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Review

Lewis acidic organoboron polymers

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Abstract

The functionalization of polymeric materials with Lewis acidic boron sites has led to exciting new opportunities in diverse areas, ranging from new polymeric catalysts to the preparation of highly luminescent materials and the design of efficient sensor systems for nucleophiles. Recent advances in the preparation of these Lewis acidic boron polymers, their coordination behavior, and some of their intriguing applications are reviewed.

Keywords: Boron; Organoborane; Organoboron polymers; Lewis acids; Sensors; Luminescent materials

1. Introduction and scope

One of the key aspects in the chemistry of organoboranes is their behavior as Lewis acids, which is a result of the empty

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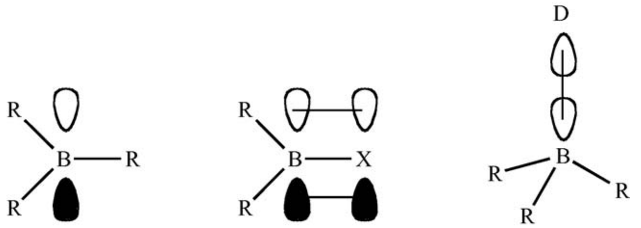


Fig. 1. Stabilization of tricoordinate organoboranes through π-bonding or formation of Lewis acid–Lewis base complexes.

p-orbital of tricoordinate boron [1]. Boron can reach the desired octet configuration either through π-overlap with a suitable substituent X or through formation of Lewis acid–Lewis base complexes (Fig. 1). These interactions have been exploited in many of the applications of organoboron compounds. For instance, interesting linear and non-linear optical properties result from overlap of the empty p-orbital on boron with extended organic π-systems [2–4]. Moreover, the photophysical properties of organoboranes show distinct changes upon coordination of nucleophiles (D), a phenomenon that has been widely used in sensor applications [5]. Similarly, the function of these organoboranes as catalysts and co-catalysts in organic synthesis is based on donor–acceptor interactions that lead to activation of the organic substrate [6–8]. Finally, donor–acceptor bonding between bifunctional organoboranes and bifunctional Lewis bases can be exploited for the (reversible) assembly of macrocycles and coordination polymers [9].

Polymeric organoboranes have recently received increasing interest since they may provide additional benefits in these areas. For instance, in the field of sensor materials, the incorporation of Lewis acidic organoboron moieties into conjugated polymers has been shown to lead to sensor signal amplification effects [10,11]. Regarding applications as catalysts, attachment of high value Lewis acid catalysts to an inert polymer backbone can provide improved stability and recoverability [12]. Moreover, the interaction of polymeric Lewis acids with Lewis base functionalized polymers may provide a new means to generate higher order polymer assemblies reversibly [13,14].

Various polymer architectures have been successfully implemented in order to realize these objectives (Fig. 2). This review will provide a survey of procedures currently available for the preparation of Lewis acidic organoboron polymers, describe their chemical and physical properties, and discuss applications of this intriguing class of polymers. Organoboron polymers in which the boron moieties do not act as typical Lewis acids are beyond the scope of this review, and the interested reader is referred to more general reviews on boron-containing polymers [15,16].

2. Side-chain functionalized polyolefins and related systems

A great deal of information has been gathered on boron-functionalized polyolefins in general [16–18]. However, in most cases the boron centers are not designed to act as Lewis acids, and surprisingly little work has been carried out on the selective functionalization of the side groups of polyolefins with Lewis acidic boron centers. A few notable exceptions that for most part involve the functionalization of polystyrene resins will be reviewed, followed by a discussion of recent contributions from our group, that allow for the facile preparation of soluble polystyrene-based organoboron polymeric Lewis acids with tunable Lewis acidity.

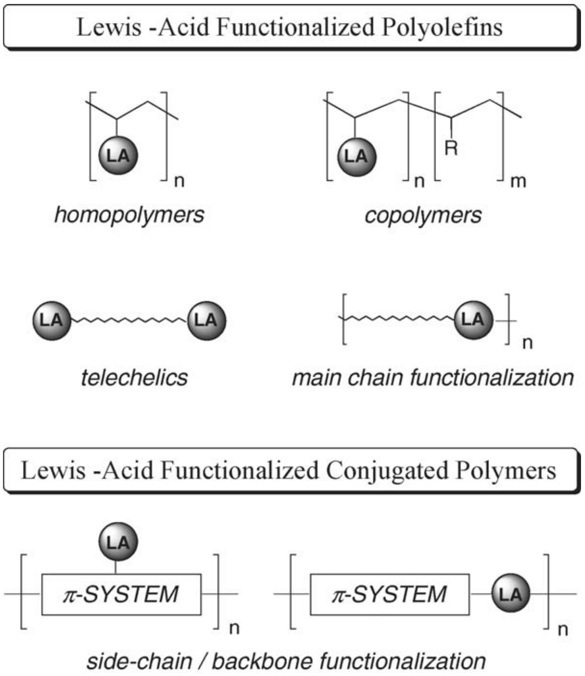


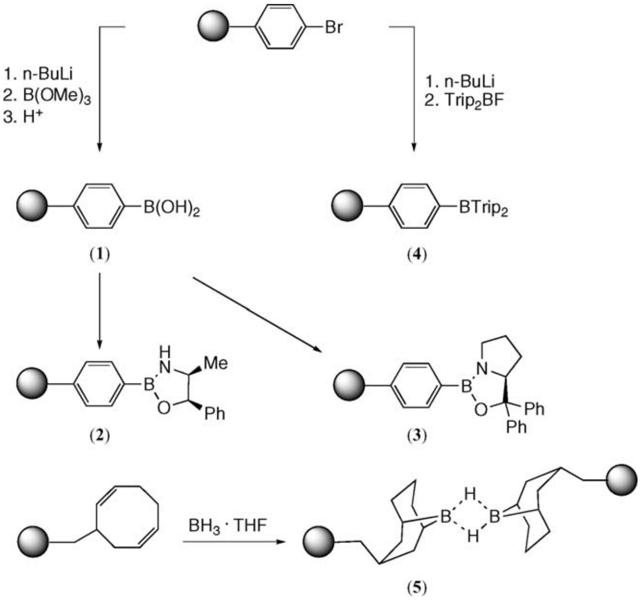
Fig. 2. Schematic representation of common designs of polymeric Lewis acids.

2.1. Synthetic methods and characterization

2.1.1. Polymer resins

Fréchet's three-step reaction sequence for the functionalization of polystyrene resins, which involves (1) bromination, (2) lithiation, and (3) quenching with electrophiles, has been widely used in the preparation of organoboron polymers (Scheme 1) [19]. A high degree of functionalization with boronic acid or other functional residues can typically be achieved if the lithiation step is carried out in aromatic solvents such as benzene or toluene rather than ether solvents [20–23]. An alternative procedure that has been studied by Thorpe et al. involves the initial mercuriation of polystyrene and related resin materials [24–27]. The resulting polystyrene boronic acid intermediate (**1**) can in turn easily be further converted to diol complexes or transformed into oxazaborolidines (**2** and **3**) that serve as catalysts in organic reactions (Scheme 1) [20,28–30].

Triarylborane-functionalized resins were prepared through similar procedures. Smith et al. reacted a brominated polystyrene resin with *n*-BuLi in benzene followed by addition of the bulky fluoroborane Trip$_2$BF (Trip = 2,4,6-tri-*iso*-propylphenyl) in THF to give polymer (**4**) [31]. In an alternative approach, treatment of Merrifield's resin with sodium naphthalenide and subsequent reaction with Trip$_2$BF resulted in formation of a diarylmethylborane resin. The resins were obtained in up to



Scheme 1. Preparation of polymer resin-supported organoboranes.

75% functional yield and converted to the respective hydroborate resins with *t*-BuLi or KH for use in the stereoselective reduction of ketones.

The preparation of polymer-supported 9-BBN (**5**) from a high loading Merrifield resin has recently been reported by Ganesan et al. (Scheme 1) [32]. A two-step procedure was applied, in which first the functionalized resin was prepared by treatment of Merrifield's resin with deprotonated 1,5-cyclooctadiene, and the product was then reacted with $BH_3{\cdot}THF$ at elevated temperature. Formation of the organoborane resin (**5**) with a loading of 3.24 mmol/g was confirmed by microanalysis and is also evident from a peak at 28 ppm in the gel-phase ^{11}B NMR, at a chemical shift similar to that of the hydrogen-bridged 9-BBN-H dimer. Several trialkylborane resins were synthesized from **5** through hydroboration of olefinic substrates.

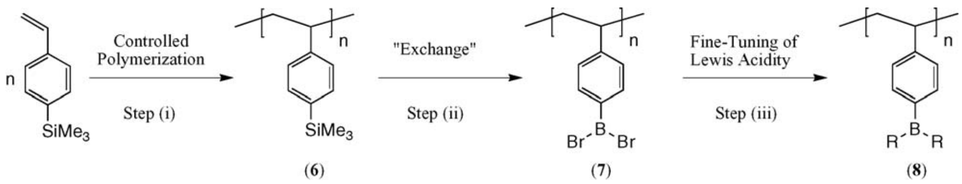
2.1.2. Linear homopolymers and random copolymers

Lithiation and mercuriation reactions have also been applied to the preparation of soluble linear organoboron polymers. However, significant cross-linking is commonly observed [24–26,28]. For instance, linear polystyrene was treated with mercuric(II) trifluoroacetate and subsequently reacted with $BH_3{\cdot}THF$ and a range of other boron hydrides including $BH_3{\cdot}SMe_2$, $BBr_2H{\cdot}SMe_2$, $BH_2Cl{\cdot}SMe_2$, 9-BBN, and HBcat (cat = catecholato). In methylene chloride very high degrees of mercuriation were achieved (up to 96%). However, the functional yield for the borane treatment was generally much lower and cross-linking was apparent [24,25]. It has also been shown that mercuriation of polystyrene occurs to a certain degree in positions other than the *para*-position of the phenyl rings [33]. Thus, polymerization of organoboron monomers can be advantageous in those cases. For instance, a soluble polymeric analog of the oxazaborolidine catalyst (**3**) has been prepared through copolymerization of *p*-vinylphenylboronic acid with styrene and subsequent treatment with α,α-diphenylprolinol [30]. This polymer-enlarged oxazaborolidine was successfully used as a recyclable reagent for borane reductions in a continuously operated membrane reactor.

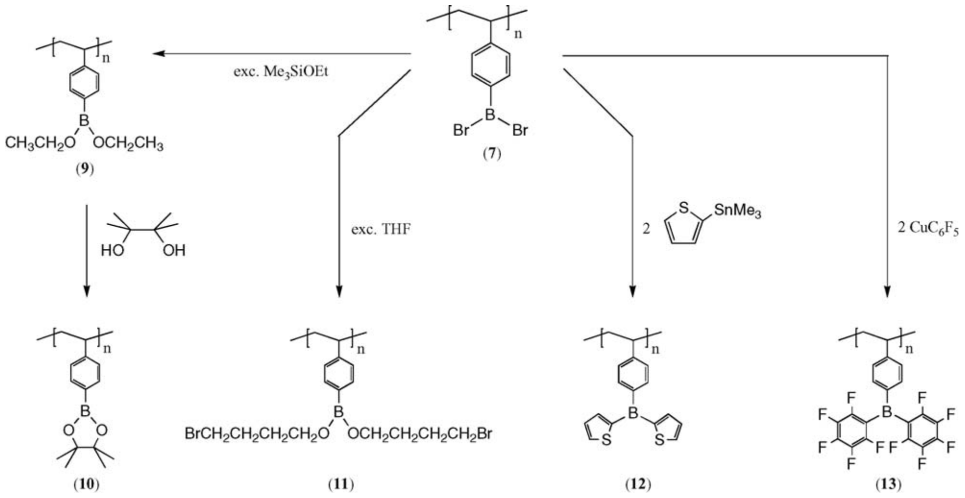
We were interested in the development of a new modular approach to organoborane polymeric Lewis acids, in which not only could cross-linking be avoided during synthesis, but also a great deal of control over the polymer architecture would be possible through use of controlled polymerization techniques [34,35]. At the same time, we wanted to be able to tune the Lewis acidity of the polymers through facile modification of the substitution pattern on boron. Our approach involves three straightforward steps: (i) the controlled (co)polymerization of the silylated functional monomer 4-trimethylsilylstyrene to give the functional polymer (**6**), (ii) the exchange of the silyl groups with the Lewis acidic dibromoboryl groups in **7**, and (iii) the fine-tuning of the Lewis acidity of the individual boron centers through high yield substituent exchange reactions (Scheme 2). The latter provides facile access to boron polymers (**8**) that show various substitution patterns and adjustable Lewis acidity.

For the preparation of the trimethylsilyl-functionalized polymer (**6**) we applied a typical protocol for atom transfer radical polymerization (ATRP), a controlled free radical polymerization technique introduced by Matyjaszewski and Xia [36]. This method provides control over the molecular weight by varying the ratio of monomer to initiator and allows for the preparation of block copolymers by chain extension with other monomers.

In the second step, a highly selective polymer modification reaction, polymer (**6**) was treated with a slight excess of BBr_3 to form the highly Lewis acidic polymer (**7**) (Scheme 2) along with the volatile by-product Me_3SiBr, which was easily removed under high vacuum. In this context it is interesting to note that silylated polystyrene (**6**) can also serve as an effective precursor to random copolymers through treatment with a deficiency of boron tribromide [37]. Multinuclear NMR studies indicated that the transformation with excess BBr_3 occurs quantitatively yielding a reactive boron polymer that is well soluble in chlorinated solvents [34,35]. This methodology thus represents an exceptionally simple and straightforward route to boron-functionalized polystyrene that avoids the use of toxic species such as mercury or tin compounds, while at the same time providing outstanding selectivity without any apparent



Scheme 2. Use of silylated polystyrene for the synthesis of organoboron polymers.



Scheme 3. Formation of organoboron polymers from dibromoborylated polystyrene.

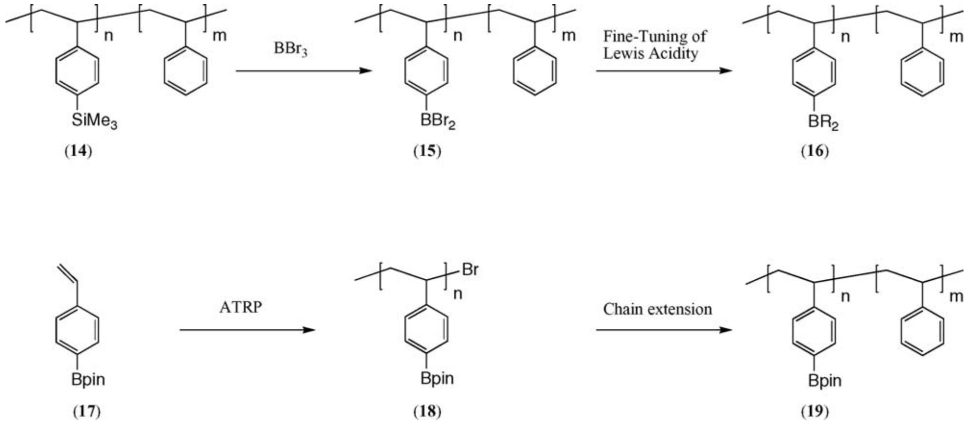
cross-linking of the polymer chains. The latter point was further confirmed through analysis of a large number of derivatives obtained upon treatment with nucleophiles as described in the following.

To gain access to polymers with centers of moderate Lewis acidity we have investigated several reagents that allow for introduction of π-donating alkoxy substituents on boron including alcohols, ethers, and silylethers (Scheme 3) [35]. Best results were obtained with strained cyclic ethers such as THF and with silylated alcohols. The polymeric alkoxyboranes (**9**–**11**) were submitted to GPC analysis, which confirmed that the molecular weight and molecular weight distribution did not change significantly from those of the silylated precursor polymer (**6**). This clearly demonstrates that both, the borylation reaction and the subsequent functionalization with nucleophiles take place without significant polymer degradation or cross-linking. Further evidence was provided by static light scattering on the boron polymer (**10**), which showed that the measured average degree of polymerization (DP) and the dispersity are nearly identical to those of the silylated precursor polymer (**6**) [34,35].

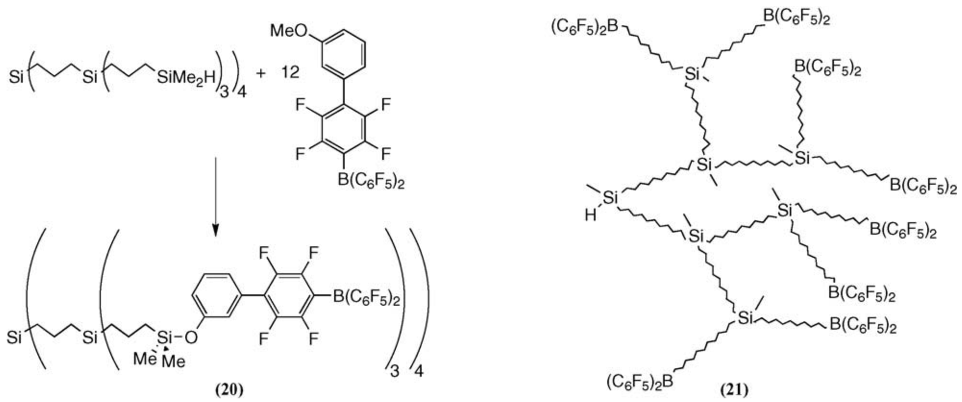
Highly Lewis acidic triarylborane polymers are accessible through reaction of **7** with stannylated arenes such as 2-trimethylstannylthiophene or 2-trimethylstannyl-5,5′-bithiophene (Scheme 3) [38,39]. We have also developed a synthetic procedure for the introduction of fluorinated aryl groups to boron halides using arylcopper reagents [40,41] and applied this methodology to the synthesis of the highly Lewis acidic organoboron polymer (**13**) [34,35].

2.1.3. Block copolymers

Organoboron random copolymers have been commonly prepared in order to "dilute" the active sites, and the synthetic procedures are typically similar to those used for the formation of homopolymers. Block copolymer architectures on the other hand are still rare. One example of the formation of organoboron block copolymers is the hydroboration of a functional block copolymer, polystyrene-*b*-polyisoprene, that contains vinyl groups in one of the constituent blocks [42]. However, the resulting organoboron block copolymer, and other related block copolymers, were not further studied, but rather directly converted to other functional block copolymers through oxidation or organometallic coupling reactions. We have investigated two different methods for the preparation of well-defined organoboron block copolymers (**16**), in which one of the constituent blocks consists of borylated styrene units (Scheme 4) [43]. In one approach we followed the procedure described



Scheme 4. Synthesis of organoboron block copolymers.



Scheme 5. Organoboron functionalized dendrimers and hyperbranched carbosilane polymers.

above for the preparation of silylated polystyrene by ATRP and then successfully performed a chain extension reaction with unfunctionalized styrene to give polymer (**14**). This procedure turned out to work very well, and a comparison of the NMR and GPC data of the silylated precursor block copolymer with the borylated product (**16**; $BR_2 = Bpin$) confirmed the high selectivity of the polymer modification procedure.

However, a possible limitation of this approach is that the second block preferably should consist of an unfunctionalized monomer in order to prevent side reactions in the silicon–boron exchange protocol. As a consequence, we have also explored an alternative route that involves the first controlled polymerization of an organoboron monomer (**17**) via ATRP (Scheme 4); the resulting boron polymer (**18**) in turn was used as a macroinitiator and extended to a block copolymer (**19**) with styrene. The GPC traces for the chain extension shown in Fig. 3 demonstrate the high efficiency of the borylated macroinitiator. Detailed kinetic studies confirmed good control and indicated quasi-living behavior for both routes [43].

2.1.4. Dendrimers and hyperbranched polymers

Perfluoroarylborane functionalized carbosilane dendrimers and hyperbranched polymers have recently been described [44,45]. Dendrimers containing a carbosilane core with up to 12 tris(perfluorophenylboryl) groups in the periphery have been assembled by Piers et al. (Scheme 5). The borane groups were attached in an elegant self-catalyzed reaction, that involves Lewis acid catalyzed silylation of the arylether derivative (**20**) [44]. High purity and nearly quantitative attachment of the arylborane moieties was confirmed by multinuclear NMR, elemental analysis, and negative ion MALDI-TOF mass spectrometry, which showed the $[MF]^-$ peaks for the fluoride adducts.

A related hyperbranched carbosilane polymer (**21**) has been developed by Rieger and Möller and co-workers [45]. Hydroboration of a vinyl-terminated poly(carbosilane) dendrimer with $[HB(C_6F_5)_2]_2$ led to the organoboron functionalized material (**21**) as indicated by ^1H NMR and FT-IR studies (Scheme 5).

2.2. Complexation and applications

Until recently very few systematic studies on the binding of nucleophiles to boron-functionalized polymers have been performed. As described above, the Lewis acidity of the polystyrene-based organoboron polymers (**7**) can be fine-tuned through high yield substitution reactions. Binding studies showed that the boron centers are indeed accessible, and tight binding of various pyridine bases to the highly Lewis acidic triarylborane polymers (**12**) and (**13**) ($R' = $ 2-thienyl, C_6F_5) has been confirmed by a strong upfield shift of the ^{11}B NMR signals [46]. Isolable polymeric donor–acceptor complexes (**22**) with pyridine ligands have been prepared (Scheme 6). A temperature-dependent equilibrium between coordinated and non-coordinated sites on the other hand is established with weaker donors such as ethers. Moreover, poly(styrene boronic

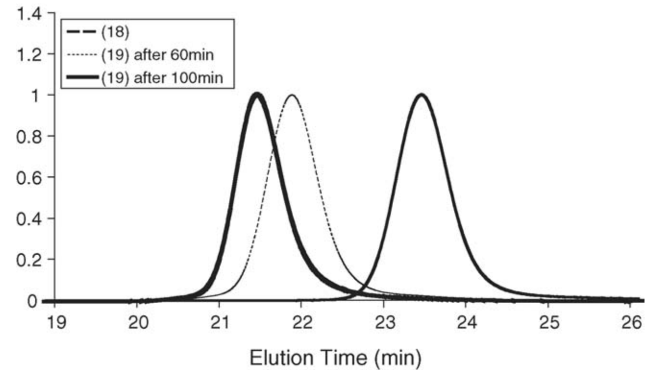
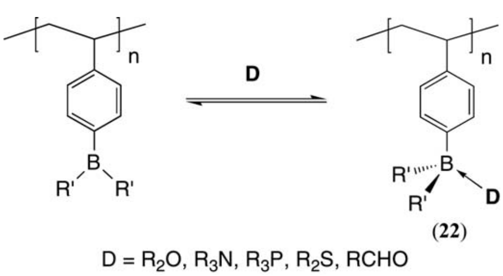
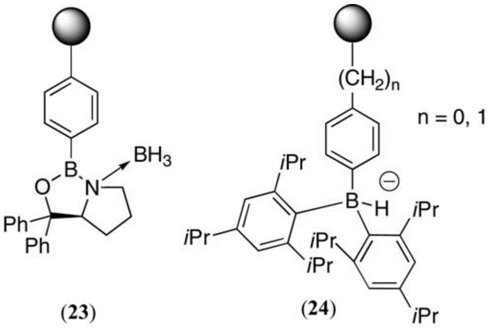


Fig. 3. GPC traces for the preparation of the organoboron block copolymer (**19**) through chain extension of **18** with styrene.

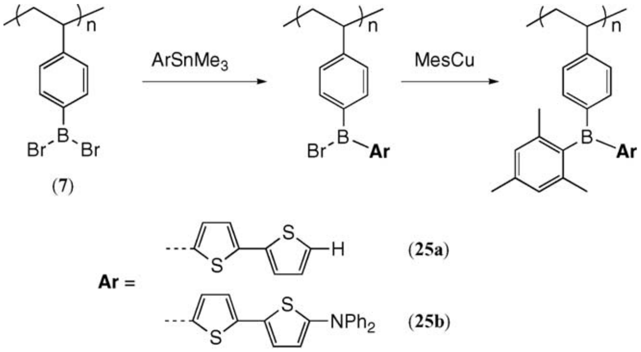


Scheme 6. Formation of polymeric complexes from soluble triarylborane polymers.



(23) **(24)**

Fig. 4. Examples of polymer-supported organoboranes as reducing agents.



Scheme 7. Luminescent polystyrene-based triarylborane polymers.

esters) (**9**, **11**; R′ = alkoxy) are only partially coordinated even in the presence of very strong bases, and no coordination of nucleophiles was detected for **10**. The fact that the Lewis acidic boron sites are readily accessible for binding of Lewis bases can be exploited for the design of new supported Lewis acid catalysts, new sensor and device materials, and in the reversible assembly of polymers [14,46,47].

2.2.1. *Applications in organic synthesis and catalysis*

2.2.1.1. Reduction and hydroboration chemistry. Polymeric oxazaborolidine resins have been extensively used in the asymmetric reduction of ketones and imines in the presence of a borane source [12]. The active species is formed upon complexation of BH_3 to the amine functionality of the oxazaborolidine moiety (e.g. **23**, Fig. 4). Similarly, hydroborates derived from arylborane resins (**24**) were shown to be effective in the stereoselective reduction of methylated cyclohexanone derivatives [31]. A reagent that was supported on Merrifield's resin (**24**, $n = 1$) displayed especially high selectivities and was readily recovered by filtration thus allowing for repeated use.

2.2.1.2. Lewis acid catalysis. Polymers containing pendent oxazaborolidine residues have also been applied as Lewis acid catalysts for asymmetric Diels–Alder reactions [48,49]. For example, excellent yields and exo:endo selectivities were observed for the reaction of methacroleine with cyclopentadiene. More recently, fluorinated arylboranes have attracted much interest as highly Lewis acid catalysts in organic synthesis and as cocatalysts in olefin polymerization. Reusable polymer-supported versions are desirable for these high value catalysts. Piers et al. demonstrated that dendrimers (**20**) that are decorated with multiple perfluorinated triarylboranes groups (4, 8 and 12) serve as effective catalysts in the hydrosilylation of acetophenone [44]. The activities in comparison to $B(C_6F_5)_3$ were found to be only slightly inferior.

The related hyperbranched carbosilane polymers (**21**) that contain bis(pentafluorophenyl)alkylborane units were investigated by Rieger and Möller and co-workers as activators in Ziegler-Natta olefin polymerization [45]. Surprisingly, despite the fact that one of the boron substituents is not fluorinated, higher activities than for $B(C_6F_5)_3$ were observed for propylene polymerization in the presence of *rac*-[1-(9-η^5-fluorenyl)-2-(5,6-cyclopenta-2-methyl-1-η^5-indenyl)ethane]zirconocene dichloride. The enhanced activities were attributed to the particular macromolecular structure of the hyperbranched polymer leading to a reduced catalyst mobility that enhances the concentration of the active species. The microstructure of the resulting polypropylene was similar to that obtained through solution phase catalysis with $B(C_6F_5)_3$ under comparable conditions.

The bis(pentafluorophenyl)boryl-substituted polymer (**13**) represents an example of a linear high molecular weight fluorinated arylborane polymer. Crotonaldehyde binding studies indicated that polymer (**13**) exhibits slightly lower Lewis acidity than the perfluorinated borane $B(C_6F_5)_3$. The latter is attributed to the fact that the polystyrene backbone in this polymer, and thus the third aryl substituents on each boron center consists of protonated phenyl rings rather than electron withdrawing C_6F_5 groups.

2.2.2. *Optical sensor materials*

The selective interaction of nucleophiles with the Lewis acid centers of organoboron polymers can be exploited in molecular recognition. Organoboron luminescent sensors rely on the modification of the electronic structure of organoboron π-systems as a result of changes in the coordination geometry from tri-coordinate to tetra-coordinate boron [5,50]. This principle has been extensively applied in highly efficient molecular sensor materials [5]; a wide range of main chain boron polymers that are highly luminescent has been reported by Chujo and co-workers and are further discussed in Section 4 of this review [51–55]. However, luminescent side-group functionalized polymers are comparatively rare [56], and little is known about organoboron polymers of this type in sensor applications. We have prepared luminescent triarylborane polymers (Ar = aromatic group with extended delocalization), in which the luminescent properties result from overlap between an extended aromatic system and the empty p-orbital on boron.

The synthesis of polystyrene-based polymers (**25**) gives access to materials that are strongly luminescent (Scheme 7). The bulky mesityl groups provide steric protection and thus lead to enhanced stability, whereas overlap of the boron p-orbital with the π-system of the bithiophene derivatives leads to strong luminescence. Thus, polymer (**25a**) exhibits blue luminescence with an emission maximum at $\lambda_{em} = 461$ nm upon excitation at

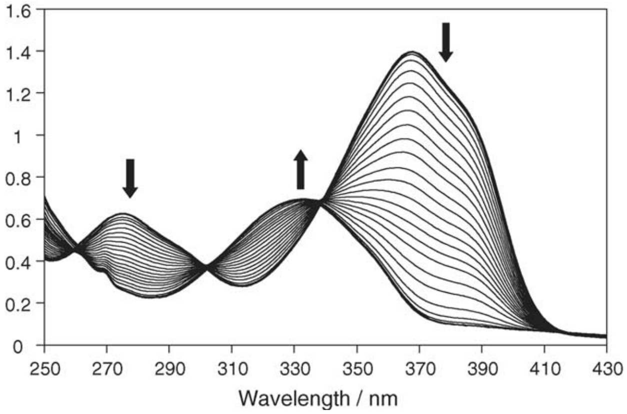


Fig. 5. Fluoride binding to polymer (**25a**) monitored by UV–vis spectroscopy.

the absorption maximum of λ = 368 nm, while **25b** emits green light (Scheme 7) [39]. Very high quantum efficiencies (ϕ_F) of up to 66% are realized for these polymers, similar to those of the respective molecular organoboron species.

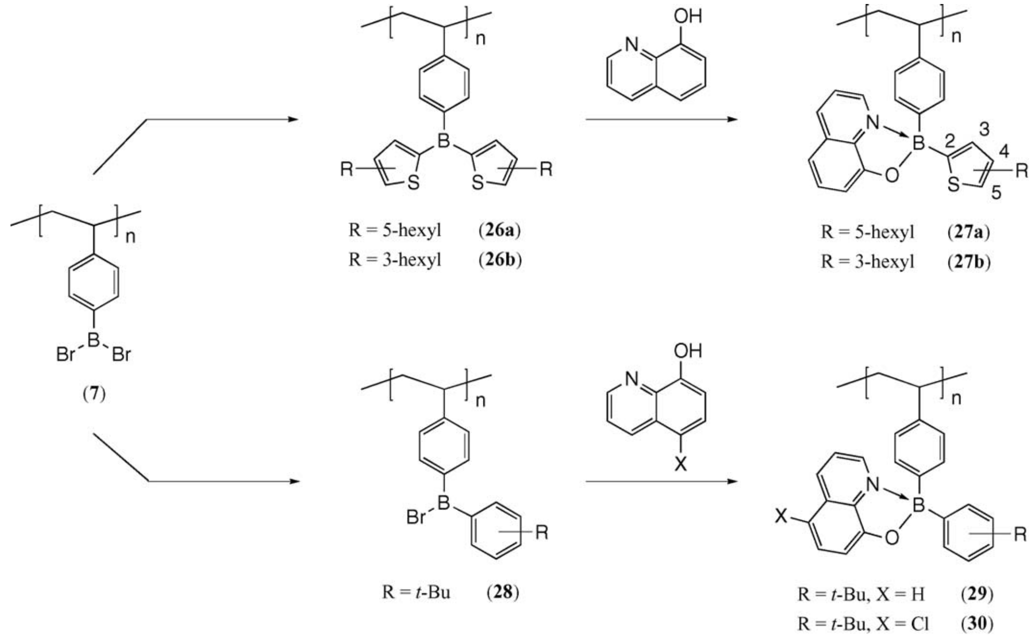
Coordination of nucleophiles to the pendent triorganoborane moieties leads to a high-energy shift of the absorption maximum and at the same time results in a decrease in the emission intensity and a shift in the emission wavelength. The binding process can thus readily be verified via spectroscopic screening. Tight binding of fluoride is evident from the large binding constants (e.g. for **25a**: $1.0 \times 10^6\ M^{-1}$) that were derived from UV–vis titration studies (Fig. 5).

2.2.3. *Luminescent organoboron chelates*

Tetra-coordinate complexes of boron have been extensively studied as new candidates for luminescent device materials [57]. For instance, the molecular organoboron species Ar_2BX (Ar = phenyl, naphthyl; X = 8-hydroxyquinolato) have been shown by Wang et al. to possess potentially useful properties as electron-conduction and light emitting components in electroluminescent devices [58,59]. The introduction of polymeric materials in this area is expected to be advantageous due to the improved processability, which would facilitate device fabrication [60].

We have prepared polymeric organoboron quinolates (**27**) via alcoholysis of one of the thiophene substituents in **26** with 8-hydroxyquinoline (Scheme 8) [47]. This transformation was found to occur with very high selectivity at the thienyl-boron rather than the phenyl-boron bond as confirmed by studies on molecular model compounds. In an alternative route, **7** was reacted in situ with 1-trimethylstannyl-4-*t*-butylbenzene at low temperature to give the mixed-substituted polymer (**28**) (Scheme 8) [61]. The latter was transformed into **29** by treatment with 8-hydroxyquinoline in the presence of an excess of triethylamine. The products were isolated by repeated precipitation into methanol and dried under high vacuum. The organoboron quinolate polymers are highly soluble in common organic solvents and show good stability in the presence of air and moisture.

The chemical composition and purity were confirmed by ^1H and ^{13}C NMR spectroscopy and elemental analysis, which indicated greater than 95% coverage with organoboron quinolate moieties. A strong upfield shift of the ^{11}B NMR signal to ca. 7 ppm confirmed the presence of tetra-coordinated boron centers (for typical triarylboranes ca. 50–70 ppm). A comparison of the light scattering data derived from in-line GPC-LS measurement of **27** and **29** with the silylated precursor polymer (**6**) showed that the average number of polymer repeat units (DP) for the quinolate polymers was essentially identical to that of the starting polymer and the polydispersities (PDIs) remained narrow.



Scheme 8. Preparation of luminescent organoboron quinolate polymers.

Table 1
Selected data of organoboron quinolate polymers

Polymer	M_W	PDI	λ_{max}(abs)	λ_{max}(em)	ϕ_F
27a	62000	1.04	392	508	0.12
27b	64000	1.06	394	509	0.14
29	127100	1.03	394	510	0.17
30	122000	1.03	409	527	0.08

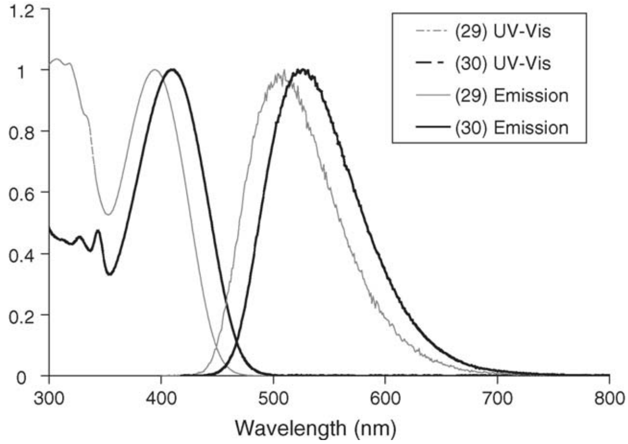


Fig. 6. Absorption and emission spectra of **29** and **30**.

Solution processing of **27** and **29** through spin coating gave smooth thin films that efficiently emit green light upon photoexcitation at the absorption maxima. Intriguingly, the emission characteristics were readily fine-tuned through the substitution pattern on the hydroxyquinoline ligand (Table 1). Polymer **29** shows an absorption maximum at 394 nm and emits at 510 nm in THF solution (Fig. 6), which is comparable with the thienyl substituted boron quinolate polymers (for **27a**: $\lambda_{abs} = 392$ nm, $\lambda_{em} = 508$ nm) and also with the molecular compound Ph_2BQ (solid state: $\lambda_{em} = 495$ nm) [58]. However, the respective chloroquinolate polymer (**30**) experiences a significant red-shift of about 16 nm in both the absorption and emission spectra ($\lambda_{abs} = 409$ nm, $\lambda_{em} = 527$ nm). These observations suggest that the nature of the boron-bound aryl group has a limited impact on the luminescence properties, but substitution on the quinolate ligand results in a very pronounced effect.

3. Side-chain functionalized conjugated organoboron polymers

The functionalization of conjugated organic polymers with Lewis acidic boron groups is intriguing since it may provide an opportunity to tune the photophysical and electrical properties of the conjugated polymer chain through binding of Lewis bases to the boryl groups. This approach can be applied to sensor applications for biologically important diol species such as glucose and dopamine, where the equilibrium between tri- and tetra-coordinate boron, and thus the optical and electrical properties of the conjugated polymer chain depend on the extent of binding of the reagent under investigation.

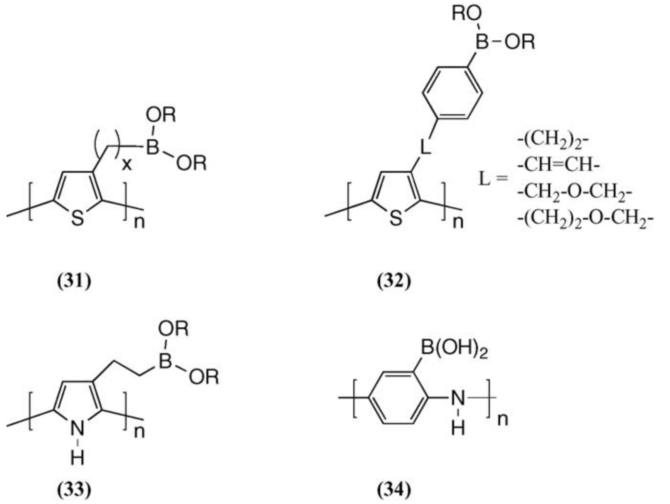


Fig. 7. Side chain organoboron-functionalized conjugated polymers (OR = OH, pinacol; $x = 0, 2, 3$).

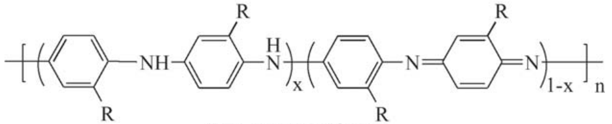
3.1. Synthetic methods and characterization

3.1.1. Electrochemical polymerisation

The research groups of Fabre et al. and Freund et al. have extensively studied the electropolymerization of boron-functionalized thiophene, pyrrole, and aniline derivatives in an effort at developing boronate-functionalized conjugated polymers (**31**–**34**, Fig. 7) [62–64]. For example, a redox-active film of polypyrrole (**33**) was electrodeposited onto a platinum electrode from acetonitrile solution [65,66]. Similarly, electrochemical polymerization of 3-anilineboronic acid in aqueous medium was used to produce thin films of poly(aniline boronic acid) (**34**) on electrodes [62,67]. The presence of fluoride ions was found to be necessary for effective electrochemical polymerization, an aspect that was attributed to the binding of fluoride to boron [62]. The latter was confirmed by a distinct upfield shift in the ^{11}B NMR spectrum of the respective monomer in acidic aqueous solution upon addition of KF. Use of high fluoride concentrations was found to lead to better stability, better adhesion properties, and increased sensitivity of the polymer-coated electrodes. Nafion is also commonly added as a polyanion that is beneficial in electrochemical polymerisations [67,68].

3.1.2. Chemical polymerisation

It has first been shown by Wolfbeis that aniline boronic acid may be copolymerized with aniline through chemical oxidation with ammonium persulfate in acidic aqueous solution leading to deposition of the respective copolymer film (**35**) [69]. More recently, Freund and co-workers found that oxidative polymerization of the fructose complex of anilineboronic acid with ammonium persulfate in the presence of fluoride leads to a self-doped water-soluble poly(aniline boronic acid). The latter could be isolated simply by reducing the fluoride concentration, which resulted in precipitation of **34** [70].



(**35**) R = H, B(OH)$_2$

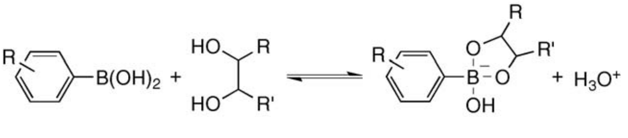
3.2. Complexation and electrochemical sensors

The complexation of boronate functionalized conjugated polymers with diols leads to a change in the coordination state of boron as illustrated in Scheme 9. This process can be monitored spectroscopically. Wolfbeis et al. reported near IR absorption studies on films of the copolymer (**35**; R = H, B(OH)$_2$), which consists of benzenoid diamine and quinone diimine groups, in the presence of various saccharides at pH 7.2. Spectral changes were most pronounced upon exposure to sorbitol and fructose. Moreover, the process was found to be reversible, though the response was relatively slow. The observations were tentatively attributed to changes in polaron delocalization and the interpolymer interactions upon saccharide binding. Reversible binding of fructose to poly(aniline boronic acid) (**34**) in the physiological range was confirmed by Freund and co-workers who found that the dihedral angle O–C–C–O of the diol moieties critically influences the binding constants and thus the selectivity [68]. Intriguingly, reversible binding of fructose to chemically polymerized **34** allowed for reversible switching between self-doped emeraldine salt form and the emeraldine base form of polyaniline [70].

Various other complexes of **34** with diols, salicylamide, and NADH have been studied [71,72]. Moreover, the formation of interchain complexes of chemically polymerized poly(aniline boronic acid) was observed in the presence of fluoride, and the resulting material was found to exhibit unprecedented hardness and thermal stability [13].

The use of **34** as conductimetric sensor for dopamine has been demonstrated by Fabre and Taillebois [73]. Moreover, an ultrasensitive composite material, prepared from polymerization of aniline boronic acid in the presence of carbon nanotubes coated with single-stranded DNA, has recently been studied by He and co-workers [74]. Upon modification of a gold electrode with this composite material, dopamine concentrations as low as 1 nM could be detected electrochemically at pH 7.4.

Finally, the boronate-functionalized polypyrrole (**33**) has been studied as a fluoride sensing material by Fabre and co-workers [65,66]. The electrochemical response was strongly modified in the presence of fluoride, whereas chloride or bromide had no effect.



Scheme 9. Binding of diols to boronic acids.

4. Main-chain functionalized organoboron polymers

Main chain functionalization of organic polymers with boron sites has been very thoroughly studied by Chujo [75]. A variety of routes to non-conjugated alkylborane polymers and π-conjugated vinyl, alkynyl and arylborane polymers have been developed. The latter have attracted much attention due to their interesting electronic and optical properties [4].

A diverse range of main chain organoboron polymers containing boron centers that are coordinated with amines through donor–acceptor bonding within the polymer main chains have also been reported by Chujo [76–85]. Moreover, the assembly of ferrocene polymers through donor–acceptor interactions has been investigated by Wagner and co-workers, who have demonstrated that diborylated ferrocenes reversibly form one-dimensional coordination polymers in the presence of aromatic diamines such as 4,4′-bipyridine [9,86–91]. However, the focus here will be on main chain organoboron polymers containing Lewis acidic tri-coordinate boron centers that are available for binding of external nucleophiles.

4.1. Synthetic methods and characterization

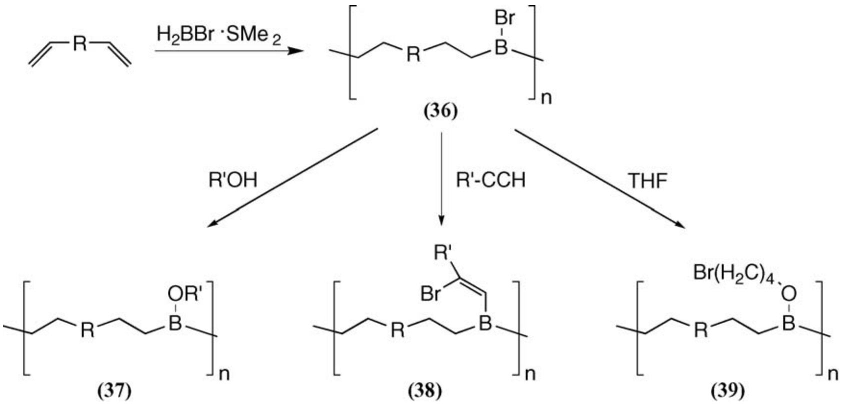
Hydroboration, haloboration and phenylboration polymerization techniques, first introduced by Chujo, have become the most versatile synthetic methods for the incorporation of tri-coordinate boron into the main chain of polymers [75]. Organometallic condensation reactions with Grignard reagents [53], organolithium species [52], and organotin precursors [11] are also very attractive, especially for the preparation of highly Lewis acidic conjugated organoboron polymers.

4.1.1. Non-conjugated polymers

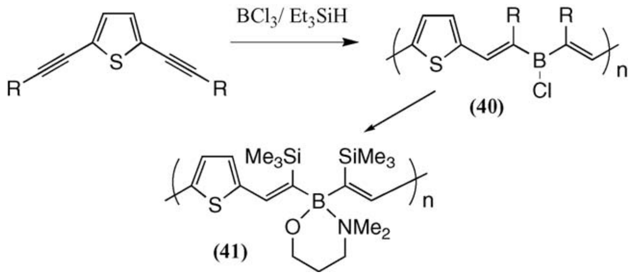
A series of alkylborane polymers (**36–39**) were prepared by Chujo et al. through hydroboration polymerization of dienes (Scheme 10) [92]. Interestingly, the reactive B–Br functionality in **36** has been successfully used for further polymer modification by reaction with alcohols, ethers or alkynes. Complexation of **36** with 1-methylimidazole has been performed by Matsumi et al. in order to generate new polymeric lithium ion conduction materials [93,94]. Other boranes, such as thexylborane have also been applied to hydroboration polymerization, and the resulting organoboron polymers have subsequently been further modified by treatment with carbon monoxide [95]. Highly stable derivatives have recently become available through polymerization of 1,7-octadiene and 1,9-decadiene, respectively, with tripylborane (TripBH$_2$) [96]. Related polymers are accessible also through hydroboration and haloboration polymerization of dialkynes [97–99].

4.1.2. Conjugated polymers

Interest in the incorporation of boron into the main chain of conjugated organic polymers is based on the expectation that extended delocalization may be observed in a polymer consisting of electron-deficient boron centers alternating with an organic π-system. Corriu et al. reported the formation of conjugated main chain organoboron polymers through hydroboration of

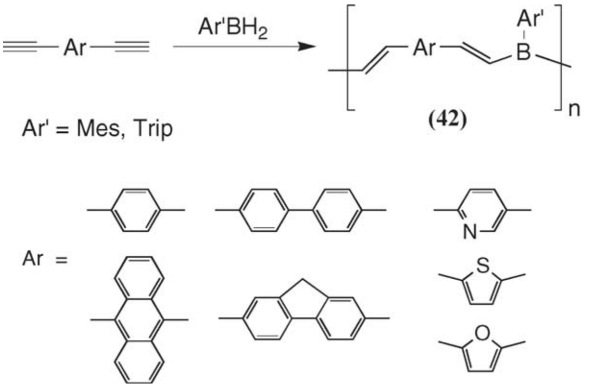


Scheme 10. Synthesis of alkylborane polymers via hydroboration polymerization of dienes; R = $-(CH_2)_2-$, $-(CH_2)_4-$, $-(CH_2)_6-$, $-CH_2C_6H_4CH_2-$, $-CH_2SiMe_2CH_2-$; R′ = Ph, *n*-Bu.



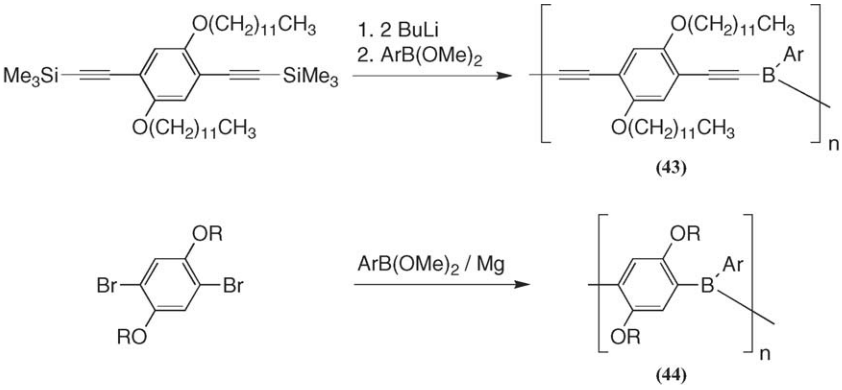
Scheme 11. Thienylenevinyleneborane polymers (R = $SiMe_3$, Ph, *t*-Bu).

2,5-diethynylthiophene derivatives with different borane sources (Scheme 11) [100]. Interestingly, differently colored polymers were obtained depending on the substituents on the alkynyl groups and the boron center itself. However, quantification of the photophysical properties and molecular weight determinations were hampered by the high sensitivity to moisture and oxygen. The chloro substituents in **40** were used for the formation of electronically stabilized boron chelates (**41**) with 3-dimethylaminopropan-1-ol.

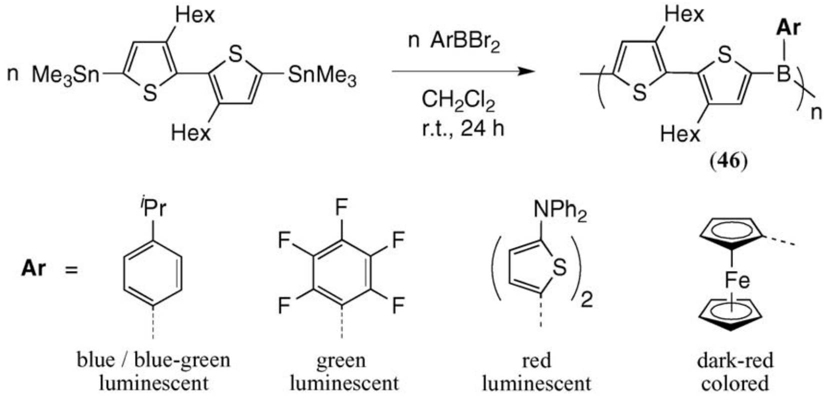


Scheme 12. Synthesis of sterically stabilized conjugated organoboron polymers via hydroboration polymerization.

Chujo and co-workers took advantage of the hydroboration of bifunctional alkynes with sterically hindered arylboranes $ArBH_2$ (Ar = Mes, Trip) for the synthesis of more stable conjugated organoboron polymers (**42**), which are structurally related to poly-*p*-phenylene vinylene (PPV) (Scheme 12) [101,102]. The bulky aryl groups on boron prevent attack of nucleophiles on boron and thus impart good environmental stability. The polymers are highly luminescent with especially large Stokes shifts for the heteroaromatic polymers containing pyridine and thiophene units in the main chain. Intriguingly, white emission was observed for the polymer derived from diethynylpyridine [102]. The latter likely can be attributed to different regiochemistry in the hydroboration of the alkynylpyridine moiety, thus leading to a more complex polymer structure. Indeed, Marder et al. recently reported that even attack at the pyridine ring may occur in the hydroboration of alkynylpyridines [103]. Unusually large third-order nonlinear optical susceptibilities were also reported for these polymers. Moreover, recent electrical conductivity measurements on a derivative of **42** consisting of fluorenylene



Scheme 13. Organometallic routes to conjugated organoboron polymers (Ar = Mes, Trip).

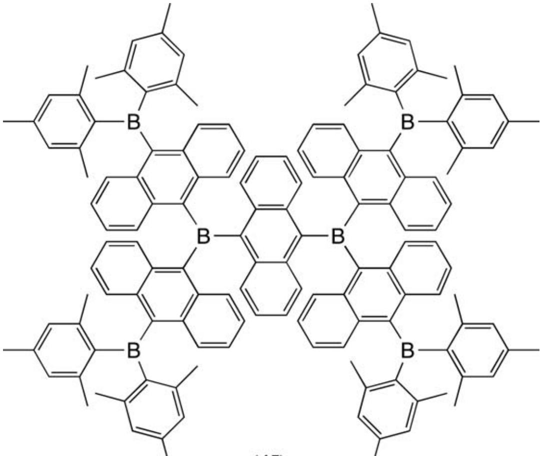


Scheme 14. Synthesis of boron-modified polythiophenes via tin–boron exchange.

bridges and tripyl substituents on boron showed an increase in conductivity from less than 10^{-10} to ca. 10^{-6} S cm^{-1} upon doping with triethylamine [104,105]. Pulsed photoexcitation experiments with an ITO-polymer–Au cell confirmed the n-type conductivity.

Many other vinyl, alkynyl, and arylborane polymers, all of which show strong fluorescence, have been synthesized by Chujo and co-workers. For example, the polycondensation of lithiated diacetylenes with aryldimethoxyboranes was used to produce blue luminescent poly(ethynylene-phenylene-ethynylene-borane)s (**43**) (Scheme 13) [106]. The fluorescent poly(*p*-phenyleneborane)s (**44**) were obtained via polycondensation of aryldimethoxyboranes with a difunctional Grignard reagent that was generated in situ (Scheme 13) [53]. The phenyleneborane polymers show absorption maxima in the range of 359–367 nm in $CHCl_3$ solution and emit blue-green light upon excitation at 350 nm.

In this context it is also interesting to note that a series of multifunctional anthrylboranes with up to six boron centers and divergently extended π-conjugation have been reported by Yamaguchi et al. [107]. The dendrimer (**45**) shows a dark red color, which is different from the bright orange color of trianthrylborane itself. The bathochromic shift was attributed to extended delocalization in this starbust oligomer. Two reversible reduction waves were found for the two different boron environments in **45**, and different binding constants were determined for the successive binding of fluoride to **45**.



(45)

We have prepared main chain polymeric Lewis acids (**46**) that contain Lewis acidic boron groups embedded into a polythiophene backbone [11]. These organoboron polymers are formed under mild conditions through tin–boron exchange reactions (Scheme 14). The polymers exhibit an intriguing variety of different photophysical properties depending on the nature of the aryl substituent on boron. Thus, with phenyl groups on boron blue (thin film) to blue–green (solution) luminescence is observed, the attachment of electron-withdrawing C_6F_5 substituents leads to bright green emission, and the aminobithiophene moieties result in orange-red luminescence, which is attributed to charge transfer in this donor–π-acceptor type structure.

Polymers (**46**) were determined to be predominantly linear in nature [108]. The latter is evident from ^{1}H NMR end-group analysis and was further confirmed by MALDI-TOF-TOF measurements. The mass spectra showed peak patterns that correlate very well with those calculated for linear polymers with $-Th_2B(Ar)-$ repeating units and bithiophene end groups (Fig. 8). The molecular weight and dispersity of polymers (**46**) were also estimated by GPC relative to PS standards which gave molecular weights ranging from $M_n = 5000$–9000 and dispersities of ca. PDI = 1.2–1.5.

4.1.3. Transition metal-containing organoboron polymers

Several examples of conjugated organoboron polymers that contain transition metals in the main chain alternating with electron deficient boron centers have been reported (Fig. 9) [55,109].

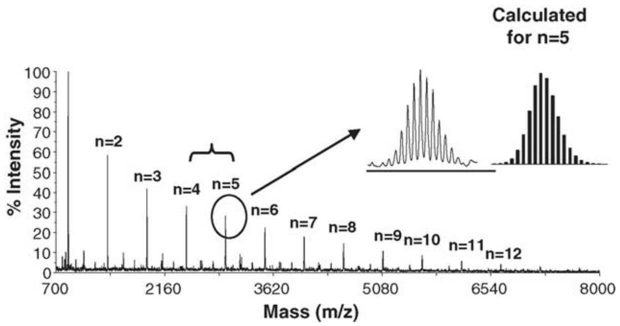
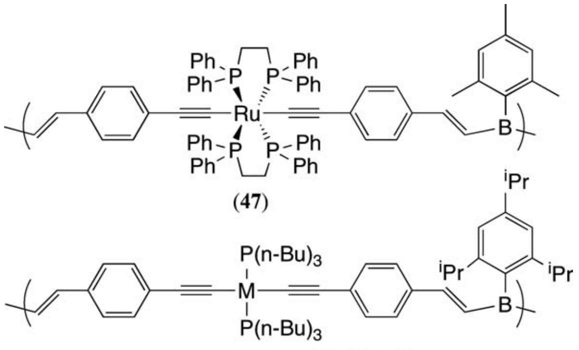


Fig. 8. MALDI-TOF-TOF spectrum of **46** (Ar = ferrocenyl; reflectron positive ion mode with benzo[*a*]pyrene as the matrix).



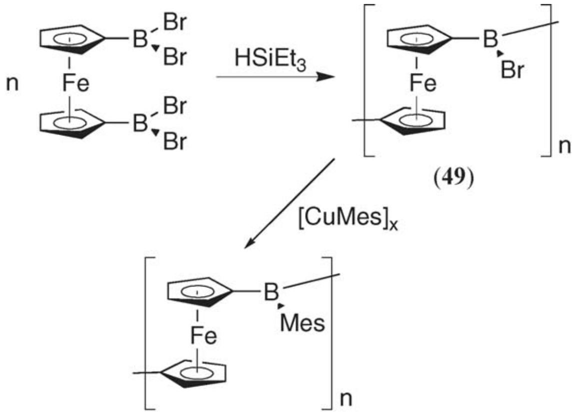
(47)

(48) M = Pd, Pt

Fig. 9. Transition metal containing organoboron polymers.

Such an arrangement is particularly interesting with regard to possible extended d_π–p_π conjugation. Indeed, incorporation of Ru alkynyl complex into the organoboron polymer backbone in **47** was reported to lead to an unusually strong bathochromic shift of 141 nm relative to the respective molecular ruthenium complex [109]. While the related Pd and Pt polymers (**48**) did not show similar red-shifted MLCT bands, those polymers were found to exhibit bright green luminescence upon excitation at 390 nm [55].

The synthesis of ferrocenylborane polymers has first been attempted by Manners and Braunschweig through ring-opening polymerization of strained ferrocenophanes [110,111]. However, the solubility of the resulting polymers was moderate, and the soluble fraction consisted primarily of low molecular weight oligomers ($n = 2$, 3). An interesting new synthetic route to ferrocenylene bridged organoboron polymers containing electron-deficient tri-coordinate boron centers has recently been discovered by Wagner et al. (Scheme 15) [112]. In a highly unusual rearrangement reaction, a reactive bromine-substituted ferrocenylborane polymer (**49**) was prepared, which in turn was readily transformed into other ferrocenylborane polymers through treatment with nucleophiles. For instance, conversion with mesityl copper led to a dark red colored material that showed an average degree of polymerization of DP = 16 according to multi angle laser light scattering studies (MALLS). MALDI-TOF-TOF measurements further confirmed the structure of polymer (**50**) and indicated the presence of both ferrocenyl and Mes_2B end groups (Mes = 2,4,6-trimethylphenyl). The iron centers in **50** are strongly interacting through the tri-coordinate boron spacers as indicated by cyclic voltammetry measurements.



(49)

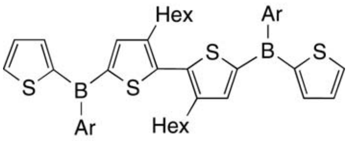
(50)

Scheme 15. Synthesis of poly(ferrocenyleneborane)s.

4.2. Complexation and optical sensors

As a result of the extended π-conjugation through the vacant p-orbital on boron, main chain organoboron polymers are promising candidates as optical sensor materials [50,113,114]. Particularly appealing is the strong potential for sensor signal amplification upon binding of an analyte to a suitable receptor within the conjugated polymer [115]. Early work by the Kaim group on the electrochemical properties of 1,4-bis(dimesitylboryl)benzene and 1,4′-bis(dimesitylboryl)biphenyl provides clear evidence for electronic communication between boron centers through a π-conjugated organic spacer moiety [116]. Two well-separated redox waves are apparent in the cyclic voltammograms. More recent studies by Shirota et al. on the respective diborylated bithiophene and terthiophene derivatives indicate a similar behavior, and those compounds have proven useful as electron conduction layers in organic light emitting devices (OLEDs) [117,118]. In order to address the question whether cooperative effects play a role in the binding of nucleophiles to such multifunctional organoboranes, we have prepared the bifunctional conjugated organoboranes (**51**) (Fig. 10). These compounds serve as model compounds that represent a fragment of the respective conjugated organoboron polymers (**46**) containing alternating bithiophene and borane moieties in the backbone. NMR spectroscopic and UV–vis titration studies clearly indicate that the individual boron centers indeed interact with each other [11]. Thus, refinement of UV–vis titration data for **51** (Ar = *i*PrPh) with pyridine for two independent consecutive binding events using the Hyperquad^{TM} program suite was successful, and the consecutive binding constants were determined to be $\lg K_{11} = 6.42 \pm 0.08$ and $\lg K_{12} = 5.57 \pm 0.08$. The result of $K_{11} = 7.0K_{12}$ indicates moderate negative cooperativity (non-cooperative system: $K_{11} = 4K_{12}$).

With regard to polymeric Lewis acids, Chujo and co-worker have studied the effect of fluoride binding to the conjugated polymers (**42**) (Ar = Mes, Trip), which were obtained through hydroboration of *p*-diethynylbenzene with $MesBH_2$ and $TripBH_2$, respectively [10]. An exciting observation was that a strong decrease in intensity and a concomitant blue shift of the absorption band at 377 nm was apparent upon addition of a fluoride source. A dramatic drop in the fluorescence intensity was



(51)

Fig. 10. Diborylated bithiophenes (Ar = *i*-PrPh, C_6F_5, Fc).

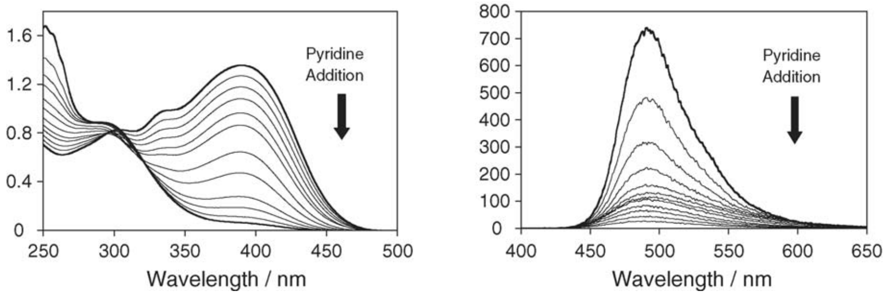


Fig. 11. Pyridine binding to boron modified polythiophene (**46**) (Ar = *i*-PrPh). UV–vis absorption spectra are shown on the left side and the corresponding fluorescence spectra on the right side.

evident upon addition of 0.5 molar equivalents of fluoride at a concentration of 10^{-6} M in $CHCl_3$. The latter indicates significant signal amplification. Moreover, high selectivity for fluoride over other halides was confirmed.

We investigated the binding of neutral nucleophiles such as pyridine to the boron-modified polythiophenes (**46**). The incorporation of readily accessible, highly Lewis acidic groups into the conjugated polymer backbone provides an opportunity for sensing of neutral Lewis basic substrates such as pyridine. We found that treatment of the thienylborane polymers (**46**) with pyridine donors results in efficient quenching of the fluorescence (Fig. 11). At low pyridine concentration, the quenching efficiency for the polymer (**46**) was enhanced by a factor of ca. 12 relative to the respective diborylated model compound (**51**). Such polymers are thus promising materials for the efficient sensing of a variety of nucleophiles.

5. Conclusions

A diverse array of new synthetic routes for the incorporation of Lewis acidic boron centers into polymer structures has recently become available. New techniques have been developed for the selective preparation of conjugated polymers that either contain boron centers in the main chain or are functionalized with pendent organoboron substituents. And the advent of living radical polymerization techniques now also provides facile access to well-defined block copolymer architectures, which hold much promise for future exploration.

The enormous variety of potential applications of organoborane polymeric Lewis acids is only beginning to be fully explored. Among the most intriguing aspects are certainly the unusual electronic properties, which pave the way for new uses in optical, electronic, and optoelectronic devices. However, more traditional areas such as Lewis acid catalysis with organoboranes still hold considerable promise, and new polymeric catalyst systems that are highly active and easy to recover are likely to emerge in the near future.

Acknowledgements

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