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Transition-metal-free approaches to poly(aminoboranes) and poly(phosphinoboranes): mechanisms, advances, and future directions

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Poly(aminoboranes) and poly(phosphinoboranes) have been of interest as inorganic analogues of poly(olefins) as early as the mid-20th century. However, their synthesis was only realised about 15 and 25 years ago, respectively. Initially, poly(aminoboranes) and poly(phosphinoboranes) were accessed *via* transition-metal-catalysed dehydropolymerisation of amine- and phosphine-borane adducts. Despite the many advances made using this method, limitations remained, particularly in the conditions required for dehydropolymerisation and in the design of effective catalysts for producing materials with controlled molar mass and specific polymer architectures. Accordingly, new routes to these materials were sought through the synthesis of reactive aminoboranes or phosphinoboranes generated *in situ* for subsequent polymerisation. In doing so, materials that were previously inaccessible by metal-mediated dehydropolymerisation were unlocked. Mechanistically, there are fundamental differences between the transition-metal-catalysed approaches and transition-metal-free reactions with reactive monomers. Understanding and research of these new mechanisms are the foundation for the development of new polymer syntheses that allow for new polymer designs. This review article discusses the new design principles and polymer synthetic concepts.

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1. Introduction

Whether naturally occurring or synthetic, polymer-based materials have played essential roles in our lives due to their



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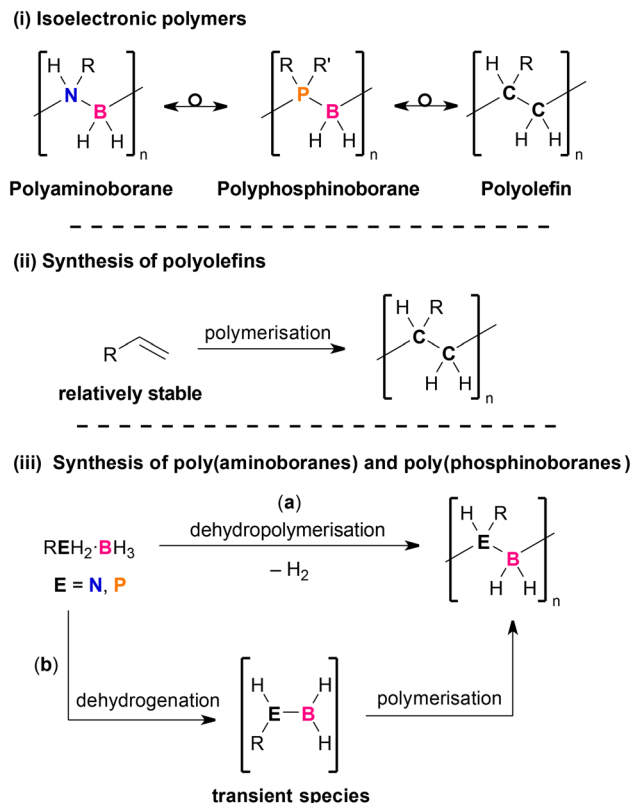
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molecular switches, switchable polymeric systems, organotin heterocycles, and group 13/15 element combinations in organic scaffolds.



Likewise, poly(aminoboranes) and poly(phosphinoboranes) are inorganic analogues of poly(olefins), where the monomer units $[\text{RNH}-\text{BH}_2]$ and $[\text{RR}'\text{P}-\text{BH}_2]$ are isoelectronic to the $[\text{RCH}-\text{CH}_2]$ units of poly(olefins) (Scheme 11).²⁷⁻³¹ Naturally, a consequence of the different atoms that comprise the main chain of poly(olefins), (C-C), poly(aminoboranes), (N-B), and poly(phosphinoboranes), (P-B), is that bond properties are also different (*i.e.*, length and polarity) leading to varied material properties (*i.e.*, stability in air, thermal properties, and polymer tacticity, *etc.*). A comparison of such properties of the carbon-parent, poly(propylene) $[\text{MeCH}-\text{CH}_2]_n$, along with poly(*N*-methylaminoborane) $[\text{MeNH}-\text{BH}_2]_n$, and poly(*P*-methylphosphinoborane) $[\text{MePH}-\text{BH}_2]_n$ is insightful, as it also immediately suggests under-researched areas in these inorganic polymers (Table 1).

Comparing across the series of bond lengths of polymer main chains and monomers, poly(olefins) and olefins have similar (Δ bond length < 0.10 Å) bond lengths to poly(aminoboranes) and aminoboranes. However, due to the presence of the larger, heavier phosphorus atom the bond lengths in poly(phosphinoboranes) and phosphinoborane monomers are sig-



Scheme 1 Overview of the structure (i) and synthesis of poly(olefins) (ii), and poly(aminoboranes) and poly(phosphinoboranes) (iii). Pathway (a) described the direct dehydropolymerisation typical of the transition-metal catalysed dehydropolymerisation of phosphine-borane adducts and pathway (b) describes two-step dehydropolymerisation where initially dehydrogenation of the precursor occurs, followed by polymerization of reactive species formed *in situ*, typical of the transition-metal catalysed dehydropolymerisation of amine-borane adducts.

Table 1 Relevant properties of common poly(olefins), poly(aminoboranes), poly(phosphinoboranes), and their precursor monomers

	[MeCH-CH ₂] _n	MeCH=CH ₂	[MeNH-BH ₂] _n	MeNH=BH ₂	[MePH-BH ₂] _n	MePH-BH ₂
E-E' bond length (Å)	1.54 (C-C) ^a	1.34 (C-C) ^a	1.63 (N-B) ^a	1.38 (N-B) ^a	1.98 (P-B) ^a	1.78 (P-B) ^b
Δ bond Length (%)	-13%	—	-15%	—	-10%	—
Bond Polarity	Apolar	Apolar	Polar	Polar	Polar	Polar
Stable in air	Yes	Yes	Yes ^c	No	Yes	No
Tacticity	A/iso/syndio	—	Unknown	—	Unknown	—
Isolated	Yes	Yes	Yes	No	Yes	No
T _m (°C)	176 ⁴³	—	—	—	—	—
T _g (°C)	-1 ⁴³	—	70 ^{41 d}	—	-24 ^{46 e}	—
T _{decomp} (°C)/(wt%)	366 (2%) ⁴⁷	—	159 (28%) ⁴¹	—	165 (5%) ⁴⁶	—

^a Bond length estimated using covalent single and double bond radii.^{48–50} ^b As the nature of P–B multiple bonding largely depends on *P*- and *B*-substituents³⁶ the calculated bond length for MePH–BH₂ is given.⁵¹ ^c Poly(*N*-methylaminoborane) has been previously reported to be unstable in air,²⁸ but a recent report states that poly(*N*-methylaminoborane) is stable in open air for at least six months as determined by nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC).⁴¹ ^d Polymer obtained by the [Rh]-catalysed dehydrocoupling of MeNH₂·BH₃.⁴¹ ^e Polymer obtained by the [Fe]-catalysed dehydropolymerisation of MePH₂·BH₃.⁴⁶ For poly(propylene), *T*_m, *T*_g, and *T*_{decomp} values for isotactic poly(propylene) are given.^{47,52,53}

nificantly (Δ bond length > 0.10 Å) larger in both the polymer and the precursor monomer. This longer bond length is reflected in the glass transition temperature (T_g) of the materials where $[\text{MePH-BH}_2]_n$ has the lowest T_g of the series of materials. However, as reflected in the relatively high T_g of $[\text{MeNH-BH}_2]_n$ (70 °C) compared to $[\text{MeCH-CH}_2]_n$ (−1 °C), there is more to consider than just bond lengths when considering T_g of these polymers. However, upon polymerisation, the elongation of the E–E' bond lengths between the monomers and the resulting polymers are all within 10–15%, with poly(phosphinoboranes) having the least drastic change in E–E' bond length (10%), and poly(aminoboranes) having the most drastic change (15%).

Another stark difference between poly(olefins), poly(aminoboranes), and poly(phosphinoboranes) is the polarisation of the monomer unit. While the $[\text{RCH-CH}_2]$ units of the main chain of poly(olefins) are largely unpolarised, in poly(aminoboranes) and poly(phosphinoboranes), the monomeric units are polarised as a consequence of the alternating heteroatoms that comprise the polymer main-chain. This is due to the electronegativity of the atoms within the monomers with Pauling electronegativity values of $\chi_B = 2.04$, $\chi_N = 3.04$, and $\chi_P = 2.19$, polarising both B–N and B–P bonds towards the group 15 element centre. Further, the presence of the heteroatoms affects the π -bond of the precursor monomers, where the C–C π -bond is much more stable (ca. 65 kcal mol^{−1})^{32,33} than a N–B (ca. 30 kcal mol^{−1})³⁴ π -bond by the bond enthalpy of the parent species (i.e. $\text{H}_2\text{E-E'H}_2$; E=E' = C or E=N and E'=B). For the parent phosphinoborane, $\text{H}_2\text{P-BH}_2$, which is non-planar due to the high barrier to inversion at the phosphorus centre (ca. 36.7 kcal mol^{−1} for PH_3),^{35–38} the bond enthalpy of the non-planar, ground state geometry is relatively low (ca. 6 kcal mol^{−1}).³⁵ However, comparing forced planar $\text{H}_2\text{N-BH}_2$ and $\text{H}_2\text{P-BH}_2$, yields bond rotation penalties of 43.2 and 40.4 kcal mol^{−1}, respectively.³⁵ Generally, the C–C π -bond is stronger than an N–B π -bond which is stronger still over a P–B π -bond.^{36,39} This is reflected in the ability to isolate the respective precursor monomers (if one presumes that in all cases this is the respective species with a double bond), where polymerisable olefins are generally bottleable and purchasable, but polymerisable aminoboranes and phosphinoboranes are not. However, all polymers are air-stable, where both poly(olefins) and poly(phosphinoboranes) are indefinitely stable.⁴⁰ Poly(aminoboranes) prepared *via* dehydropolymerisation using $[\text{Rh}(\text{L})(\text{NBD})\text{Cl}]$ ($\text{L} = (\text{iPr}_2\text{PCH}_2\text{CH}_2)_2\text{NH}$; NBD = norbornadiene) as a catalyst are air-stable for at least six months.⁴¹ However, it should be noted that in some syntheses, poly(aminoboranes) are reported to be air-sensitive and are stored under inert conditions,^{28,42} so their stability may be related to the presence (or lack thereof) of residual contaminants.

The bulk properties of polymeric materials arise, in part, from their molecular structures. One important property to consider is the positioning (stereochemistry) of the monomer units in the polymer with respect to one another, known as tacticity. Tacticity affects the thermodynamic properties such as the melting temperature, but also the solubility or mechani-

cal parameters like stiffness. For poly(olefins), atactic, isotactic, and syndiotactic polymers can be produced, depending on how the monomers are incorporated into the growing polymer chain.⁴³ However, for poly(aminoboranes) and poly(phosphinoboranes) tacticity has mostly been invoked for explaining heteronuclear nuclear magnetic resonance (NMR) spectra. Specifically, broad ¹¹B and ¹³C{¹H} NMR signals for poly(aminoboranes),^{41,44} and broad ³¹P NMR signals for heterotactic triads in poly(phosphinoboranes).^{45,46} The synthesis and characterisation of a stereoregular poly(aminoborane) or poly(phosphinoborane) has not yet been realised. Further, to the best of our knowledge, all samples prepared of poly(aminoboranes) and poly(phosphinoboranes) are amorphous solids, indicated by the lack of melting temperatures observed in their differential scanning calorimetry traces.

In terms of thermal stability, poly(aminoboranes) are much less stable than poly(phosphinoboranes) and poly(olefins). In a sample of $[\text{MeNH-BH}_2]_n$ produced by Rh-catalysed dehydrocoupling, nearly 30% mass loss of $[\text{MeNH-BH}_2]_n$ had occurred by 159 °C by thermal gravimetric analysis (TGA).⁴¹ However, for the comparable poly(phosphinoborane), $[\text{MePH-BH}_2]_n$, only 5% mass loss has occurred at 160 °C,⁴⁶ and for poly(propylene), $[\text{MeCH-CH}_2]_n$, less than 5% mass loss occurred by 366 °C.⁴⁷

Accordingly, the applications of these inorganic polymers are distinct from their organic counterparts. While polyolefins are typically used as container or structural materials, poly(aminoboranes) and poly(phosphinoboranes) have (potential) uses related to their inorganic main chain. For example, poly(aminoboranes) have been proposed as polymers for piezoelectric thin films due to their intrinsically asymmetric polymer main-chain, where for a poly(olefin) to be used in the same manner, monomer polarity would have to be introduced *via* fluorinated substituents.⁵⁴ Similarly, poly(phosphinoboranes) have been sought as flame retardants due to their ability to self-extinguish upon combustion as a result of their high phosphorus and boron content.^{55,56} In contrast, for flame retardancy to be introduced to poly(olefins), high loadings of additives are needed.⁵⁷

Just as the applications of poly(aminoboranes) and poly(phosphinoboranes) differ from poly(olefins), so does their synthesis. While olefin monomers are typically stable enough to be isolated and used directly to access a poly(olefin) (Scheme 1ii), the same is impossible for poly(aminoboranes) and poly(phosphinoboranes). Therefore, instead, these inorganic polymers are generally accessed through the metal-mediated dehydropolymerisation of either the precursor amine- or phosphine-borane adduct, which has been reviewed in detail (Scheme 1iii).^{30,31,58} Mechanistically, the metal-catalysed dehydropolymerisation of phosphine-borane adducts differs from that of amine-borane adducts. For phosphine-boranes, both dehydrogenation and P–B coupling events occur on-metal within their catalytic cycles (route a). However, for amine-borane adducts, a dehydrogenative catalytic cycle generates transient aminoboranes *in situ*, which then undergo polymerisation (route b).

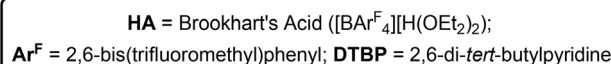


2.1 Overview of metal-mediated dehydropolymerisation

2.2 Metal-free generation of reactive aminoboranes *in situ*

The metal-free dehydropolymerisation of amine-borane adducts was not realised until 2014. Metal-free strategies to these materials rely on the generation of reactive aminoboranes *in situ* which then undergo polymerisation.

2.2.1 Deprotonation of amine-boronium salts. In 2014, the Manners group reported on the deprotonation of amine-boronium salts (**3Me**; [MeNH₂·BH₂(OEt₂)] [BAR^F₄] Ar^F = 1,3-bis(trifluoromethyl)phenyl) to access reactive aminoboranes *in situ* (Scheme 2). These intermediary aminoboranes (**3Me**; MeNH=BH₂) then undergo polymerisation.⁶¹ Immediate measurement of a ¹¹B NMR spectra obtained of the reaction mixture between [MeNH₂·BH₂(OEt₂)] [BAR^F₄] and an excess of 2,6-di-*tert*-butylpyridine in a cooled (−10 °C) NMR spectrometer revealed a triplet (¹J_{BH} = 130 Hz) at 37.1 ppm, indicative of the presence of free aminoborane (MeNH=BH₂). This assignment was based on similar ¹¹B NMR signals observed for the closely related Me₂N=BH₂.^{62,63} Further evidence for the generation of free aminoborane in solution was obtained through a trapping reaction with cyclohexene, where a small

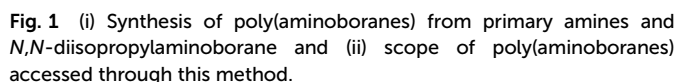


Scheme 2 Synthesis of poly(aminoboranes) through the deprotonation of an amine-boronium salt.

fraction of $\text{MeNH}=\text{BCy}_2$ was obtained as evidenced by an ^{11}B NMR spectrum of the reaction product ($\text{MeNH}=\text{BCy}_2$; $\delta(^{11}\text{B})$: 45.4 ppm). Characterisation of the polymeric material obtained using gel-permeation chromatography (GPC) and dynamic light scattering (DLS) revealed that only low molar mass material was obtained ($M_n \leq 5 \text{ kg mol}^{-1}$). Further analysis of the polymeric materials using negative mode electrospray ionisation mass spectrometry (ESI-MS) revealed that the major product was linear poly(aminoborane) (**4Me**) with amine end caps ($\text{MeNH}_2\text{--}[\text{BH}_2\text{--MeNH}]_x\text{--H}$ ($x \leq 49$)), but a small amount of cyclic oligomers ($([\text{MeNH--BH}_2])_x$) were also detected. Despite only accessing relatively low molecular weight materials, this work showed that, upon generation, reactive aminoboranes themselves could undergo polymerisation into soluble poly(aminoboranes).

2.2.2.2 *N,N*-Diisopropylaminoborane as a “BH₂” source. In 2017, the Alcaraz group discovered that the reaction between iPr₂N=BH₂ (**4iPr₂**) and primary amines (**5R**: RNH₂) resulted in the formation of poly(aminoboranes) (**2R**: [RNH–BH₂]_{*n*}) and *N,N*-diisopropylamine (**5iPr₂**) (Fig. 1i). This was shown to work for several *N*-alkyl amines including *N*-allylamine (**5R**: RNH₂; R = Me, Et, Pr, Bu, allyl). Further, random copolymers were accessed through simultaneous generation of both aminoboranes *in situ* ([EtNH–BH₂]_{*n*}-*r*-[RNH–BH₂]_{*n*}; R = Bu, Pr). Additionally, as this reaction is performed in neat conditions and at low temperatures, polymers of extremely high molecular weight ($M_w \leq 5\,450\text{ kg mol}^{-1}$, $D = 6.9$) could be obtained. Characterisation of homopolymeric materials by negative mode ESI-MS revealed oligomers corresponding to RNH₂–[BH₂–RNH]_{*x*}–H and RNH₂BH₂–(RNH–BH₂)_{*x*}–H (R = Me, Et, Pr, Bu, allyl).

The Alcaraz group later reported further on this transformation, elaborating on its mechanism.⁴⁴ In a theoretical study they confirmed that the BH₂ transfer is preceded by primary amine coordination of the borane of iPr₂N=BH₂, and a N-to-N



The authors also expanded the scope of accessible poly(aminoboranes) through this route to include alkyl groups with benzyl, trimethylsilyl (SiMe₃), *n*-hexyl, and the bicyclic-alkyl (mertanyl) functional groups (Fig. 1ii). Thus, through careful choice of reaction conditions, high-molecular weight poly(aminoboranes) with a wide variety of *N*-substituents can be accessed without the presence of transition-metal-based impurities.

3.1 Overview of metal-mediated dehydropolymerisation

Since then, other metal-based phosphine-borane dehydropolymerisation catalysts based on iron,^{66,67} rhodium,^{68–70} and iridium⁷¹ centres have been reported. However, these catalysts require high temperatures and long reaction times to produce high molar mass polymers (≥ 90 °C, ≥ 16 h). Alternatively, the titanium-catalysed polymerisation of a trimethylamine-stabilised phosphanylborane (**8tBu**, $t\text{BuPH-BH}_2\cdot\text{NMe}_3$) was recently reported, which occurs under ambient conditions.⁷² However, this reaction has not produced polymers other than $[t\text{BuPH-BH}_2]_n$. The field of transition-metal-mediated phosphine-borane dehydropolymerisation has been recently reviewed.^{30,58}

3.2 Metal-free synthesis of poly(phosphinoboranes)

As a point of reference, purely thermal phosphine-borane dehydrocoupling can be considered, which is both metal-free and free of any other additive. In such a reaction, phosphine-borane adducts are heated at or above 150 °C, resulting in loss of hydrogen and formation of P–B bonds to access cyclic and oligomeric materials.^{73,74} Later, in 2003 Gaumont and co-workers reported the ambient condition dehydrogenative coupling of P–B bonds using tris(pentafluorophenyl)borane, accessing low molecular weight materials ($M_n \leq 3 \text{ kg mol}^{-1}$).⁷⁵ However, only recently high molecular weight poly(phosphino-boranes) were synthesised without relying on metal-mediated dehydropolymerisation.

3.2.1 Stoichiometric routes

3.2.1.1 *Polymerisation of phosphanylboranes.* It was not until 2015 that high molecular weight poly(phosphinoboranes) were synthesised without relying on transition-metal-mediated dehydropolymerisation. This advancement built on earlier work from the Scheer group, where they had accessed the trimethylamine-stabilised parent phosphanylborane ($\text{H}_2\text{P}-\text{BH}_2(\text{NMe}_3)$).⁷⁶ They proposed that, upon release of trimethylamine from the stabilised phosphanylborane, reactive phosphinoboranes (**9R**: $\text{RPH}-\text{BH}_2$) are produced *in situ*. Thus, in a collaboration between the Scheer and Manners groups, a trimethylamine-stabilised *P*-tert-butylphosphanylborane (**8tBu**, $t\text{BuPH}-\text{BH}_2(\text{NMe}_3)$) was prepared, and then polymerised (Fig. 3, route A).⁴⁵ The polymerisations were performed at relatively mild conditions (22–40 °C, 48 h). The authors were able to synthesise high molar mass [$t\text{BuPH}-\text{BH}_2$]_n (**7tBu**), as determined by GPC ($M_n = 35 \text{ kg mol}^{-1}$; $D = 1.6$). Later, the scope of

The result of the deprotonation was shown to be significantly impacted by the choice of base. When Hünig's base was used to deprotonate phosphine-(triflimido)boranes, only *P*-monosubstituted polymer (PhPH-BH₂)_{*n*} was obtained as

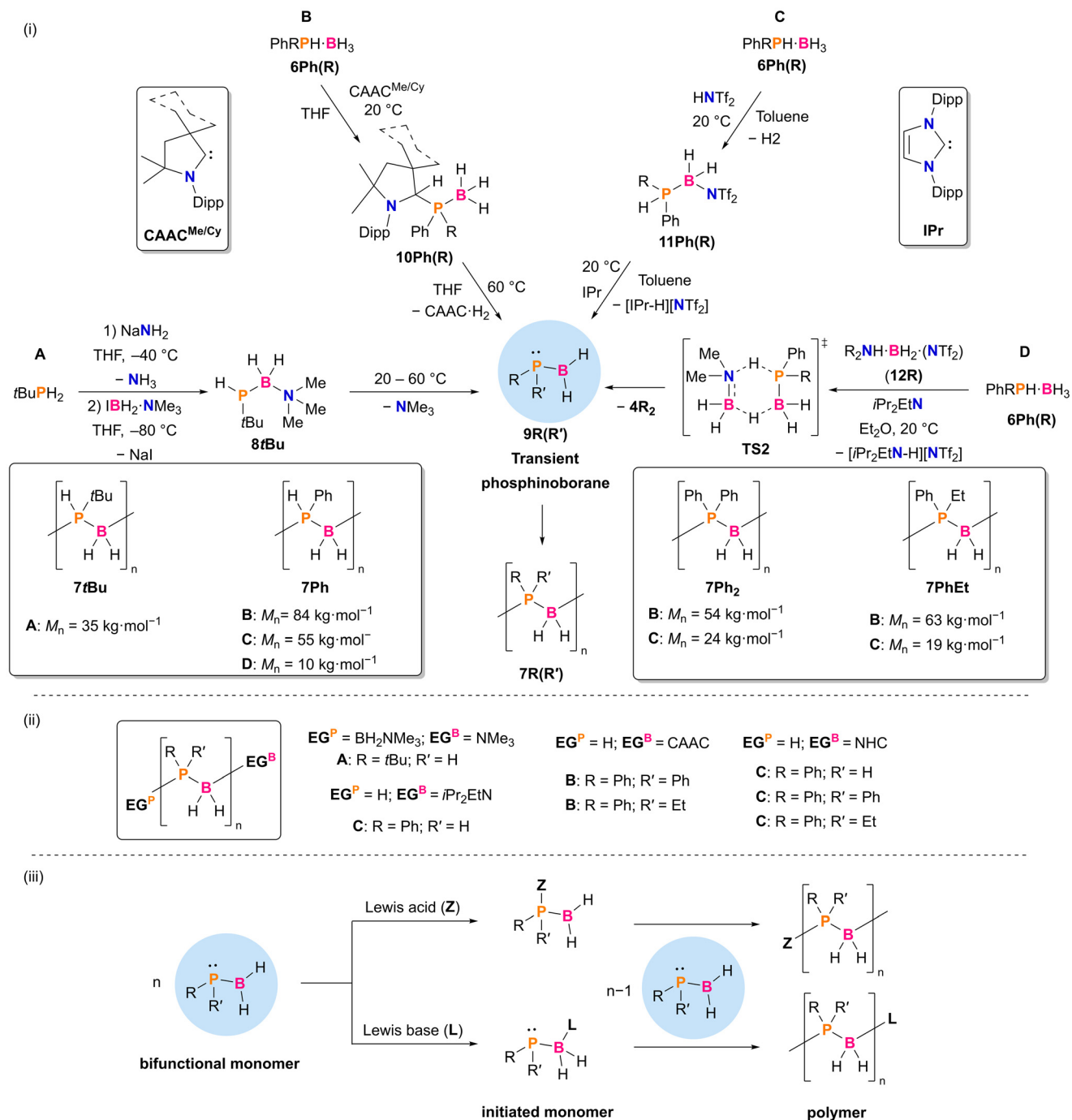


Fig. 3 An overview of the synthesis of poly(phosphinoboranes) via the synthesis of phosphinoborane monomers *in situ* through stoichiometric reactions. (i) The four pathways to yield poly(phosphinoboranes) through the synthesis of phosphinoborane monomers are given. Pathway A depicts the synthesis of $t\text{BuPH-BH}_2(\text{NMe}_3)$ and its subsequent polymerisation via thermally driven cleavage of the B–N bond.⁴⁵ Pathway B depicts the dehydro-polymerisation of phosphine-borane adducts using CAACs, showing the initial P–H bond insertion reaction, followed by the generation of phosphinoborane and CAAC- H_2 .⁸¹ Pathway C depicts the synthesis of phosphine-(triflimido)borane adducts, followed by their deprotonation to access poly(phosphinoboranes). Pathway D depicts the reaction between aminoboranes and phosphine-borane adducts to result in the formation of phosphinoboranes and amine-borane adducts.⁸³ (ii) The end groups observed by ESI-MS in the isolated polymer materials from the four pathways are given. Below each set the substituents at phosphorus are indicated for routes A–C. (iii) The proposed mechanism^{81,82} for the polymerisation of phosphinoboranes generated *in situ*, where Lewis acids or Lewis bases can coordinate chain ends to suppress the formation of low molecular weight materials and yield high molar mass products.

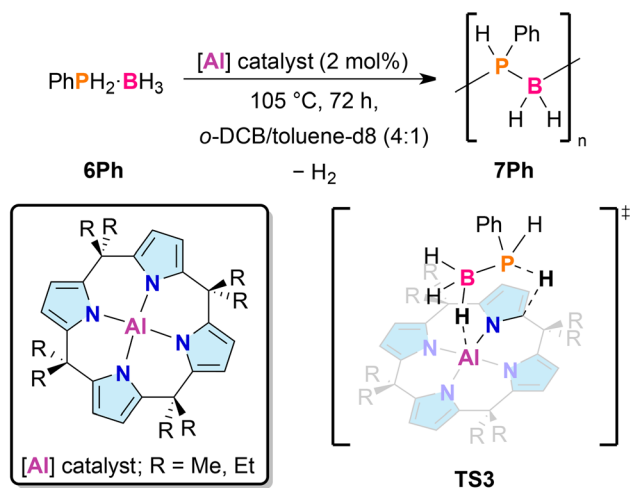


Fig. 4 Dehydropolymerisation of $\text{PhPH}_2\text{-BH}_3$ using calix[4]pyrrolato aluminate as a catalyst. The proposed intermediate where P–H bond is acidified via a B–H–Al interaction (TS3) is also shown.

determined by NMR spectroscopy and GPC. Further, analysis of the GPC chromatograms revealed that the material had a bimodal mass distribution, where most of the product was of low molar mass (*ca.* 30% high molar mass material). Attempted polymerisation of *P*-disubstituted phosphinoboranes using Hünig's base instead results in the formation of what was tentatively assigned as Lewis base capped linear dimers ($\text{PhPH}_2\text{-BH}_2\text{-PhPH-BH}_2(\text{L})$; $\text{L} = \text{iPr}_2\text{EtN}$, H , NTf_2) based on heteronuclear NMR spectra that were similar to known dimers ($\text{PhRPH-BH}_2\text{-PhRP-BH}_3$, $\text{R} = \text{Ph}$, Et).^{40,81}

When an *N*-heterocyclic carbene was used as the base for deprotonation of phosphine-(triflimido)boranes, *P*-disubstituted polymers were obtained. Characterisation of all polymers produced by NMR spectroscopy resulted in the materials indistinguishable by earlier studies.⁸¹ However, comparing the GPC traces from the materials obtained from deprotonations using NHCs revealed that the materials obtained had a high fraction ($\geq 50\%$) of high molar mass material. As both Hünig's base and NHCs are sufficiently basic to deprotonate phosphine-(triflimido)boranes, the ability to access *P*-disubstituted polymers only with NHCs implies that the base also has a role in the addition polymerisation of phosphinoborane monomers. This was further supported by end-group characterisation using ESI-MS, where NHCs were observed as end-groups (*i.e.* $\text{H-[PhRP-BH}_2\text{]}_n\text{-NHC}$, $\text{R} = \text{H}$, Ph , Et) in isolated polymer samples (Fig. 3ii). Similar to the CAAC-mediated route, the authors were able to trap a reactive phosphinoborane through the reaction of two equivalents of NHC with $t\text{Bu}_2\text{PH-BH}_2(\text{NTf}_2)$, generating $t\text{Bu}_2\text{P-BH}_2(\text{NHC})$.⁸² Therefore, this study cemented that to access *P*-disubstituted polymers, the generation of *P*-disubstituted phosphinoboranes *in situ* cannot be the only requirement for accessing their polymers.

3.2.1.4 Dehydropolymerisation of phosphine-borane adducts using aminoboranes as H_2 -acceptors. A significant challenge in the dehydropolymerisation of phosphine-borane adducts has

been the requirement for the harsh conditions. The other methods described above require either the synthesis of specialised phosphinoborane precursors, or are still rather inefficient transformations from the perspective of atom economy. Recently, however, a strategy using reactive amino-boranes to accept hydrogen from phosphine-borane adducts has been introduced, which occurs under ambient conditions.⁸³

This development built upon earlier work from the Manners group, in which amine-borane adducts were shown to undergo hydrogen transfer reactions with *N,N*-diisopropylaminoborane (**4iPr₂**).^{84,85} In this process, **4iPr₂** accepts hydrogen from *N,N*-dimethylamine-borane through a six-membered transition state involving a stepwise, concerted N-to-N and B-to-B hydrogen transfer. Computational studies determined that the hydrogen transfer from *N,N*-dimethylamine-borane to **4iPr₂** is endergonic, but the overall reaction is driven forward by the dimerisation of the reactive *N,N*-dimethylaminoborane formed in solution.

Motivated by these findings, similar hydrogen transfer reactions were explored between reactive aminoboranes and phosphine-borane adducts.⁸³ These studies showed that only sufficiently reactive aminoboranes accepted hydrogen from phosphine-borane adducts, as **4iPr₂** was shown to be unreactive. However, generation of *N,N*-dimethylaminoborane (**4Et₂**) or *N,N*-diethylaminoborane (**4Me₂**) in solution by the deprotonation of their respective amine-(triflimido)boranes (**12R₂**, $\text{R} = \text{Me}$ or Et) enabled the dehydrocoupling of $\text{PhPH}_2\text{-BH}_3$ (**6Ph**) or $\text{Ph}_2\text{PH-BH}_3$ (**6Ph₂**). These reactions afforded either $[\text{PhPH-BH}_2]_n$ (**7Ph**) or $\text{Ph}_2\text{PH-BH}_2\text{-Ph}_2\text{P-BH}_3$ under ambient conditions (20°C , $\leq 24\text{ h}$) (Fig. 3, route D). However, the polymer produced was of modest molar mass ($M_n = 10\text{ kg mol}^{-1}$, $D = 1.6$). A computational study suggested the hydrogen follows an analogous six-membered transition state to that observed for amine-borane adducts, proceeding *via* P-to-N and B-to-B hydrogen transfer (Fig. 3, TS2). Importantly, this transformation represents the first example of the direct dehydrogenation of phosphine-borane adducts under ambient conditions.

3.2.2 Sub-stoichiometric routes

3.2.2.1 Dehydropolymerisation of phosphine-borane adducts using an aluminate catalyst. Calix[4]pyrrolato aluminate has recently gained attention as a main-group-element-centred Lewis acidic anion that has unique reactivity due to its square planar coordinative environment. This environment allows for aluminum-ligand interactions with polar substrates such as carbon monoxide (CO) and carbon dioxide (CO_2).^{86,87} In a recent collaboration between the Manners and Greb groups, calix[4]pyrrolato aluminate was shown to catalyse the dehydropolymerisation of *P*-phenylphosphine-borane.⁸⁸ This was achieved under similar conditions explored for metal-mediated catalytic dehydropolymerisation of phosphine-borane adducts ($[\text{Al}] = 0.3\text{--}10\text{ mol\%}$, $t = 24\text{--}72\text{ h}$, $T = 105^\circ\text{C}$).⁸⁸ The materials obtained were of high molecular weight and had typical dispersity values for poly(phosphinoboranes) (**7Ph**: $M_n = 14\text{--}43\text{ kg mol}^{-1}$; $D = 1.54\text{--}2.00$). Thus, polymers with molecular weights and dispersity values matching those produced by metal-



mediated catalysis could be produced, but instead using a main-group element centred catalyst.

Computational studies into the mechanism suggested that the aluminate species acidifies the P–H bond of the phosphine-borane adduct *via* aluminium binding of one of the hydride substituents on borane (Fig. 4, TS3), delivering a proton to 2-position of the pyrrole ring. The basic nature of the 2-position of the pyrrole in calix[4]pyrrolato aluminate was confirmed experimentally through reactions with either a sub-stoichiometric (0.6 eq.) of phosphine-borane adduct (**6Ph**) or a stoichiometric amount of HNTf₂, producing the protonated ligand still bound to aluminium.

3.2.2.2. Thermal dehydropolymerisation in the presence of Lewis acid-base pairs. The essential role of Lewis acid and Lewis base pairs in the dehydropolymerisation of phosphine-borane adducts was cemented in a recent study from the Manners group.⁸⁹ Here it was shown that high temperature dehydropolymerisation of PhPH₂·BH₃ (**6Ph**) performed in the presence of sub-stoichiometric (5 mol%) LiOTf, LiNTf₂, Mg(OTf)₂, or BH₃·SMe₂ performed as well as those performed with the state-of-the-art transition metal catalyst, Cp(CO)₂FeOTf (Fig. 5i).⁶⁶ Further, phosphine-borane dehydropolymerisation was performed without any additives in 2-MeTHF, under normal catalytic dehydropolymerisation con-

ditions (2 M, 100 °C, 24 h) to access high molar mass, low dispersity polymer (**7Ph**: $M_n = 81 \text{ kg mol}^{-1}$, $D = 1.66$).

The ability to access high molar mass [PhPH–BH₂]_n (**7Ph**) without any additives in 2-MeTHF, implies that all that is necessary to access high molar mass material exists either in the precursor phosphine-borane adduct, or 2-MeTHF. It is believed that a small amount of phosphine-borane dissociates *in situ* at elevated temperatures, providing both a Lewis acid (borane) and a Lewis base (phosphine, 2-MeTHF). Further, it was revealed that performing dehydropolymerisation reactions with added BH₃·SMe₂, a source of BH₃, decreased the time needed for full dehydrogenation of PhPH₂·BH₃ (**6Ph**), suggesting it is potentially involved in dehydrogenation as well. End-group analysis revealed polymers with PhPH₂ or BH₂(SMe₂) end groups in positive mode-ESI (*i.e.*, H–[PhPH–BH₂]_x–PPhH₂ and Me₂S·BH₂–[PhPH–BH₂]_x–H) and polymers with BH₃ end groups in negative mode-ESI (*i.e.*, BH₃–[PhPH–BH₂]_x–H) (Fig. 5ii). This supports the role of borane sources (*i.e.* PhPH₂·BH₃ and BH₃·SMe₂) in both the dehydrogenation and polymerisation steps.

On this basis, the authors proposed that monomers can either undergo a self-initiation and polymerisation, or, initiation *via* reactions with Lewis acids or Lewis bases *in situ* as depicted in Fig. 3(iii). In addition, reversible coordination

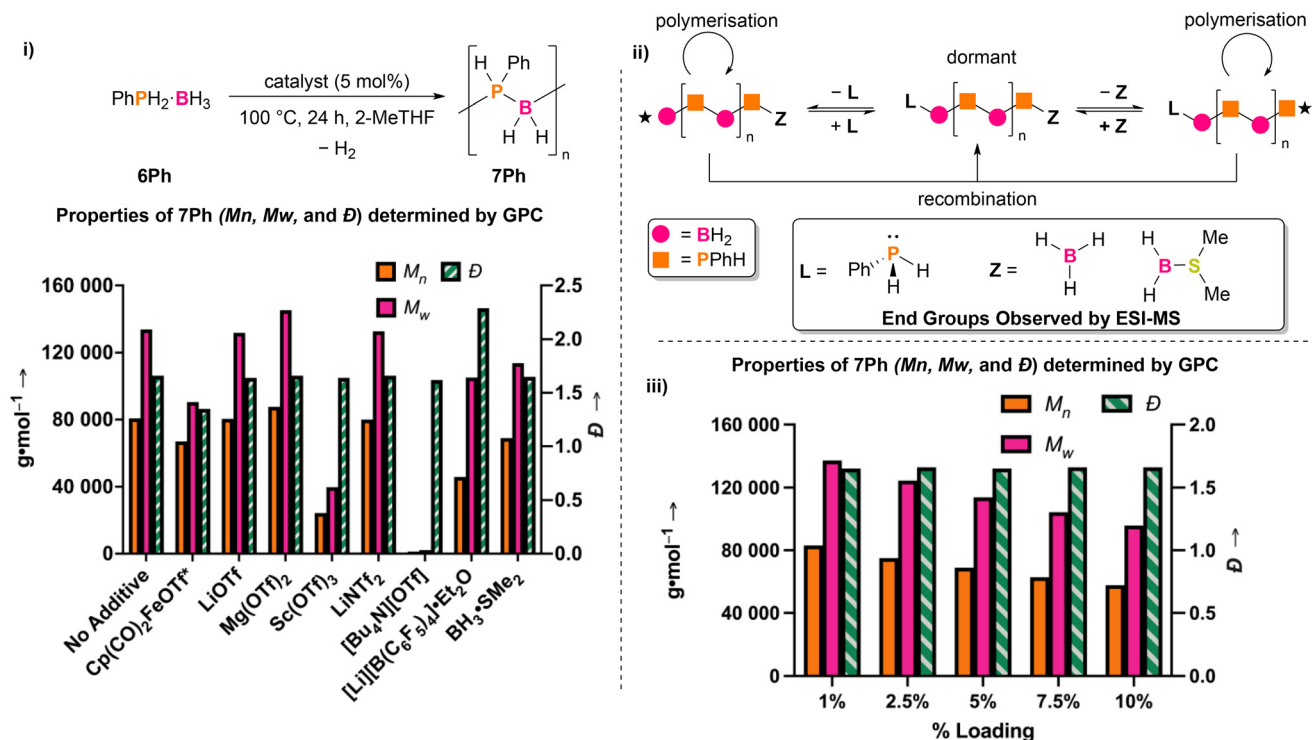


Fig. 5 Overview of the thermal dehydropolymerisation of phosphine-borane adducts in the presence of Lewis acid-base pairs. (i) Synthesis of poly(phosphinoboranes) using commercially available salt additives in 2-MeTHF, where M_n , M_w , and D values are plotted in a bar chart below.⁸⁹ *The value for Cp(CO)₂FeOTf is given from a polymerisation performed in dioxane.⁶⁶ (ii) Mechanism for the polymerisation of phosphinoborane chains mediated by Lewis acids (Z) and Lewis bases (L) where reactive exposed termini are labelled with a 5-point star. (iii) Bar chart of M_n , M_w , and D values obtained from the dehydropolymerisation of PhPH₂·BH₃ with 1 to 10 mol% loading of BH₃·SMe₂, with the same conditions as listed in (i). Bar charts shown in (i) and (iii) are reproduced from ref. 84 with permission from the Royal Society of Chemistry.

Table 2 Summary of the synthetic routes to poly(aminoboranes) and poly(phosphinoboranes). Section numbers correspond to the more detailed discussions in-text

Method (section)	Scope	Conditions	M_n (kg mol ⁻¹) and $\bar{D}$	Features
Synthesis of poly(aminoboranes)				
Transition-metal-free routes				
Deprotonation of amine-boronium cations (2.2.1) ⁶¹	[MeNH-BH ₂] _n	1 min, 20 °C, Et ₂ O (0.3 M)	$M_n \leq 5$ $\bar{D} = \text{n/a}$	Rapid generation of aminoboranes; unexplored substrate scope
Reaction of primary amines with iPr ₂ N=BH ₂ (2.2.2) ^{44,94}	[RCH ₂ N-BH ₂] _n ; R = H, alkyl, aryl, silyl, cycloalkyl	2 h, -40 °C, neat	$M_n \leq 790$ $\bar{D} = 1.2\text{--}10.2$	Broad scope of nitrogen substituents
Transition-metal-catalysed dehydropolymerisation (selected examples)				
Titanium-catalysed dehydropolymerisation (2.1) ⁴²	[RNH-BH ₂] _n ; R = Me, benzyl, allyl	1 h, 20 °C, toluene (0.2 M), 4 mol% [Ti]	$M_n \leq 235$ $\bar{D} = 1.3\text{--}2.3$	Polymers accessed with <i>p</i> -halogenated benzylic <i>N</i> -substituents
Rhodium-catalysed dehydropolymerisation (2.1) ³¹	[MeNH-BH ₂] _n	0.5–2 h, 20 °C, THF (1–5 M), 0.01–1.0 mol% [Rh]	$M_n \leq 78$ ¹ $\bar{D} = 1.3\text{--}2.3$	Polymerization can be performed in open air; molar mass control through added [BH ₂ (NMe ₂ H) ₂]Cl; unexplored substrate scope
Synthesis of poly(phosphinoboranes)				
Transition-metal-free routes				
Using stoichiometric reagents				
Polymerization of <i>t</i> BuPH-BH ₂ (NMe ₂) (3.2.1.1) ⁴⁵	[<i>t</i> BuPH-BH ₂] _n	48 h, 22–40 °C, neat or toluene (<i>ca.</i> 0.3 M)	$M_n \leq 35$ $\bar{D} = 1.6\text{--}1.9$	Limited to only [<i>t</i> BuPH-BH ₂] _n
Reaction of PhRPH-BH ₃ with CAAC (3.2.1.2) ⁸¹	[PhPR-BH ₂] _n ; R = H, Ph, Et	4 h, 20–110 °C, THF or toluene (0.1–2.5 M)	$M_n \leq 60$ $\bar{D} = 1.1\text{--}1.6$	<i>P</i> -Disubstituted material only at 60 °C; bimodal material isolated; small fraction (<i>ca.</i> 10%) of high M_n polymer
Deprotonation of PhRPH-BH ₂ (NTf ₂) (3.2.1.3) ⁸²	[PhPR-BH ₂] _n ; R = H, Ph, Et	4 h, 20 °C, toluene (2 M)	$M_n \leq 55$ $\bar{D} = 1.3\text{--}1.6$	Bimodal material isolated; large (≥50%) fraction of high M_n polymer
Reaction of PhRPH-BH ₃ with aminoboranes (3.2.1.4) ⁸³	[PhPH-BH ₂] ₂	24 h, 20 °C, Et ₂ O (2 M)	$M_n = 10$ $\bar{D} = 1.8$	Direct dehydrogenation of phosphine-borane adducts; unexplored substrate scope
Using sub-stoichiometric reagents				
Aluminate-catalysed phosphine-borane dehydropolymerisation (3.2.2.1) ⁸⁸	[PhPH-BH ₂] _n	24–72 h, 105 °C, 4 : 1 <i>o</i> -DCB & toluene- <i>d</i> ₈ (1 M), 0.3–10 mol% [Al]	$M_n \leq 43$ $\bar{D} = 1.1\text{--}1.6$	Operates <i>via</i> ligand-aluminium cooperative dehydrogenation of phosphine-borane adducts; unexplored substrate scope
Thermal dehydropolymerisation with Lewis acid base pairs (3.2.2.2) ⁸⁹	[PhPH-BH ₂] _n	24 h, 100 °C, toluene or 2-MeTHF (2 M); 1–10 mol% additive	$M_n \leq 92$ $\bar{D} = 1.4\text{--}2.3$	Uses commercially available additives; molar mass control through BH ₃ ·SMe ₂ loading; unexplored substrate scope
Transition-metal-catalysed dehydropolymerisation (selected examples)				
Iron-catalysed dehydropolymerisation (3.1) ^{46,66,95}	[RPH-BH ₂] _n ; R = alkyl, aryl, ferrocenyl	24 h, 100 °C, toluene or dioxane (0.6 M), 0.1–10 mol% [Fe]	$M_n \leq 67$ $\bar{D} = 1.5\text{--}1.7$	Chain-growth coordination-insertion mechanism; molar mass control based on [Fe] loading
Rhodium-catalysed dehydropolymerisation (3.1) ^{69,70}	[RPH-BH ₂] _n ; R = Ph, <i>n</i> -hexyl	19–66 h, 100 °C, toluene (1.25 M), 1–3 mol% [Rh]	$M_n \leq 127$ $\bar{D} = 1.2\text{--}1.6$	Step-growth, reversible-chain transfer mechanism; capable of producing AB block copolymers

of reactive tertiary phosphine or borane termini moderates the reactivity of chain-ends, in a manner reminiscent of living radical olefin polymerisations (Fig. 5ii).^{90–93} This allows for continued polymer growth through addition reactions when either polymer end is exposed, and also allows for complementarily reactive growing polymers to recombine into a higher-molar-mass dormant species.

Experimental evidence supported this mechanism. Firstly, isolated polymer samples were dissolved in minimal 2-MeTHF and heated for 24 hours further, resulting in an increase in molecular weight and dispersity (**7Ph**: $M_n = 149$ kg mol⁻¹, $\bar{D} = 2.40$). This behaviour is consistent with pseudo-living character, in which polymers undergo continued growth. Molecular weight control was also demonstrated through BH₃·SMe₂ loading (Fig. 5iii). An increase in BH₃·SMe₂ loading resulted in

a reduction of the M_n of the resulting material (*i.e.* **7Ph**: $M_n = 83$ kg mol⁻¹ with 1 mol% BH₃·SMe₂ loading to $M_n = 57$ kg mol⁻¹ with 10 mol% BH₃·SMe₂ loading). This effect was attributed to a higher fraction of dormant chains *in situ*, which undergo fewer propagation events. Thus, it was shown that high molar mass **7Ph** with tuned M_n could be produced using BH₃·SMe₂ as an additive.

4. Overview and future directions

As our requirements of materials become more sophisticated, so do the materials themselves. Accordingly, synthetic methods to access new materials needs to continue to grow. This has been the case in the synthesis of poly(aminoboranes)



and poly(phosphinoboranes), especially within the past decade. Herein we have described the advancements made in the transition-metal-free synthesis of poly(aminoboranes) and poly(phosphinoboranes). The routes described within this review with their scope, reaction conditions, typical polymer masses, and features to each method are given in Table 2.

Generally, these routes focus on the generation of transient aminoboranes or phosphinoboranes *in situ* which then undergo polymerisation. This is analogous to the polymerisation process for poly(olefins), but rendered much more complicated by the low thermal and kinetic stability of the BN and BP monomers compared to olefins. However, through thorough characterisation of isolated polymer samples and carefully designed experiments, significant headway has been made in the understanding of the individual polymerisation step, apart from dehydrogenation of precursor adducts. Mechanistically, trapping of reactive species, including the monomers as well as ESI end-group analysis has been most insightful. It appears that the new generation of catalysts act by stabilising the end groups of the growing polymers, either as Lewis acids or Lewis bases. Together with a judicious choice of solvent, chain termination events can be reduced, reminiscent of keeping a growing polymer chain dormant, but alive in pseudo-living radical polymerisations of olefins. These individual breakthroughs are all part of the larger goal of absolute control over polymer microstructure for these inorganic polymers (*i.e.*, degree of polymerisation, tacticity, monomer substitution). We predict that the next wave of discovery for poly(aminoboranes) and poly(phosphinoboranes) will be largely concerned with gaining control over the polymer architecture in a way that is already well known for poly(olefins).

While much has been achieved, these polymers are still mostly of interest in academia, and their application outside of synthetic laboratories are in their infancy. We believe this is in part due to the historic synthetic barrier to access these materials. However, the synthetic routes described within this review are capable of producing polymeric materials of high molecular weight and low dispersity using routine laboratory reagents. Thus, while there is still progress to be made in having a greater understanding of the polymerisations, we are of the opinion that the synthetic chemistry for poly(aminoboranes) and poly(phosphinoboranes) are now of sufficient maturity for bulk property analysis, allowing for a better understanding of their structure-property relationships. Further, these transition-metal-free routes offer the opportunity to determine the true effect of metal-doping on bulk polymer samples. We therefore encourage the broader scientific community to explore these fascinating materials in more depth, confident that their potential is only beginning to be realised.

Author contributions

Conceptualisation: M. A. W.; funding acquisition: M. A. W., A. S.; project administration: M. A. W., A. S.; resources: M. A. W., A. S.; supervision: A. S.; visualisation: M. A. W.;

writing – original draft: M. A. W.; writing – reviewing and editing: M. A. W., A. S.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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