of the polar functionality on the reactivity can be minimised by implementing a methylene spacer between the double bond and the functionality, but these monomers are less abundant and therefore more expensive.[1] Another problem that can hamper TM catalysed copolymerisation is β-heteroatom elimination of the functional group, which has been observed for vinyl acetate, vinyl halides and vinyl ethers.[1,5] Aside from this, after insertion of the polar monomer, the functional groups can coordinate to the metal centre leading to the formation of stable chelates, breaking-up of which significantly slows down further insertions. Nevertheless, despite these possible problems, successful examples of direct copolymerisation have been reported and the number of publications has rapidly grown in the past few years. The field of transition-metal catalysed copolymerisations has been the subject of several reviews.[1,5,6,48,57–59] The following sections will give an overview of the current state-of-the-art with respect to controlled synthesis of functional copolymers *via* direct copolymerisation of non-functionalised olefins and polar vinyl monomers.

3.4.2.1 Early transition-metal catalysts. As stated above, ETM catalysts require the use of protecting strategies for incorporation of functional groups. Consequently, this approach requires post-polymerisation reactions to obtain the desired functionalities. These protecting strategies mainly involve coordination of aluminium species to the polar groups, since aluminium is compatible with and often required for successful Ziegler/Natta or metallocene catalysis.[1] This approach has been used for the synthesis of polyethene and polypropene bearing amine,[60–62] ester (Scheme 13),[63–68] ether,[69,70] alcohol (Scheme 14),[61,62,64,65,70–78] thiol[62] and acid functionalities,[64,65,73,74] although in almost all cases the polymerisation activity of the catalyst system dropped significantly compared to the homopolymerisation of ethene/propene. Removal of the aluminium protection group is easily achieved by acid cleavage during polymer work-up. This approach has been protected in several patents (see *e.g.* Boffa[1] for examples).

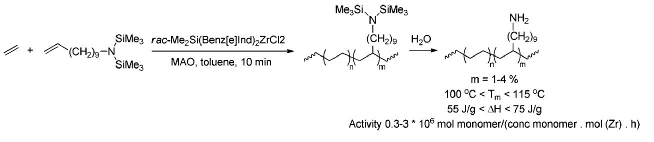
Amine functionalities have also been protected with trimethylsilyl (TMS) groups (Scheme 15),[79,80] since monomers containing



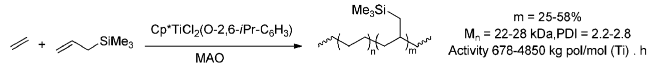
Scheme 13 ETM-catalysed direct copolymerisation of ethene and ester-functionalised vinyl monomers. The functional group is protected *in situ* with aluminium.



Scheme 14 Synthesis of polyethene containing alcohol functionalities *via* direct copolymerisation with aluminium-protected OH-functionalised monomers.



Scheme 15 ETM-catalysed copolymerisation of ethene and silyl-protected amine-functionalised monomers.

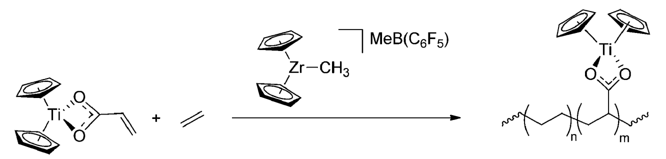


Scheme 16 Silyl-functionalised polyethene synthesised *via* direct copolymerisation catalysed by ETM complexes.

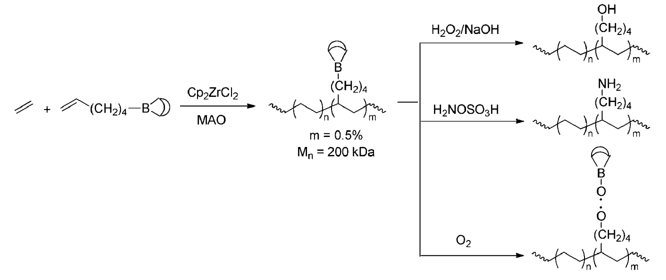
silyl functionalities can easily be copolymerised with ethene or propene using ETM catalysts (Scheme 16).[81–86] Different protection strategies have also been applied for copolymerisation with acrylates, since acrylate monomers are the most difficult to be copolymerised with non-polar olefins due to the formation of inactive *O*-enolate complexes or π-allyl-η^3-complexes after insertion of the acrylate monomer into the M–C bond.[1,5] Formation of these inactive species can be circumvented by the use of acrylate salts as monomers, formed by complexation of the acrylate anions to metallocene cations (Scheme 17).[87] In this way, the synthesis of aminofunctional linear low density polyethene (LLDPE) could be realised.

Another approach that has been applied in combination with ETM catalysts is functionalisation *via* borane monomers. Borane functionalities do not hamper ETM catalysed polymerisation, and since they are easily modified they form an excellent starting point for the introduction of various functionalities. Chung *et al.* reported formation of random copolymers of ethene and propene with vinyl monomers containing 9-borabicyclononane (9-BBN) functionalities.[88–91] These pendant borane functionalities could be converted to a variety of functional groups (Scheme 18), including alcohols, amines, halogens and radical species that can serve as initiators for the synthesis of graft copolymers (*vide infra*, Section 5.2).

However, all the above-described examples deal with polar monomers containing several methylene groups as spacers between the $C{=}C$ double bond and the polar group. Very few examples of direct copolymerisation of polar vinyl monomers without this additional spacer have been reported for ETM catalysis, thereby limiting this approach to a selected class of monomers. Aside from this, the incorporation of polar monomers is rather low (in general less than 5%) due to diminished reactivity of the polar monomers compared to the non-functionalised analogues (similar to the lower reactivities of α-olefins), and the distribution along the polymer backbone is difficult to tune.



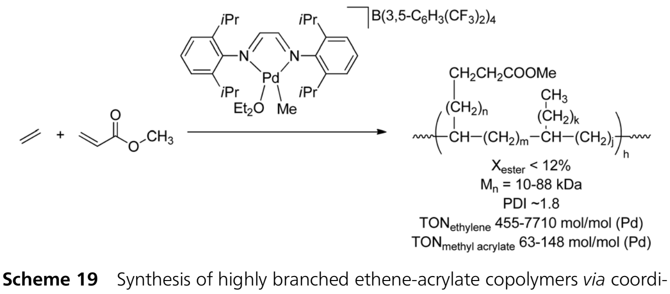
Scheme 17 Direct copolymerisation of ethene and acrylate salts formed by complexation with metallocene cations.



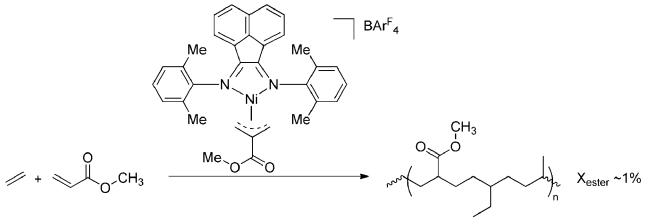
Scheme 18 Functionalisation of polyethene *via* ETM-catalysed direct copolymerisation with borane-containing monomers, followed by subsequent functionalisation steps.

3.4.2.2 Late transition-metal catalysts. Late transition-metal (LTM) catalysts are able to incorporate polar vinyl monomers that bear the polar functionality at the vinylic position, directly attached to the $C{=}C$ double bond, *via* direct copolymerisation with non-polar olefins, without the need for protection. The most successful examples have been reported for nickel and palladium catalysts.[5,92]

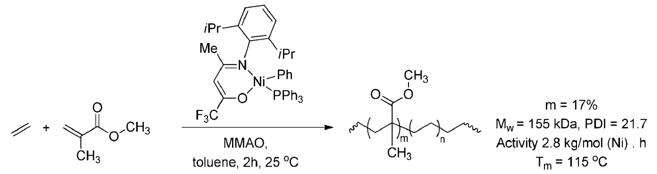
Palladium catalysts bearing α-diimine ligands are highly active in ethene homopolymerisation and the scope of this reaction has been extended to copolymerisations of ethene/propene with acrylates,[93–95] acrylic acid,[48] methyl vinyl ketone,[93] and monomers bearing acetyl functionalities (Scheme 19).[96] These systems yield highly branched copolymers (typically 100 branches per 1000 carbon atoms) due to rapid β-hydride elimination followed by reinsertion (*i.e.* chain walking), and the polar monomers are mainly located at the end of the branches. Incorporation of polar monomers up to 12% was achieved by varying the monomer feed ratio, although the polymerisation efficiency decreased significantly upon incorporation of the polar monomers. The incorporation of polar monomers could be increased to more than 20% by slightly modifying the catalyst, *i.e.* by blocking the axial positions.[95] For none of these systems consecutive insertions of polar monomers were observed, and the system proved to be inactive towards homopolymerisation of polar vinyl monomers. Copolymerisation of olefins with methyl methacrylate could not be achieved with these Pd-diimine catalysts and this feature was ascribed to the very low insertion rate of methacrylates.[97,98] Acrylonitrile and other nitrogen-containing monomers also hampered copolymerisation, most likely *via N*-coordination of the monomers to the catalyst.[48] The catalyst system is more tolerant to functional groups if additional methylene spacers are present between the $C{=}C$ double bond and the functionality similar to the ETM systems discussed above.[99] Although this approach is viable, it is not a unique feature of these Pd-diimine catalysts and therefore of minor importance.



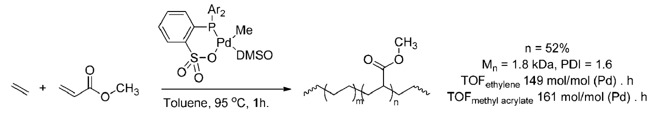
Scheme 19 Synthesis of highly branched ethene-acrylate copolymers *via* coordination/insertion polymerisation catalysed by a Pd-diimine complex.



Scheme 20 Copolymerisation of ethene and methylacrylate catalysed by a Ni-diimine catalyst.



Scheme 22 Copolymerisation of ethene and methyl methacrylate catalysed by a Ni[N–O] complex.



Scheme 23 Synthesis of ethene–methyl acrylate copolymers showing consecutive acrylate insertions, obtained *via* coordination/insertion polymerisation using a Pd[P–O] catalyst.

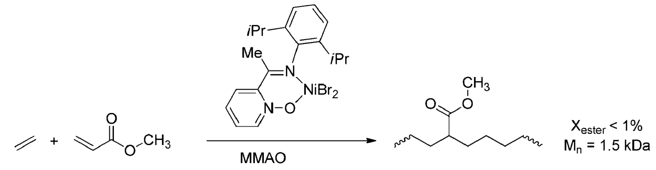
The corresponding nickel-diimine catalysts showed far less activity in the copolymerisation of olefins and polar vinyl monomers, due to strong coordination of the oxygen functionalities in the polar monomers to the metal centre, thereby poisoning the catalyst.[100] This problem can be overcome by applying quite harsh polymerisation conditions (high temperatures (120 °C) and pressures up to 340 bar), and in this way copolymers of ethene and methyl acrylate were obtained with around 1% incorporation of the polar monomers (Scheme 20).[101,102] In contrast to the above-mentioned Pd systems, these Ni catalysts give rise to copolymers with a wider range of microstructures, from moderately linear (*i.e.* 30 branches per 1000 carbon atoms) to highly branched, and the incorporation of acrylates takes place mainly in-chain. These Ni systems and their behaviour in copolymerisation reactions with polar monomers have mainly been discussed in the patent literature (for examples, see *e.g.* Nozaki[5] and Ittel[48]).

To overcome the problem of *O*-coordination to the oxophilic Ni center, several anionic ligands have been used to achieve copolymerisation of ethene and methyl acrylate, mainly based on [P–O], [P–N] or [N–O] coordination to the metal centre.

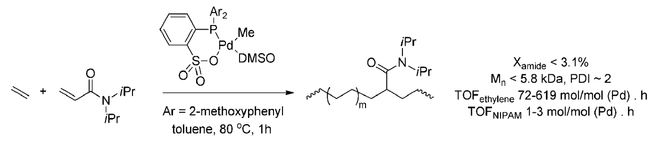
Application of these catalysts in combination with Lewis acids as cocatalysts resulted in the formation of moderately linear low-M_w copolymers ($M_n \sim 1500$ Da) with rather low amounts of polar functionalities (<1%), although the methyl acrylate units are incorporated in the polymer backbone rather than at the branches (Scheme 21).[103–105] The main advantage of these systems is that they allow copolymerisation of olefins with methyl methacrylate, and copolymers with a MMA content up to 17% could be obtained (Scheme 22).[106–109] Papers dealing with MMA contents of 80% have been reported as well, but these high acrylate contents point in the direction of radical polymerisation rather than sole coordination/insertion polymerisation.[110]

Along these lines, palladium complexes bearing phosphine–sulfonate [P–O] ligands have been applied in copolymerisation reactions of ethene and several acrylates, giving rise to linear copolymers with acrylate incorporation up to 17%.[57,111–114] The degree of branching in the copolymers is very low (1 branch per 1000 carbon atoms), giving rise to truly linear copolymers with the polar monomers positioned along the polymer backbone. No consecutive acrylate insertions were observed for these systems Recently it was found that by slightly modifying the catalysts, the acrylate incorporation can be increased up to 52% giving rise to consecutive acrylate insertions (albeit up to 3 or 4) (Scheme 23).[115] Unfortunately, the M_w of the corresponding copolymers decreased drastically (to as low as 2 kDa) upon incorporation of acrylate. This approach has been extended to the copolymerisation of ethene and a variety of co-monomers, including acrylonitrile,[116] vinyl ether,[117] vinyl acetate,[118] acryl amides (Scheme 24),[119] acrylic acid,[120,121] vinyl sulfones[122] and allylic monomers containing functional groups.[123,124]

The above-described examples emphasise the potential of this approach and the number of publications has rapidly grown in the past few years. The tolerance of these catalysts towards a large variety of functional groups makes them excellent candidates for the synthesis of copolymers of olefins and polar vinyl monomers. Up to now, Pd[P–O] systems have only been applied for copolymerisations with ethene. Another drawback is the limited occurrence of consecutive polar monomer insertions, which limits the potential of this approach for block copolymer synthesis. However, since the research in this field is still ongoing, future improvements of the catalysts and polymerisation conditions are expected to broaden the scope of these catalyst systems further.



Scheme 21 Synthesis of low-M_w copolymers of ethene and methylacrylate obtained with a Ni catalyst bearing a [N–O] ligand.



Scheme 24 Pd[P–O]-catalysed copolymerisation of ethene and *N*-isopropylacrylamide (NIPAM).

4 Chain-end functionalised copolymers

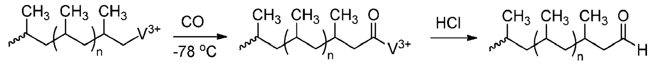
Chain-end functionalisation is a key step in polyolefin synthesis, since this is the starting point for constructing more complex macromolecular architectures such as block copolymers and graft copolymers from the otherwise unreactive polyolefin chains (*vide infra*). Polyolefins bearing a terminal functional group at either one end or both ends (*i.e.* telechelic polymers) are prepared by three general methods: controlled end-capping of living TM-catalysed polymerisation (a), *in situ* chain transfer reactions during TM catalysed coordination polymerisation (b), or modification of preformed unsaturated chain ends (c).[3,6,125,126] These approaches are discussed in the following paragraphs, with emphasis on those examples that have been exploited for the synthesis of more complex macrostructures.

4.1 End-capping of living polymerisations

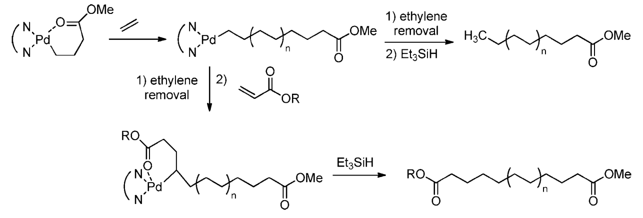
Although end-capping of living polymerisation is the classical approach for introducing terminal functionalities, this approach is less suitable for end-functionalisation of polyolefins with polar groups.[3] Aside from being metal-consuming and thus of limited practical value, this approach requires the use of very specific catalysts under certain polymerisation conditions and, in fact, not many examples have been reported.[127] Living coordination polymerisation of polypropene was achieved using a vanadium catalyst at a very low temperature (−65 °C) and syndiotactic polypropene end-capped with iodine was obtained by addition of I_2 at the end of the polymerisation.[128–131] Aldehyde-functionalised polypropene was prepared in a similar process by reaction with carbon monoxide (Scheme 25).[132,133]

End-capped polyethene was obtained by using a cobalt catalyst bearing *para*-substituted phenyl groups.[134] These phenyl groups are able to initiate living coordination polymerisation of ethene, thereby introducing the terminal functionality in the initiation step. More recently, this approach has been extended to the synthesis of acrylate-functionalised polyethenes *via* living coordination polymerisation at selected palladium-diimine catalysts.[135,136] Pd complexes chelated by one acrylate unit were able to initiate living polymerisation of ethene, thus allowing end-functionalisation of polyethene in the initiation step. This approach has also been used for the synthesis of telechelic polyethenes, in which the second end functionality was introduced by insertion of an acrylate unit after the polymerisation reaction (Scheme 26).[136]

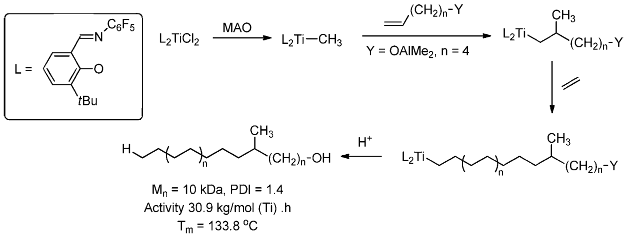
Introduction of functional groups during the initiation step is not limited to the use of LTM catalysts. ETM catalysts bearing phenoxyimine (FI) ligands were used to obtain both polyethene and polypropene end-capped with aluminium or silyl functionalities, which can be converted to hydroxyl end groups (Scheme 27).[137]



Scheme 25 Synthesis of aldehyde-functionalised polypropene by end-capping of living vanadium-catalysed polymerisation by carbon monoxide.



Scheme 26 Synthesis of polyethene functionalised with an acrylate unit at either one or both chain ends *via* end-capping of living polymerisation catalysed by palladium.

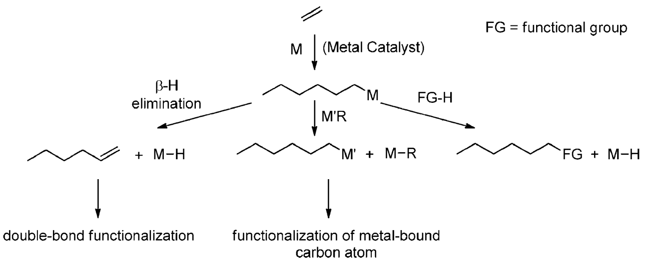


Scheme 27 Introduction of functional groups during the initiation of polyethene growth using a titanium catalyst bearing phenoxyimine (FI) ligands.

Similar to the LTM systems above, this method can be extended to the synthesis of telechelic polymers by insertion of functionalised monomers after polymerisation of the non-functionalised monomers.

4.2 Chain-transfer reactions

End-functionalisation *via* chain transfer is the most efficient approach for obtaining polyolefins bearing a terminal functionality. The process is very metal-efficient, since each catalytically active species produces multiple polymer chains, all bearing the desired end functionality. The overall polymerisation efficiency is therefore retained, while the molecular weight of the resulting polymers can be tuned by varying the chain-transfer agent (CTA) to monomer ratio ([CTA]/[monomer]). Different varieties of chain-transfer reactions have been applied for this purpose and a general overview is given in Scheme 28. A well-known chain transfer reaction in polyolefin synthesis (often the cause of formation of low-M_w materials) is β-hydride elimination, yielding polyolefin chains with vinylic end groups that can be further modified through chemical transformation reactions. Chain transfer to a (main-group) metal, either catalytic



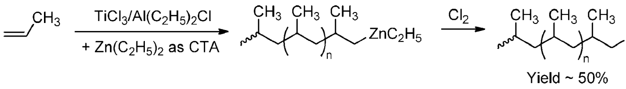
Scheme 28 General overview of chain-transfer reactions that can be used for end-functionalisation of polyolefins.

or irreversible, is a different approach that is of growing importance due to the well-understood behaviour of ETM/metal alkyl catalyst systems in polyolefin synthesis. By taking advantage of the reactivity of the newly formed metal–carbon bonds different functional groups can be introduced and examples of this approach will be provided in the following paragraphs. Another chain-transfer approach is direct introduction of functionalities using suitable (functionalised) chain-transfer agents (CTA) that terminate the growing polymer chain with a functional group while the catalyst is simultaneously re-activated for the formation of a new polyolefin chain.[3,6] The field of chain-transfer reactions in polyolefin synthesis has recently been reviewed by Marks.[138]

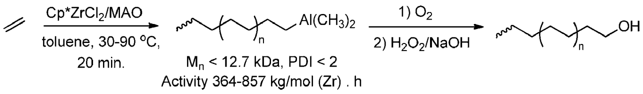
Chain transfer of the growing polymer chain to a second (main-group) metal present in the polymerisation mixture has already been known for a long time[139] and is mainly observed for ETM catalysts that operate in cooperation with zinc and main-group metal alkyl compounds. Under certain conditions this chain transfer occurs in a catalytic fashion, giving rise to a process called chain-shuttling or catalytic chain-transfer polymerisation (CCTP).[140] This approach is very suitable for obtaining polyolefin chains that are fully end-capped with a (main-group) metal, although the non-catalytic version of this chain-transfer process has also been successfully used for end-functionalisation of polyolefins. Chain transfer from ETM catalysts to zinc yielding Zn-alkyl terminated polypropene was first utilised to synthesise polypropenes with a variety of functional groups (hydroxyl,[141,142] carbonyl,[143] halogen,[143] vinyl[144,145] or amine groups[146]), making use of the high reactivity of Zn–C bonds towards many reagents (Scheme 29). *Catalytic* chain transfer from ETM catalysts to zinc has also been applied and led to the synthesis of polyolefins bearing alkyne or azide functionalities.[147] For a more general overview of the potential of catalytic chain transfer to zinc in polymerisation, see *e.g.* Gibson,[148] Arriola[149] and Sita[150] and references therein. Transfer to zinc has also been used in combination with LTM catalysts, yielding hydroxyl-terminated polyethene.[151]

Similar results are obtained when ETM catalysed polymerisations are conducted in the presence of aluminium alkyls, leading to polyolefins bearing hydroxyl groups (Scheme 30).[152–158]

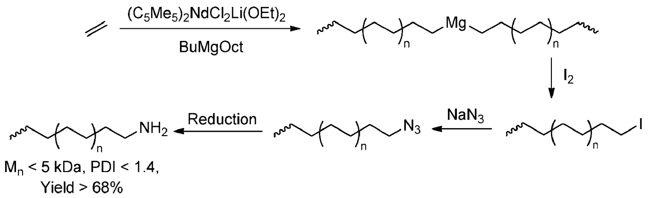
Transfer to magnesium followed by subsequent functionalisation has been exploited for lanthanide catalysts, giving rise to polymers with various functionalities,[159] such as[152] alkoxyamine-functionalised polymers,[160,161] polymers bearing thiocarbonyl functionalities[162] and azide-functionalised polyethene (Scheme 31).[163]



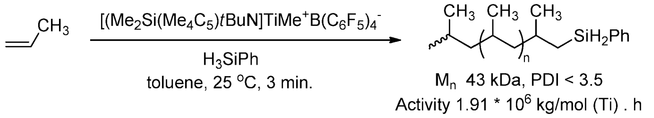
Scheme 29 Polypropene end-functionalised with halogen functionalities *via* intermediate chain transfer to zinc.



Scheme 30 Synthesis of hydroxy-functionalised polyethene *via* ETM catalysis in combination with chain transfer to aluminium.



Scheme 31 End-functionalisation of polyethene *via* lanthanide catalysis in combination with catalytic chain transfer to magnesium alkyls.

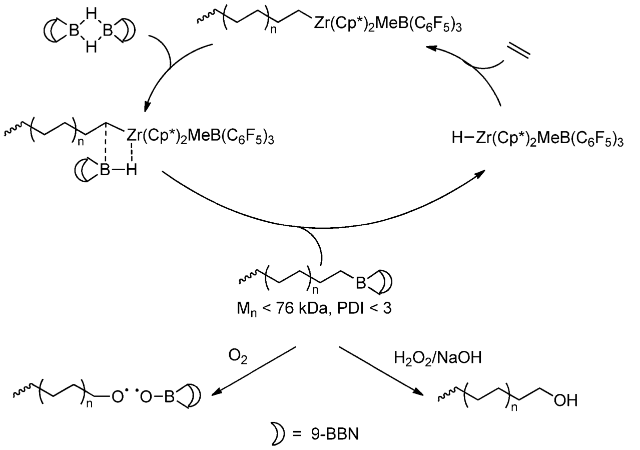


Scheme 32 Chain transfer to silanes as effective method for the synthesis of silyl end-capped polypropene.

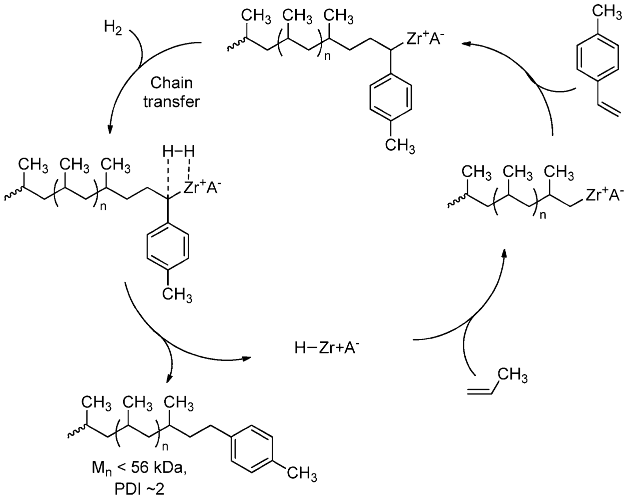
In the presence of various silanes, chain transfer of the growing polymer chain to the silyl functionality can occur from both ETM and lanthanide catalysts (Scheme 32).[164–167] This process is versatile, and both polyethene and polypropene bearing a wide range of silyl functionalities have been prepared. Although this should in principle be a good starting point for the synthesis of polyolefins with a variety of other functionalities,[168] additional modifications of the silyl functionalities were not reported.

Chain-transfer to organoboranes leads to the formation of polymers with a terminal borane functionality and a corresponding metal-hydride species, which is still active towards polymerisation. Chung and Xu reported formation of polyethene terminated with a 9-BBN moiety, obtained *via* chain-transfer from ETM catalysts to the 9-BBN dimer.[169,170] The borane functionalities can be oxidised to yield polyolefins with a terminal hydroxyl group,[169] but more interesting is their ability to be used as initiators in free radical polymerisation *via* controlled oxidation (Scheme 33). This allows the formation of block copolymers *via* coordination/insertion polymerisation in combination with subsequent free radical polymerisation (*vide infra*).

Another chain-transfer reaction that is of interest is the transfer to styrene derivatives (in particular *p*-methylstyrene) that in turn can function as initiators for the growth of polar polymer segments (*vide infra*, Section 4.3). These styrene functionalities can be introduced by first inserting the styrene-derivative *via* a coordination/insertion mechanism, followed by chain transfer to hydrogen, yielding the styrene-terminated polymer chain and a metal-hydride catalyst (Scheme 34).[171–173] These systems benefit from the low activity of the ETM catalysts towards the incorporation of styrenes and, in fact, the system becomes inactive after insertion of the styrene-derivative. Chain-transfer to hydrogen is necessary to regenerate catalyst and allow the formation of additional polymer chains.



Scheme 33 Functionalisation of polyethene with a terminal borane group and subsequent transformations into a hydroxyl functionality and a suitable initiator for radical polymerisation.

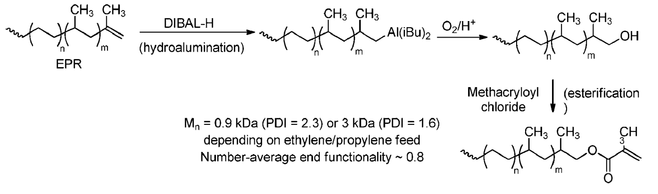


Scheme 34 Chain transfer of a growing polypropene chain to *p*-methylstyrene.

This approach works for both polyethene and polypropene and several functionalised styrene-derivatives have been used, including styrenes bearing chloride and amine groups.[172]

4.3 Functionalisation of unsaturated chain ends

Functionalisation of polyolefins by chemical modification of preformed unsaturated chain-ends has been applied for the introduction of several functionalities, mainly *via* hydroboration, hydrosilylation and hydroalumination reactions.[3,126] However, this approach has several disadvantages, which limits its potential for the synthesis of end-functionalised polyolefins. The chain-end unsaturation of the preformed polyolefins needs to be nearly quantitative to ensure complete functionalisation, although several ETM systems exist to date that mainly terminate *via* β-hydride elimination (*e.g.* $Et(Ind)_2ZrCl_2$ that has been applied by Chung[174]). The subsequent chemical transformations are hampered by the very low concentration of the double bonds in the polymer mixture and, even more importantly, by the poor solubility of these polymers in the reaction medium/solvent associated with the use of these reagents.[6,125]

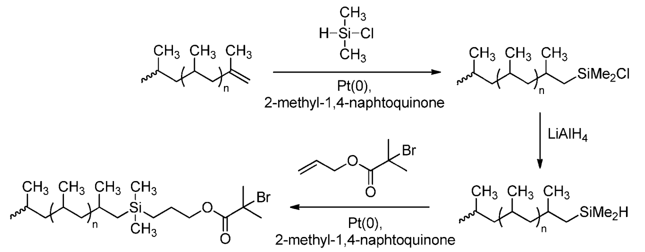


Scheme 35 Hydroalumination of an unsaturated ethene–propene copolymer used for the introduction of a methacryloyl functionality.

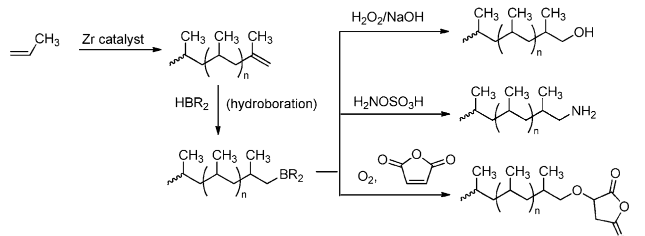
Hydroalumination and subsequent oxidation have been used to functionalise polypropene with a hydroxyl group.[157,175] Later, this approach was used for hydroxy-functionalisation of ethene–propene copolymers (EPR), followed by further conversion of the hydroxyl group to a methacryloyl functionality suitable for copolymerisation reactions (Scheme 35).[175] Introduction of halogen functionalities at the chain end was also achieved *via* this method.[176]

Hydrosilylation reactions have been applied for converting the unsaturated chain ends of polypropene into a suitable initiator for radical polymerisation (Scheme 36),[177] in order to synthesise block copolymers (*vide infra*).

Hydroboration is by far the most successful transformation reaction, which has been attributed to the advantageous reactivity and solubility of dialkylborane reagents in hydrocarbon media.[6] Polypropene or polyethene-*co*-hexadiene bearing an unsaturated chain end was transformed into borane-functionalised polypropene by a hydroboration reaction with alkylboranes.[174,178] Subsequent transformations of these newly formed polypropenes led to the formation of polyolefins end-functionalised with hydroxyl,[174,178] amine,[174] silyl[174] or maleic anhydride functionalities[179,180] (see Scheme 37).



Scheme 36 Formation of a polypropene macro-initiator for radical polymerisation by hydrosilylation of an unsaturated chain end.



Scheme 37 End-functionalisation of polypropene *via* hydroboration reactions converting the unsaturated chain ends.

5 Segmented copolymers: block and graft copolymers

Segmented copolymers (*i.e.* block copolymers and graft copolymers) are highly desirable materials, since they offer a large quantity of functional groups while preserving the original properties of the non-functionalised polyolefin chain (*e.g.* crystallinity, melting point and hydrophobicity). Both block and graft copolymers are ideally suited to act as compatibilisers in polymer blends, where the functionalised segment(s) provide(s) good adhesion to polar surfaces and the non-polar segment interpenetrates into polyolefin homopolymer domains.[6,181] Segmented copolymers may exhibit phase separation at the microscopic level, whether in the melt, solid state or solution (for an example, see Fig. 3).[181,182] Although phase separation of segmented copolymers is a spontaneous process driven by thermodynamics,[183] the ordering of the crystalline domains in thin films can be influenced in various ways depending on the desired properties and potential applications (for an overview see Hamley[184]). Due to the more simple molecular architecture of block copolymers compared to graft copolymers, the morphologies of (di)block copolymers exhibit a long-range lattice order while morphologies of graft copolymers often lack this long range order.[185] This long-range order makes block copolymers excellent materials for applications in microelectronics, *e.g.* as integrated circuits (for a review on the applications of block copolymers in electronics, see Kim *et al.*[186]) Another phenomenon mainly observed for block copolymers is self-assembly in solution, which is studied extensively as a mimic for protein folding, although its potential reaches much further than that.[187] However, most applications are based on functional polymers other than polyolefins and this field is therefore not discussed in detail.

5.1 Synthesis of block copolymers

The synthesis of block copolymers based on polyolefins is rather difficult and often occurs in a multi-step fashion, involving two or more mechanistically distinct polymerisation techniques.[188] Most techniques are not compatible with the large differences between polar and non-polar vinyl monomers, thereby hampering block copolymer synthesis *via* sequential monomer addition based on the same polymerisation mechanism.[189] Radical polymerisation by sequential monomer addition is hampered by the lack of reactivity towards non-polar alkenes (and especially ethene) compared to polar vinyl monomers.[49] TM catalysed block copolymer synthesis is limited by either the high oxophilicity of early TM catalysts or the low reactivity of late TMs towards polar monomers. Therefore, most successful synthesis pathways for block copolymers are based on transformation reactions, involving cross-over between distinct polymerisation mechanisms. A general overview of such transformation reactions is given in Fig. 4, including cross-over pathways that are not suitable for the synthesis of functionalised polyolefins.[188] Using this cross-over approach, first, monomer A is fed to the system, which is pre-polymerised *via* a suitable mechanism. The growing chain-end is converted into a suitable initiator for polymerisation of monomer B *via* a different mechanism, and several different functionalities have been discussed in Section 4.2. Polymerisation of B can occur (a) *via* the direct fresh feed of B into the prepolymer solution using the prepolymer directly as a macroinitiator, or (b) by isolation of the pre-polymer and applying that as macro-initiator in a second step (Scheme 38). The former method is convenient since it occurs in one pot, although this method can only be successful if the end-functionalisation of the first pre-polymer occurs almost quantitatively and selectively to prevent fouling of the reaction mixture by homopolymers of A. The second approach yields exclusively block copolymers, although this requires the sometimes cumbersome isolation and purification of prepolymers of A.[49,190]

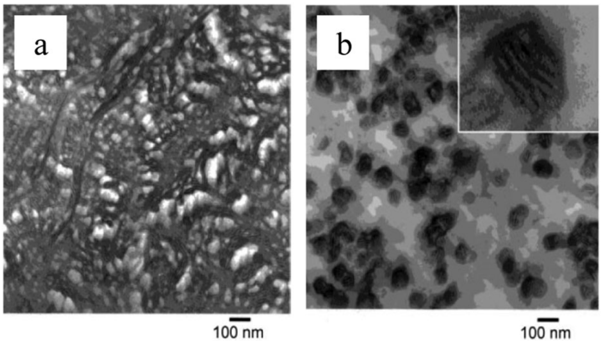


Fig. 3 TEM pictures of polypropene-polymethylmethacrylate block-copolymers (PP-*b*-PMMA) showing phase separation at the microscopic level, with different morphologies for a PMMA content of 60% (a) and 75% (b).[181] (Reproduced with permission; Copyright 2003 Wiley)

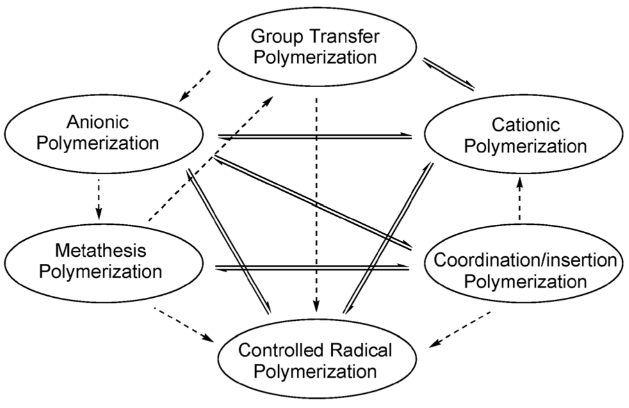
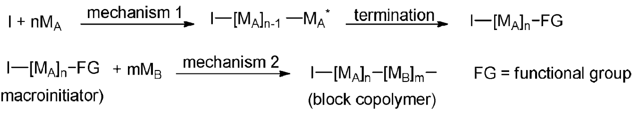
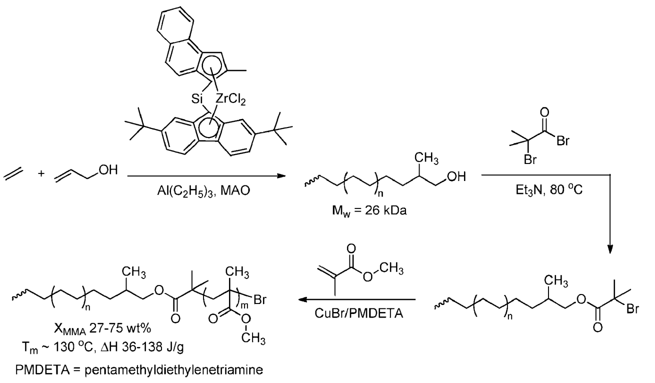


Fig. 4 Mechanistic transformations in living/controlled polymerisation aimed at the synthesis of block copolymers. Solid lines indicate pathways suitable for the synthesis of functional polyolefins, while pathways indicated with dashed lines are not.



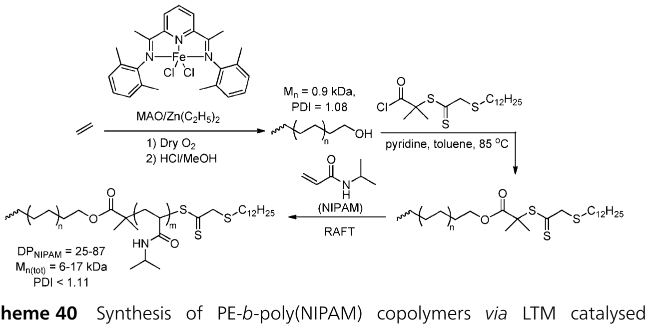
Scheme 38 Schematic representation of copolymer synthesis *via* mechanistic transformation reactions.



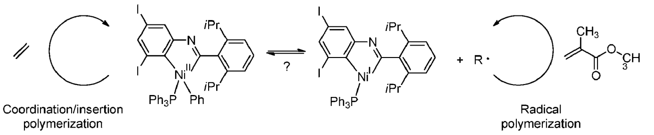
Scheme 39 PE-*b*-PMMA copolymer synthesised *via* ETM catalysed coordination/insertion polymerisation followed by cross-over to radical polymerisation.

The two main transformation pathways for the synthesis of functional block copolymers based on vinyl monomers are cross-over reactions between catalytic coordination/insertion polymerisations and either radical polymerisations or conjugate addition mechanisms.[6,49,58,125] Cross-over to radical mechanisms is mainly described for block copolymers of ethene/propene and acrylates. The non-polar block is formed by catalytic coordination polymerisation at either early[151,169,170,177,181,191–196]or late TM catalysts,[151,197–199] or lanthanide complexes,[161,162] followed by subsequent transformation of the chain end into a radical initiator suitable for acrylate polymerisation (Scheme 39 (ref. 200) and Scheme 40). Several possibilities for transforming the chain end into a suitable initiator have been discussed above (Section 4.2). A drawback of this approach is the rather limited control over the polymerisation in terms of stereoselectivity due to the use of radical polymerisation.

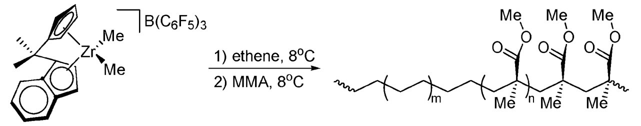
Very recently, Monteil and coworkers developed a pathway for the synthesis of multiblock copolymers from ethene and acrylates, based on a reversible shuttling process, going back and forth from catalytic insertion polymerisation to radical polymerisation (Scheme 41), occurring at the same metal (Ni) center.[201,202] This so-called dual radical/catalytic polymerisation allows the synthesis of multiblock copolymers of various compositions that can be tuned by varying the feed ratio of both monomers and the absolute ethene pressure. As stated above, the stereoselectivity of the consecutive polar monomer insertions is moderate as a result of the underlying radical mechanism.



Scheme 40 Synthesis of PE-*b*-poly(NIPAM) copolymers *via* LTM catalysed coordination/insertion polymerisation and subsequent radical polymerisation.



Scheme 41 Reversible shuttling process between a Ni^{II} species responsible for coordination/insertion polymerisation of ethene and a Ni^{I} species active in controlled radical polymerisation of acrylates. Multiple shuttling cycles result in the formation of ethene-acrylate multiblock copolymers.

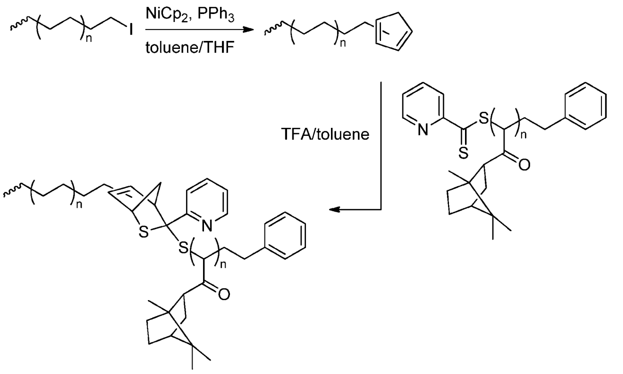


Scheme 42 Ethene–methylmethacrylate (MMA) copolymerisation produced by mechanistic cross-over from coordination polymerisation to addition polymerisation using an ETM metallocene catalyst.[210]

Transformation of coordination/insertion polymerisation to addition polymerisation of acrylates (*i.e.* metal-catalysed anionic polymerisation) is limited to the use of lanthanide (metallocene)[203–209] or early-TM metallocene[210,211] catalysts for the synthesis of the non-polar block (for an example, see Scheme 42). Polymerisations of the polar monomers, to some extent, take place stereoselectively, allowing the synthesis of isotactic and syndiotactic (rich) blocks.[210,212] However, this approach is only unidirectional: due to mechanistic incompatibilities block copolymers can only be obtained starting with the non-polar block. Copolymerisation attempts starting with acrylate polymerisation only lead to the formation of homopolymers.[58] This also implies that this cross-over approach is not suitable for the synthesis of statistical, random copolymers, which is a major drawback.

A different approach to the synthesis of block copolymers is linking two preformed polymer segments together *via* a coupling reaction. Despite the fact that coupling reactions of any kind are widely available and can nowadays be applied very efficiently for coupling of polymers (for a review see *e.g.* Schubert *et al.*[213]), this approach is not often used for linking non-polar polyolefin segments and segments functionalised with polar groups. This is due to the very limited abundance of polyolefin segments terminated with a functionality suitable for coupling reactions, since the field of end-functionalisation of polyolefins has only recently started to bloom (see Section 4.2). Nevertheless, this approach will likely gain importance in the near future and the first successful example of coupling polyethene segments to polyacrylates *via* (hetero) Diels–Alder chemistry has been reported (Scheme 43).[214]

The above-mentioned examples clearly emphasise the need for the development of alternative synthesis pathways for polar/non-polar block copolymers that allow more control over the synthesis and preferably do not require multiple consecutive reaction steps. Despite recent progress there is clearly room for optimisation in block copolymer synthesis.



Scheme 43 Formation of a block copolymer by coupling a preformed non-polar and a preformed polar segment *via* a hetero Diels–Alder reaction.

5.2 Synthesis of graft copolymers

For similar reasons as discussed above for the synthesis of block copolymers, graft copolymers are generally prepared *via* transformation reactions involving two mechanistically distinct polymerisation mechanisms. Whereas this is rather straightforward in the case of block copolymers (*i.e.* involving modification of one chain end), the synthesis of graft copolymers is more challenging since it requires modifications on multiple sites along the polymer backbone. Nevertheless, graft copolymers based on polyolefins have been described in the literature and the section below gives an overview of their synthesis pathways.[125]

Three general methods exist for the synthesis of graft copolymers: grafting onto (a), grafting from (b) and grafting through (c) approaches (Fig. 5) (for a more general review on graft copolymers see *e.g.* Hadjichristidis[215] and Huang[216]).

5.2.1 Grafting onto. The "grafting onto" approach requires the synthesis of a polymer backbone with randomly placed functionalities, as well as the formation of end-functionalised polymers bearing functional groups with a complementary reactivity to those of the main chain. Coupling of the two functionalities in a separate step leads to the synthesis of graft copolymers in which the end-functionalised polymers become branches of the main chain. In principle, this technique is very suitable for obtaining graft copolymers based on polyolefins, since it allows the synthesis of the polymer backbone and the branches in separate steps (and thus by different polymerisation mechanisms). Although this approach has been used to couple polyolefins to several other polymer segments (*e.g.* Li *et al.*[217]), to our knowledge, no examples of this approach exist in the literature covering the synthesis of polyolefin-*graft*-poly(polar vinyl monomer) copolymers.[216]

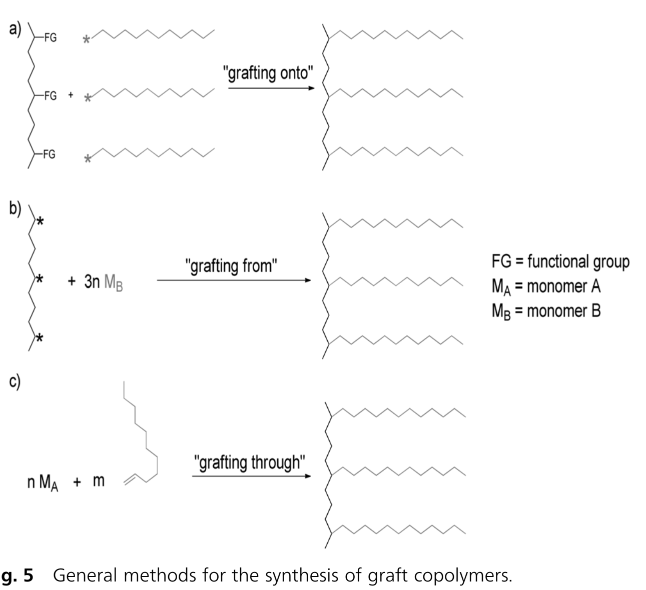
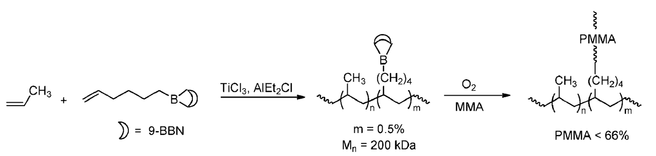
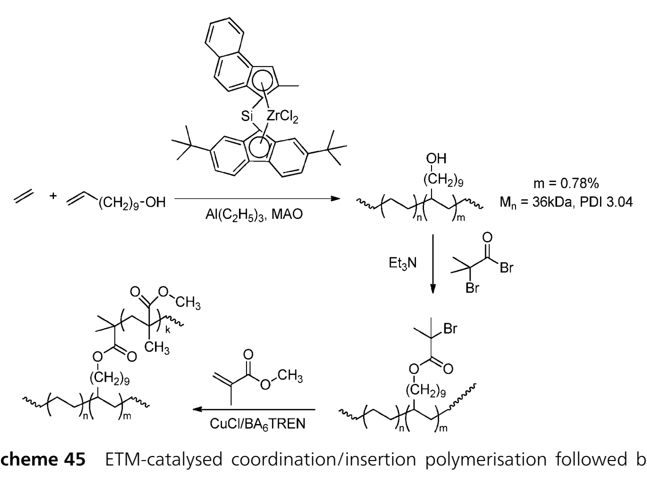


Fig. 5 General methods for the synthesis of graft copolymers.

5.2.2 Grafting from. The second approach, "grafting from", involves the synthesis of a polymer backbone bearing randomly placed functionalities, which can serve as an initiator for the polymerisation of a second monomer *via* a different mechanism. Similar to block copolymer synthesis, the most successful transformations are those based on catalytic coordination/insertion polymerisation of the polyolefin backbone, combined with radical polymerisation to form the functionalised branches.[3,125] The polymer backbone is synthesised *via* ETM-catalysed insertion polymerisation and the functionalities are incorporated *via* direct copolymerisation of selected functional monomers with either ethene or propene (or both). The nature of the co-monomer depends highly on the desired follow-up polymerisation reaction to form the polymeric branches. Common functionalities are *p*-methylaryl (for an example, see Chung *et al.*[218]) 9-borabicyclononane (9-BBN, see Scheme 44),[89,91] alkoxyamine,[219] hydroxyl (Scheme 45)[220,221] and vinylic groups,[174,222] some of which



Scheme 44 Synthesis of PP-*g*-PMMA copolymers *via* ETM catalysed coordination/insertion polymerisation followed by peroxyborane-initiated radical polymerisation. The borane initiation sites were incorporated in the polymer backbone *via* direct copolymerisation of borane-functionalised monomers with propene.



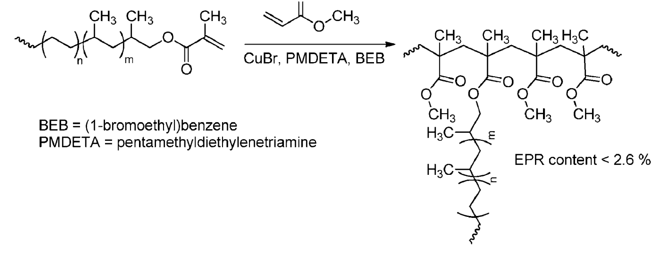
Scheme 45 ETM-catalysed coordination/insertion polymerisation followed by ATRP for the preparation of PE-*g*-PMMA copolymers.

require additional transformations in order to serve as initiator in subsequent radical polymerisation of the polar monomers. Although some of these examples are formally outside the scope of this review, they contribute to a better understanding of the possible ways to functionalise polyolefins and are therefore included in this section. Various forms of radical polymerisation have been applied, including peroxyborane-initiated radical polymerisation (Scheme 44),[90,223] nitroxide-mediated radical polymerisation (NMRP)[219] and atom-transfer radical polymerisation (ATRP) (Scheme 45),[220–222] leading to the formation of polyolefin-*graft*-polyacrylate copolymers.

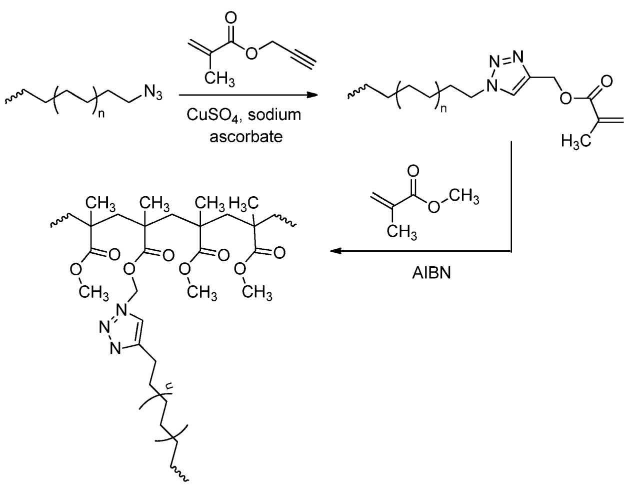
The polar segments can also be introduced by cross-over to anionic polymerisation from *e.g.* *p*-methylstyrene functionalities,[218] although examples in this field are scarce due to the special conditions required for incorporation of polar monomers.[224] Although the above-mentioned examples indicate that the "grafting from" approach has proven to be successful for the synthesis of graft copolymers, a major drawback of this method is that it requires multiple reaction steps.

5.2.3 Grafting through. In the "grafting through" or macro-monomer approach a polymer–oligomer chain with a polymerisable end group is formed, that can be copolymerised with other monomers to yield graft copolymers. The polyolefin macro-monomer is synthesised *via* coordination polymerisation using either ETM (Scheme 46)[151,175] or LTM[135] catalysts, and the end group is transformed into a methacryloyl functionality that can be copolymerised with other acrylate monomers *via* ATRP. The polyolefin segment can also be prepared *via* catalytic chain shuttling polymerisation using lanthanide/magnesium catalysis.[163] After introduction of a suitable functionality *via* "click" chemistry, these macro-monomers were copolymerised with other acrylates *via* radical polymerisation (Scheme 47).

The "grafting through" approach yields polyacrylate-*graft*-polyolefin copolymers, thus being complementary to the graft copolymers obtained *via* the "grafting from" method. The length of the grafts and the grafting density can easily be tuned by changing the degree of polymerisation of the side chains and the polymer backbone, respectively, allowing the synthesis of graft copolymers in a controlled way.[216] However, this approach has several drawbacks. Due to the incompatibility of the monomers and the high viscosity of the polymerisation medium the conversions of the ATRP reaction are generally low, leading to the presence of unreacted macro-monomers in the copolymer mixture that need to be removed in additional steps. Similar to the systems discussed above, the "grafting through" process occurs in a multi-step fashion, although the sensitivity of the catalytic systems to the functionalities necessary for ATRP (*i.e.* halogens) often requires several additional transformations, making this approach somewhat more cumbersome.[125]



Scheme 46 PMMA-*g*-PE/PP copolymers obtained by copolymerisation of MMA with PE/PP macro-monomers *via* the "grafting through" approach. For the synthesis of the macro-monomer, see Scheme 35.

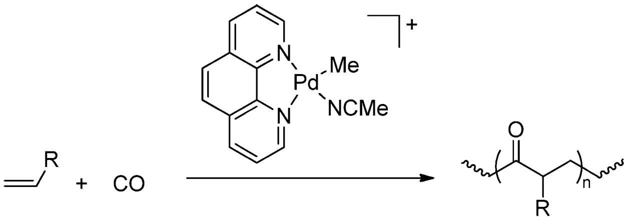


Scheme 47 PE macro-initiator prepared *via* catalytic chain-shuttling (see also Scheme 31) and subsequent 'click' reaction with propargyl methacrylate. The obtained macro-monomer was used in a radical copolymerisation with methylmethacrylate to obtain PMMA-*g*-PE copolymers.

6 Alternative polar monomers

The above-described examples illustrate that the most successful routes towards functionalised polyolefins involve, at some point, polymerisation *via* a coordination–insertion mechanism, catalysed by transition metals. Transition-metal catalysis offers the advantages of more controlled polymerisations, *e.g.* in terms of polymer microstructure and stereoregularity. However, attempts to obtain functionalised polyolefins solely by transition-metal catalysed coordination–insertion processes have met only limited success (*vide supra*). This has to do with the large differences of non-polar olefins and polar vinyl monomers in their reactivity towards different metals. Therefore, the development of alternative pathways to introduce functionalities directly into the growing polymer chain *via* a transition metal catalysed process, based on monomers other than polar vinyl compounds is of growing importance. One such approach is the use of so-called C1 monomers that build up a polymer chain with one backbone-carbon unit at a time, as an alternative to traditional olefinic monomers or C2 monomers that extend the growing polymer chain by two carbon units at each insertion step.

The most widely used C1 monomer is carbon monoxide (CO) and ample examples exist in the literature describing *co*- and *ter*-polymerisations of CO and olefins formed *via* migratory-insertion processes, leading to successful introduction of ketone

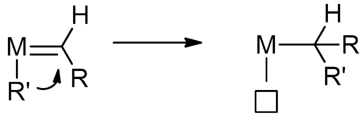


Scheme 48 Synthesis of alternating CO-olefin copolymers *via* a coordination/insertion mechanism catalysed by Pd catalysts.

functionalities in the polymer chain (Scheme 48) (for a review on this topic see *e.g.* Drent,[225] Bianchini,[226] Sen[227] and Nozaki[5]). However, this approach is obviously not suitable for the direct synthesis of a wider variety of functionalised polymers without the need for any further modifications.

Carbenes (*i.e.* CRR' units) can be regarded as a more versatile class of C1 monomers since they allow incorporation of a wider variety of functionalities by varying the substituents. Carbenes are readily generated from diazo compounds[228] and other carbene precursors (*e.g.* ylides of sulfoxides[229] and α,α-dihalocarbons). Diazo compounds are excellent and widely applied carbene precursors due to their ease of preparation and their relative 'green' character: the only byproduct upon carbene generation is dinitrogen, while other carbene precursors give rise to formation of byproducts that are not so easily removed from the reaction mixture (*e.g.* dmso).[230,231] The *large scale applicability* of carbene precursors is somewhat limited in substrate scope due to some potential safety hazards associated with some diazo compounds. Many diazo compounds are toxic, and some of them are even potentially explosive under certain conditions.[232] Especially aliphatic diazoalkanes are very unstable and require handling at low temperatures and low concentrations. Diazocarbonyl compounds (diazoketones or diazoesters), on the other hand, are much more stable and quite safe to work with. Hence they are frequently applied as carbene precursors in several organic transformations, even in large scale industrial reactions. They are excellent substrates for the introduction of highly-functionalised carbon units, since a wide variety of substituted diazocarbonyl compounds is readily available *via* well-defined synthesis routes developed in the past decades.[233] Because the handling of aliphatic carbene precursors is more problematic, much recent effort has been put into the development of safer alternative methods that allow either *in situ* generation of the inherently unstable *aliphatic* diazo compounds (for a review see Fulton *et al.*[234]) or avoid the use of diazo compounds entirely (for a review see *e.g.* Müller[235]). The availability of these alternative methods to generate (aliphatic) carbenes will certainly stimulate further research into the use of carbenes in (catalytic) organic transformations in general.

In the presence of transition metals, carbenes can undergo migratory insertion into TM–C bonds, similar to insertions of alkenes and CO[236,237] (Scheme 49) and this elementary step has received quite some recent interest as a tool for the introduction of functionalities. While some main-group metals and several Lewis acids are suitable for the generation of carbenes and catalysis of the subsequent migratory insertion reactions, the most successful results were obtained with late transition-metal (LTM) catalysts and at these metal centres migratory insertions occur both in a stoichiometric and in a catalytic fashion.[238]

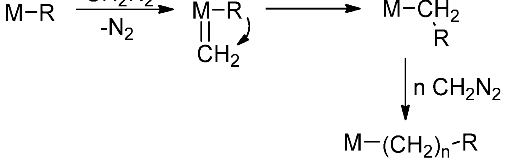


Scheme 49 Migratory insertion of carbenes.

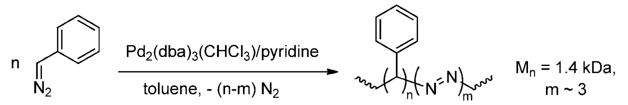
6.1 Carbene polymerisation

If the reactions are carried out using an excess of carbene precursor with respect to the metal catalyst, multiple carbene insertions can occur resulting in the formation of oligomers or polymers (provided that the rate constant for carbene insertion is larger than that for elimination–termination processes or follow-up reactions). As such, metal-catalysed insertions of carbenes provide a viable pathway for the synthesis of densely functionalised polymers that (so far) cannot be synthesised in any other way. The following sections give an overview of the development of TM catalysed coordination/insertion polymerisation based on carbenes. The whole field of so-called 'C1 polymerisation' including catalysis by non-LTM systems has recently been reviewed by de Bruin *et al.*[239] and Ihara.[240]

6.1.1 Polymers from diazo-alkanes and phenyl diazomethane. Reports dealing with the polymerisation of diazoalkanes date back to the early 1900's and although many different metals have been attempted as catalysts for this reaction, most of the earlier reports deal with the activity of copper[241,242] and gold[243–245] (Scheme 50). With both metals high molecular-weight polymers were obtained (*i.e.* M_w up to 50 kDa for polymers of diazomethane) and this topic has been reviewed in the 1970's.[242,246] The activity of other metals is less extensively studied, but there are some reports mentioning the activity of nickel,[247] iridium[248] and palladium[249] towards polymerisation of diazoalkanes. The behaviour of the nickel system is rather unique, since it produces exclusively high-M_w polymers without the formation of byproducts (*i.e.* dimers and oligomers) and the catalyst remains active after all monomers have been converted.[247] The use of palladium catalysts, on the other hand, leads to formation of small amounts of low-M_w oligomers containing large amounts of azo-groups, indicating that the reaction is not fully selective towards carbene insertion (Scheme 51).



Scheme 50 General mechanism for polymerisation of diazomethane by TM catalysts.



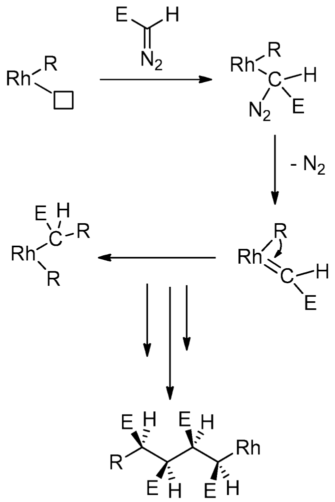
Scheme 51 Polymerisation of phenyl diazomethane by $Pd_2(dba)_3(CHCl_3)$.

Aside from the above-described homogeneous catalysts also some heterogeneous metal surfaces catalyse the polymerisation of carbenes (Au, Cu, Ti, Fe, Mg, W, Ni, V, Mn, Ta, Pt, Co, Zn, Cd, Cr, Al, Mo; listed in order of decreasing yield), with thin films of gold being the most active.[243,250–252] In a way, these polymerisation reactions, involving multiple migratory carbene insertion steps, also model key steps of hydrocarbon formation in Fischer–Tropsch synthesis.[253,254]

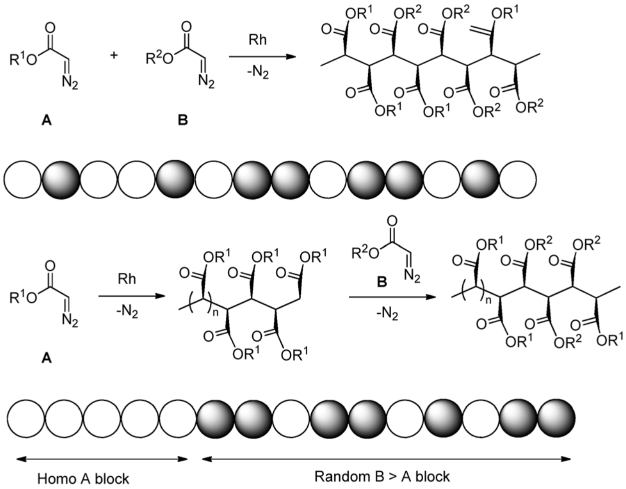
6.1.2 Polymers from carbenes bearing polar functionalities. C1 polymerisation of carbenes bearing polar functionalities is much more challenging due to the increased stability of the corresponding carbene precursors and most metal catalysts form only the corresponding dimers from these precursors.[247,255,256]

From 2003 on Ihara and co-workers investigated the polymerisation of diazo compounds bearing polar functionalities catalysed by a variety of Pd^{II} catalysts. They successfully subjected diazoesters,[249,256–259] diazoketones[249,260–262] and diazoacetamides[263] to so-called 'poly(substituted methylene) synthesis', which allowed them to obtain various highly-functionalised oligomers/polymers in either homo- or co-polymerisation processes, yielding low M_w atactic material. These results indicate that the catalyst system is not sensitive to the presence of functional groups in the monomer, emphasizing the wide range of applicability of this technique towards the synthesis of functional materials. Recently the authors have shown that higher-M_w polymers of diazoesters (up to 24 kDa) could be obtained in reasonable yields by applying a $Pd^0(NHC)/BPh_4^-$ system as a catalyst.[258,259] This approach has been extended to the synthesis of poly(ether ketone)s[264] and poly(ester ether ketone)s[265] by reaction of diazoketones with aromatic diols/cyclic ethers and diacids/cyclic ethers respectively (Fig. 6).

Stereoselective polymerisation of diazoesters was achieved by applying rhodium(diene) catalysis, giving rise to high-M_w, highly syndiotactic (co)polymers in high yields (up to 95%) (Scheme 52). The remaining products are atactic oligomers (M_w ~ 1200 Da) and dimers.[266–270] Using this approach, a variety of functionalised carbene precursors could be polymerised in a stereoselective way, such as *n*-butyl diazoacetate, 3-butenyl diazoacetate,[270] benzyl diazoacetate and ^{t}Bu-diazoacetate, and the reaction allows the synthesis of random and [homo-A]-[random-B > A]-type block copolymers (Scheme 53).[268] The resulting syndiotactic polymers are highly crystalline materials that reveal both thermotropic and lyotropic liquid crystalline properties.[268,270] The M_w of the polymers can be tuned by varying the Rh catalyst and the polymerisation conditions.[268] Recently, it was shown that these Rh catalysts are also able to copolymerise functionalised carbenes with non-functionalised carbenes generated from either diazomethane[271] or sulfoxonium ylides[272] (Scheme 54). The resulting



Scheme 52 Rh-mediated carbene polymerisation: formation of syndiotactic polymers from diazo-esters.



Scheme 53 Random and [homo-A]-[random-B > A] block copolymers synthesised *via* Rh-mediated carbene polymerisation.

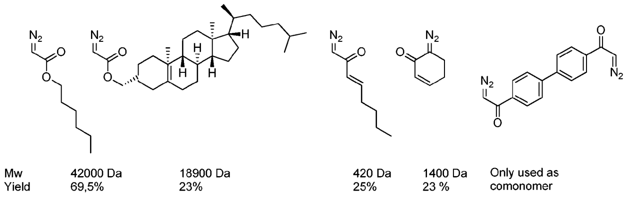
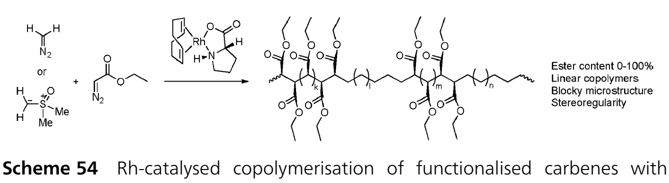
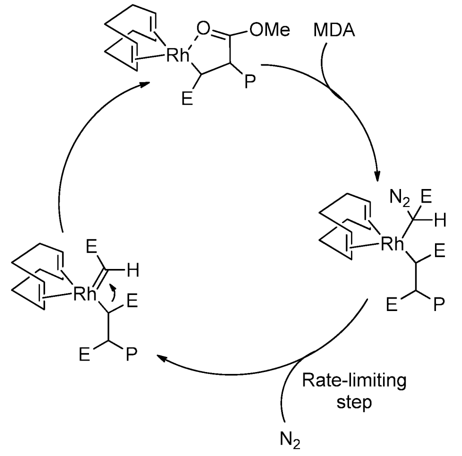


Fig. 6 Structure of some diazo compounds attempted as monomers in the Pd catalysed carbene polymerisation.



Scheme 54 Rh-catalysed copolymerisation of functionalised carbenes with either diazomethane or dimethylsulfoxonium ylide, yielding copolymers with a blocky microstructure.



Scheme 55 Proposed mechanism for the Rh-mediated polymerisation of polar functionalised carbenes, proceeding *via* a migratory insertion pathway (P = growing polymer chain, E = COOMe).

copolymers exhibit a blocky microstructure and the functional-group content can be tuned in a large window by varying the feed ratio of the two monomers. Copolymerisation of functionalised carbenes with ethene is also possible, albeit leading to quite inhomogeneous polymer mixtures.[273] These results emphasise the potential of this new technique for the development of new materials that are up to now inaccessible *via* traditional olefin polymerisation.

This Rh-mediated carbene polymerisation has the advantage of giving stereoregular (syndiotactic) polymers with high molecular weights from polar C1 monomers,[239] whereas other C1 polymerisation techniques mainly yield atactic and/or low-M_w material. This approach seems to work exclusively with Rh catalysts. Most of the corresponding iridium analogues did not show polymerisation activity towards carbenes, with only one exception.[266,274] No other metals able to polymerise carbenes in a stereoselective manner have been reported. The stereoregularity of the polymers obtained by Rh catalysis is, according to DFT calculations, most likely a result of chain-end control during the propagation steps, since the Rh catalysts used in these reactions are non-chiral.[266] The reaction proceeds *via* a migratory insertion mechanism (Scheme 55)[266] and no or little chain transfer seems to occur.[275–278] Most recently, detailed mechanistic studies revealed that the active species responsible for this polymerisation is a Rh^{III}(allyl)(alkyl) species (Fig. 7) that can be formed by modifications of rather simple Rh^{I}(diene) precursors (*e.g.* 1,5-cyclooctadiene (cod) derivatives) under the applied reaction conditions.[267,277,279] These findings are expected to lead to future improvements of this approach in terms of yields, initiation efficiencies of the catalysts and in the synthesis of stereoregular polymers with different tacticities. This clearly indicates that this new reaction has not yet been exploited at its full potential.

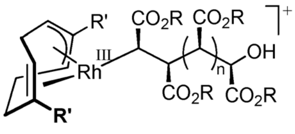


Fig. 7 Rh^{III}(allyl)(alkyl) species proposed as active species for the Rh-catalysed stereoselective polymerisation of diazoesters.

7 Concluding remarks

The research area reviewed here has seen a remarkable amount of activity over the past decade, resulting in the development of a variety of improved methods that allow the synthesis of functional polyolefins in a more controlled way. Each pathway described in this review has its own advantages and limitations and its potential for the synthesis of functional polyolefins has been described in detail.

Despite many recent advances in this field, the synthesis of functional polyolefins in a controlled way with tuneable amount of functionalities still remains a challenge. Randomly functionalised copolymers are still the most difficult to prepare in a controlled way, although advances in the field of late transition-metal catalysed polymerisation allow nowadays the synthesis of these materials *via* a direct copolymerisation reaction of non-functionalised olefins and functional polar monomers. This approach is somewhat limited with respect to incorporation of large amounts of polar functionalities, since consecutive insertions of polar monomers take place only up to three or four times. Attempts to improve the catalysts used in this process are still ongoing, so we expect this technique to gain more potential in the future. Recent advances in the field of metathesis polymerisation allowed the synthesis of analogues of these randomly functionalised polyolefins with very precise control over the distribution of functionalities along the polymer backbone. The resulting polymers have shown to be excellent structures for studying the effect of functional-group distributions on the crystal packing and physical properties. Chain-end functionalised polyolefins are readily available *via* a variety of pathways, although this approach benefits most from the recent advances in the field of chain-transfer reactions, which allow almost quantitative chain-end functionalisation. The resulting materials are excellent starting points for the synthesis of block and graft copolymers in which the functional fragments are synthesised in a sequential reaction step *via* a different reaction mechanism. So far, these materials are not available *via* a single reaction mechanism due to the intrinsic reactivity differences between polar vinyl monomers and non-functionalised olefins. However, as stated above, advances in the field of late transition-metal catalysis might lead to the development of pathways for the synthesis of block and graft copolymers *via* a coordination/insertion mechanism in the (near) future.

To overcome some of these challenges, alternative pathways that lead to analogues of functional polyolefins are continuously being developed. One such promising alternative is the use of functionalised carbenes (C1 monomers) instead of the traditional polar vinyl monomers for the insertion of the polar functionalities. These carbenes can be polymerised to high molecular weight, highly stereoregular and densely functionalised polymers in a transition-metal catalysed process.

Acknowledgements

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