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Polymers and the p-block elements

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REVIEW

Polymers and the p-block elements[‡]

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A survey of the state-of-the-art in the development of synthetic methods to incorporate p-block elements into polymers is given. The incorporation of main group elements (groups 13-16) into long chains provides access to materials with fascinating chemical and physical properties imparted by the presence inorganic groups. Perhaps the greatest impedence to the widespread academic and commercial use of p-block element-containing macromolecules is the synthetic challenge associated with linking inorganic elements into long chains. In recent years, creative methodologies have been developed to incorporate heteroatoms into polymeric structures, with perhaps the greatest advances occurring with hybrid organic-inorganic polymers composed of boron, silicon, phosphorus and sulfur. With these developments, materials are being realized that posess exciting chemical, photophysical and thermal properties that are not possible for conventional organic polymers. This review focuses on highlighting the most significant recent advances whilst giving an appropriate background for the general reader. Of particular focus will be advances made over the last two decades, with emphasis on the novel synthetic methodologies employed.

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1 Introduction

Perhaps the greatest impact of 20th century synthetic chemistry is the sudden ubiquity of polymeric materials in our daily lives. It is difficult to imagine modern society without synthetic textiles, electronics, disposable packaging, and structural materials. The pervasiveness of plastics, rubbers and fibres is all the more impressive considering that the vast majority of these products are made primarily from organic polymers (composed almost entirely of carbon). Given the great breadth of properties and applications of long chains composed solely of combinations of carbon, nitrogen and oxygen, the potential for polymers including other p-block elements is inconceivable. The inclusion of inorganic elements into linear macromolecules opens the door to materials with unique physical and chemical properties that are not attainable with purely carbon-based systems.

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Despite these exciting prospects, the field of inorganic polymer chemistry remains at a much more primitive stage of development. Until late in the last millennium, the field was dominated by three classes of macromolecules: polysiloxanes (**A**), polyphosphazenes (**B**), and polysilanes (**C**, Fig. 1). Research on these commercially relevant polymers remains a hotbed of activity due to their unique properties such as excellent thermo-oxidative stability and high flexibility at low temperatures. Recently, poly(ferrocenylsilane)s (**D**) have emerged as a fourth major class of inorganic polymer.
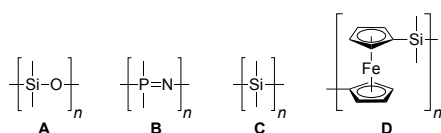
Fig. 1 Four main classes of macromolecules composed of p-block-elements in the main chain.

The relative dearth of p-block polymers can, in part, be attributed to an absence of sophisticated methods available to link inorganic functionalities into long chains. In contrast, the preparation of carbon-based polymers is aided by the maturity of synthetic organic chemistry. Thus, the major challenge facing researchers in the area of p-block element-containing macromolecules is the development of general synthetic methods to link inorganic elements together. Although recent growth in polymers composed purely of inorganic backbones is modest, an explosion of growth in the field of inorganic-organic hybrid polymers is currently underway.

The basic strategies to incorporate inorganic elements (E or A) into polymers are the same as those used to prepare organic polymers (Fig. 2). Chain growth methods offer the advantage of giving high molecular weights even at low monomer conversion, however, they require either (i) unsaturated monomers for addition polymerization or (ii) rings for ring-opening polymerization (ROP). For purely inorganic systems, multiply bonded species are often difficult to obtain and require large, polymerization inhibiting, substituents. Likewise, suitably strained inorganic ring compounds are often inaccessible. Step growth methods suffer from the need for high purity monomers in strict stoichiometric ratios to achieve high molecular weights. Meeting these requirements is particularly challenging for p-block monomers, which are often difficult to obtain in high purity due to their tendency to be air- and moisture-sensitive. Despite these limitations, catalytic methods such as dehydrogenative coupling have emerged for the preparation of polymers by routes (iii) and (vi). In addition, the use of organic spacers, as depicted by routes (iv) and (v), has grown in popularity due to the proliferation of catalytic organic coupling chemistry.
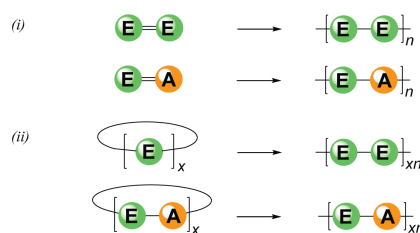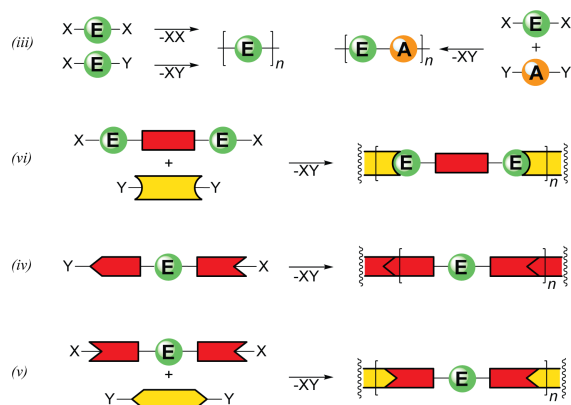
Fig. 2 Well-established synthetic methods used to prepare polymers as applied to generic p-block elements (E and A).

In this review, a survey of the rapidly growing field of p-block element-containing polymers will be detailed. Emphasis will be placed on advances in synthetic methodologies towards linear macromolecules containing main group elements within the main chain. Where possible, the exciting properties of these novel materials will be highlighted. Although the reader will be provided with a brief historical background and context, recent breakthroughs will be the main focus. For previous reviews and books in the general areas of inorganic, metal-containing and organometallic polymers, the reader is directed to the following references.[1]

2 Group 13 elements

Incorporating the triels into long chains poses a considerable synthetic challenge due to their metallic character and the additional complexity imparted by forming dative, ionic and covalently-bonded structures. As a consequence, the heavier elements of the group are often found in coordination polymers. Boron occupies a unique place in polymer chemistry due to its electron deficiency and its ability to function as a Lewis acid. Thus, boron-containing polymers exhibit fascinating properties, particularly in the areas of optoelectronics and sensors. The incorporation of organoboron moieties into polymers with π-conjugated frameworks is currently undergoing rapid growth. For more details, the reader is referred to these excellent recent reviews that focus on the synthesis and properties of boron-containing macromolecules.[2] By contrast, the development of covalent

macromolecules containing the heavier elements of group 13 is in its infancy.

2.1 Boron

2.11 Poly(borazylene)s and poly(cyclodiborazane)s

There has been a longstanding interest in inorganic boron-containing polymers such as the poly(borazylene)s (e.g. **1** and **2**, Fig. 3). These macromolecules are of particular importance as precursors to boron-nitride ceramics.[3, 4] In many instances, these materials consist of either short chain oligomers or highly cross-linked networks and, thus, are difficult to study using conventional polymer characterization techniques. Approaches involving linear macromolecules derived from vinyl borazine display increased solublilty and have also found application as ceramic precursors.[5]
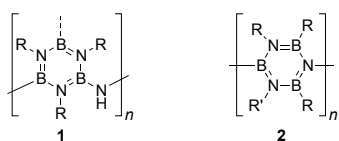

Fig. 3 Common structural forms of poly(borazylenes).

The hydroboration of bridged dicyano monomers with boranes provides an efficient route to poly(cyclodiborazane)s (**3**, Scheme 1), the first polymers with cyclic B_2N_2 rings in the polymer main chain.[6, 7] This methodology permits the incorporation of novel functionalities, such as disilanes (**3a**: M_n = 4 800 − 9 400 g mol^{-1}, PDI = 1.5 − 1.6)[8] or oligothiophene (**3b-e**: 1 800 − 4 200 g mol^{-1}, PDI = 1.4 − 2.8)[9] spacers. These polymers are of potential interest for their novel photophysical properties. In particular, bathochromic shifts are observed with increasing thiophene chain length (**3b**: λ_{max} = 387 nm; **3e**: 426 nm; R = Mes), each polymer exhibits fluorescence in solution (**3a**: λ_{em} = 434 nm, **3b-e**: 451 − 536 nm; R = Mes), and a film of **3b** showed yellow emission in the solid state.
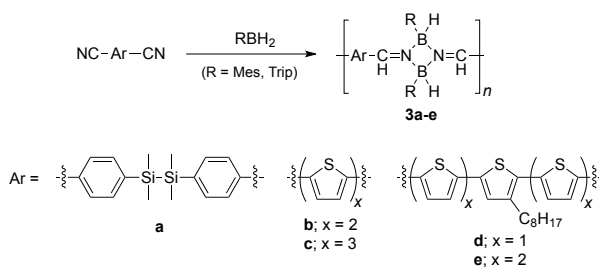

Scheme 1 Synthesis of poly(cyclodiborazane)s with disilane and oligothiophene spacers.

2.12 Polymers containing organoboron heterocycles

An attractive organoboron motif that can be incorporated into the macromolecular framework is the quinolate ligand. Both the boron-quinolate and the π-conjugated spacer are separate chromophores that independently account for the emissive properties of these materials. These exciting macromolecules are often highly fluorescent and the color

emitted is tunable by varying the nature of the substituent on the quinolate ring.

Originally, B-quinolate polymers were synthesized by Sonogashira cross-coupling of arylenediynes and bis(*p*-iodophenyl) organoboron quinolates (Scheme 2).[10] The isolated polymers **4a** (M_n = 3 200 g mol^{-1}, PDI = 1.7) and **4b** (M_n = 20 700 g mol^{-1}, PDI = 2.4) were strongly absorbing in the visible region (λ_{max} = 375 nm) and exhibited green-blue fluorescence (λ_{em} = 486-512 nm) in solution and solid state. The measured solution quantum yields (Φ) for **4a** and **4b** were 0.26 and 0.27, respectively.

4a; R = C_6H_{13}
4b; R = $C_{12}H_{25}$
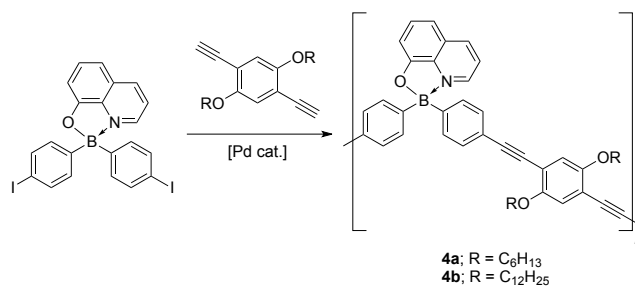
Scheme 2 Synthesis of organoboron quinolate polymers using Sonogashira cross-coupling.

This methodology has subsequently been expanded to include similar organoboron polymers containing quinolates,[11] benzo[*h*]quinolates,[12] aminoquinolates,[13, 14] quinolone thiolates,[15] quinolone selenates,[15] and 1,3-diketones.[16] Alternatively, a boron-induced ether cleavage of an arylmethoxide has been used to incorporate quinolate moieties into the backbone (Scheme 3).[17] In this example, polymerization occurs when bromoborane moieties cleave the methyl group of the bifunctional 8-methoxyquinoline, forming boron quinolate polymer **5** (M_n = 14 300 g mol^{-1}, PDI = 1.20). Another strategy to polymers of this type involves the post-polymerization formation of the boron quinolate moiety.[18, 19]


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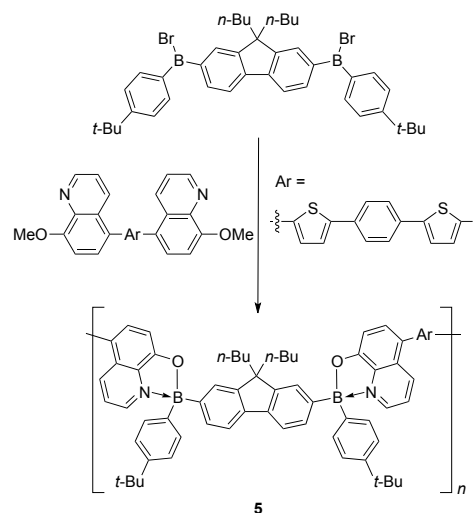
Scheme 3 Synthesis of an organoboron quinolate macromolecule using boron-induced ether cleavage.

One of the most common boron-containing motifs in conjugated polymers is the BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) system. This is because in both molecular and macromolecular chemistry, compounds containing BODIPY groups are typically highly emissive.[20] Polymers containing BODIPY have been prepared using Sonogashira cross-coupling.[21-26] Suzuki[27-31] and Stille[32] cross-coupling reactions have been used to make additional BODIPY polymers with aromatic spacers that are attractive for their potential photovoltaic applications. A BODIPY homopolymer, **6**, was synthetized by nickel(0)-mediated coupling of a dibromo-precursor (M_n = 2 630 g mol^{-1}, PDI = 1.59, Scheme 4).[32]
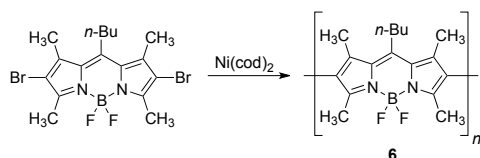

Scheme 4   Method for the preparation of a macromolecule with BODIPY functionalities in the main chain.

Similarly, pyrazabole-containing derivatives have been synthesized by Sonogashira coupling using aryl diynes and iodated pyrazaboles as comonomers.[33, 34] The resultant materials are fluorescent and possess excellent quantum yields ($\Phi \leq 0.67$).

A route to macromolecules containing cyclic 1,2-azaborines (i.e. 1,2-BNC$_4$R$_6$, a benzene analogue) in the main chain was recently reported using a Suzuki coupling of an azaborine A-B-type monomer (A = Br, B = Bpin).[35] Employing a palladium(II) catalyst in basic conditions provided the highest molecular weight (M_n = 3 150 g mol^{-1}, PDI = 1.3). The absorption spectrum of the poly(azaborine) (λ_{max} = 475 nm) was consistent with significant π-conjugation within the main chain.

2.13 Poly(aminoborane)s

Recently, boron-nitrogen compounds have received considerable attention due to their potential for hydrogen storage.[36, 37] Poly(aminoborane)s have been prepared from the catalytic dehydrocoupling of amine-boranes (Scheme 5). When employing a rhodium(I) or rhodium(III) precatalyst, the reaction is hindered by the formation of cyclic oligomers (R$_2$NBH$_2$)$_x$ (x = 2 or 3) or borazines ([RNBH]$_3$).[38, 39] In contrast, when N-methylamine-borane (MeNH$_2$·BH$_3$) was treated with an iridium(III) catalyst, soluble polymeric material **7** was obtained within minutes [**7** (R = Me): M_n = 55 200 g mol^{-1}, PDI = 2.9, Scheme 5].[40]
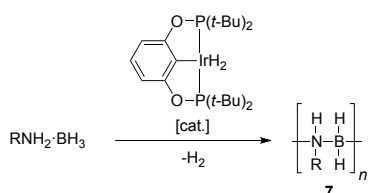
Scheme 5   Dehydrocoupling of amine-borane adducts using an iridium(III) catalyst to afford poly(aminoborane)s.

Mixtures of different amine-boranes and the aforementioned iridium(III) catalyst have given random aminoborane copolymers but substrate scope is limited to N-alkyl-substituted monomers.[40, 41] The use of unsubstituted [NH$_2$BH$_2$]$_n$ [**7** (R = H)] as a precursor to boron nitride ceramics through pyrolysis has been demonstrated (Fig. 4). The copolymerization of MeNH$_2$·BH$_3$ with NH$_3$·BH$_3$ has also been accomplished, however, the molecular weights of these materials were low (M_n = 12 000 − 14 000 g mol^{-1}) and PDIs were high (up to 11). Insight into the mechanism of catalytic dehydrocoupling of amine-boranes has been gained through both experimental[42-45] and theoretical[46, 47] studies. In a recent article, a metal-free polymerization of N-methylamine-borane was reported.[48] Stoichiometric addition of [H(OEt$_2$)$_2$][B(C$_6$F$_5$)$_4$] to MeNH$_2$BH$_3$ resulted in the formation of an amine-boronium cation which, upon the addition of excess base, forms the corresponding poly(aminoborane). Analysis of the reaction products by ESI-MS showed a degree of polymerization of up to 49 (ca. 2 100 g mol^{-1}).

Fig. 4   Pellet of poly(aminoborane) **7** (R = H) (a) after pyrolysis at 900 °C, (b) before pyrolysis. The Euro coin is shown for scale. Reproduced from Ref. 40 with permission of John Wiley and Sons.

2.14 Poly(phosphinoborane)s

The attempted synthesis of poly(phosphinoborane)s dates back to the mid-1950s with the thermal dehydrocoupling of phosphine-borane adducts at 200 °C. The first high molecular weight poly(phosphinoborane) (**8**: M_w = 33 300 g mol^{-1} determined by static light scattering, Scheme 6) was produced using the rhodium(I)-catalyzed dehydrocoupling of PhPH$_2$-BH$_3$.[49] The choice of monomer is critical as similar attempts to polymerize Ph$_2$PH-BH$_3$ using a rhodium(I) catalyst afforded only 6- and 8-membered phosphinoborane heterocycles. Subsequent to this initial breakthrough, the preparation and characterization of poly(phosphinoborane)s bearing a variety of substituents on phosphorus was reported (e.g. 4-BuC$_6$H$_4$, 4-DodecC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$, i-Bu).[50, 51] In each case, only monomers derived from primary boranes are capable of forming high molecular weight materials. Poly(phosphinoborane)s exhibit high thermal and oxidative stability.
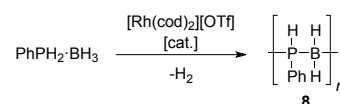
Scheme 6   Dehydrocoupling of phenylphosphine-borane adduct to make poly(phosphinoborane) using a rhodium(I) catalysis.

Recently, the dehydrocoupling of phosphine-borane adducts using an iron(II) catalyst was presented.[52] The molecular weights were dependent on the loading of FeCp(CO)$_2$OTf catalyst. Micropatterns of the resulting polymers were fabricated on silicon wafers by soft-lithography.

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The progress of the [Cp$_2$Ti]-catalyzed oligomerization of PH$_2$BH$_2$NMe$_3$, a BP analogue of ethylene, has been followed step-by-step at the metal center.[53] These results may serve as a model to future catalyst developments for dehydropolymerization.

The metal-free addition polymerization of phosphinoboranes stabilized by Lewis bases has just appeared.[54] This method provides a route to P-alkyl poly(phosphinoborane)s with reasonable molecular weight with low polydispersity (M_n = 27 800 – 35 000 g mol^{-1}, PDI = 1.6 - 1.9) under mild conditions. A head-to-tail microstructure is postulated.

2.15 Poly(arylene/vinylene/ethynylene borane)s

In a pioneering study, the synthesis of solution-processable organoboron polymers by the haloboration of terminal diynes with boron tribromide was described.[55] The resultant polymer featured divinyl bromoborane linkages with alkyl spacers (**9**: M_n = 5 200 g mol^{-1}, PDI = 3.27, Fig. 5). Although moisture-sensitive, the labile B-Br bonds presented an opportunity for further functionalization. Just a year later saturated polyalkyleneboranes (e.g. **10**: M_n = 19 000 g mol^{-1}, PDI = 1.46) were reported, synthesized by hydroboration of dienes with *t*-hexyl borane.[56] A later report described the synthesis of poly(thienyldivinylene borane)s (e.g. **11**: M_n = 2 700 g mol^{-1}) by hydroboration of 2,5-diethynylthiophene derivatives with a BCl$_3$/Et$_3$SiH mixture.[57]
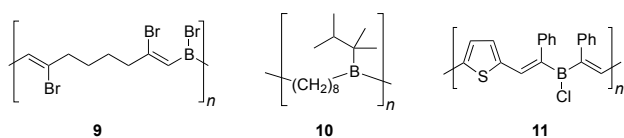

Fig. 5   Selected examples of the first poly(vinylene borane)s and poly(alkylene borane)s.

The difficulty in handling the aforementioned materials prevented detailed investigation of their properties. The introduction of steric bulk within poly(vinylene borane)s by employing Mes[58-60] or Trip[61, 62] substituents at boron vastly increased moisture stability in comparison to the previously used *t*-hexyl or halogen groups.

A route to poly(arylenevinylene borane)s (**12a-e**) using an intriguing haloboration-phenyl transformation in the polymerization step has been demonstrated by the reaction of aromatic diynes with Ph$_2$BBr (Scheme 7).[63] In this example, the borane acts as a difunctional monomer by adding both a bromo and a phenyl group across the dialkyne. A variety of polymers with different aryl spacers were prepared with distinctly different molecular weights (M_n) varying from 1 000 g mol^{-1} (**12c**) to 7 500 g mol^{-1} (**12e**). The PDIs varied from 2.3 to 4.3.
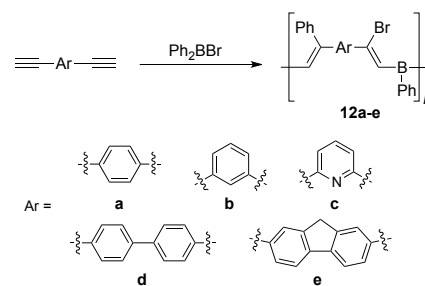

Scheme 7   The copolymerization of arylenediynes and bromodiphenylborane to afford poly(arylenevinylene borane)s.

Poly(*p*-phenylenediethynylene borane)s **13a** and **13b** have been prepared by the reaction of a dilithiated diethynylphenylene and aryldimethoxyboranes (Scheme 8).[64] gel permeation chromatography (GPC) of the air- and moisture-stable polymers revealed a modest molecular weight (**13a**: M_n = 2 700 g mol^{-1}, PDI = 1.3; **13b**: M_n = 2 000 g mol^{-1}, PDI = 1.1). Polymer **13b** absorbs at 397 nm, significantly bathochromically shifted compared to the trimethylsilylated dialkyne monomer (345 nm), suggesting significant π-conjugation through the boron atoms.
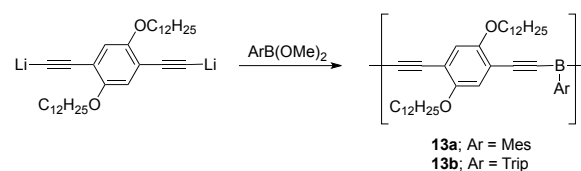
Scheme 8   Condensation polymerization of lithiated arylenediyne and arylboronate ester to afford poly(*p*-phenylenediethynylene borane)s.

A key contribution has appeared that describes the synthesis of air- and moisture-stable poly(*p*-phenylene borane)s **14** (Ar = Trip) by the reaction of TripB(OMe)$_2$ with various 1,4-dibromo-2,5-dialkoxybenzene derivatives in the presence of magnesium metal (Scheme 9).[65] The absorption maxima (350-360 nm) for the polymer show a bathochromic shift when compared to molecular models, consistent with π-conjugation through the boron atoms. Polymer **14** (Ar = Trip, R = *n*-Dodec) strongly emitted blue-green light (λ_{em} = 487 nm) upon irradiation at 350 nm. These exciting poly(*p*-phenylene borane)s were obtained in modest molecular weights and narrow polydispersity (M_n *ca.* 3 000 g mol^{-1}; PDI = 1.2). Other derivatives of **14** displayed similar photophysical properties, albeit with lower molecular weights and isolated yields.
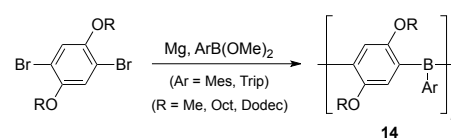
**Scheme 9**   Synthesis of poly(arylene borane)s by polycondensation of di-Grignard reagents and arylboronate esters.

Incorporating a fluorene moiety as the aryl linker increases the conjugation length, thereby giving access to macromolecules with desirable photophysical properties. Poly(fluorenylene borane)s have been synthesized by

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condensing 2,7-bis(trimethylstannyl)fluorene and 2,7-bis(dibromoboryl)fluorene (Scheme 10).[19] The resultant polymers contain labile B-Br bonds that are readily arylated using mild organocopper(I) reagents. This macromolecular substitution affords air- and moisture-stable materials (**15a** and **15b**: M_n = 8 800 − 10 400 g mol^{-1}, PDI = 1.61 − 1.68). Interestingly, these materials are strongly absorbing (λ_{max} = 390 nm) with the absorbance maximum being red-shifted compared to dihexylfluorene ($\Delta\lambda$ = 80 nm) and 2,7-bis(dimesitylboryl)-9,9-diethylfluorene ($\Delta\lambda$ = 20 nm). Both **15a** and **15b** fluoresce with strikingly high quantum yields (Φ = 0.81 and 0.84, respectively). These materials are attractive for "turn off" chemosensor applications showing a high sensitivity towards fluoride and cyanide but no response to chloride and bromide anions. A similar polymerization strategy has been used in the synthesis of poly(arylene borane)s (**16a**-**c**) featuring a 2,2'-bithiophene spacer (Scheme 10).[66] Polymers **16a** and **16c** have moderate quantum yields (Φ = 0.21 and 0.15, respectively) and show "turn off" emission upon the addition of pyridine whilst **16b** is non-emissive.
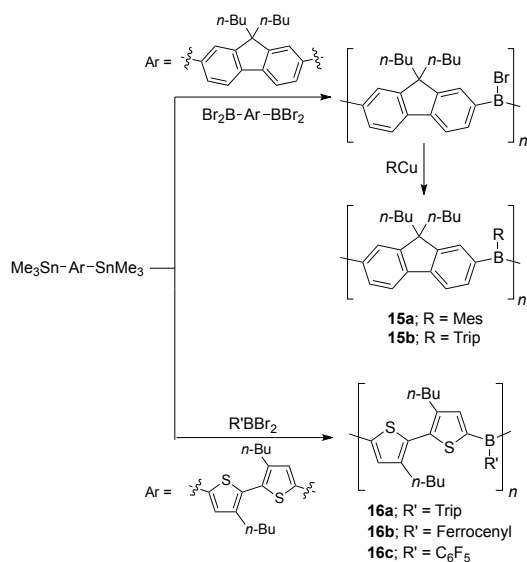
Scheme 10 Methods to prepare main chain π-conjugated organoboron polymers with fluorene and 2,2'-dithiophene spacers.

2.16 Poly(9,10-diboraanthracene)s

The incorporation of 9,10-diboraanthracene moieties into long chains ensures significant π–conjugation due to the rigidity of the diboraanthracene ring. The hydroboration polymerization of 9,10-dihydro-9,10-diboraanthracene with various 1,4-diethynylbenzene linkers affords polymers **17a** and **17b** with predominately *E*-configuration (Scheme 11).[67] The air-sensitive polymer **17b** exhibits multiple absorption maxima (λ_{max} = 410, 349, and 290 nm) and emits green light (λ_{em} = 518 nm) both in solution and in the solid state (Fig. 6).
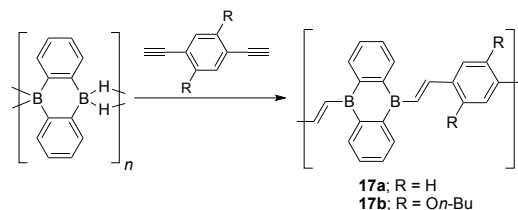
Scheme 11 Synthesis of poly(9,10-diboraanthracene)s by hydroboration polymerization.
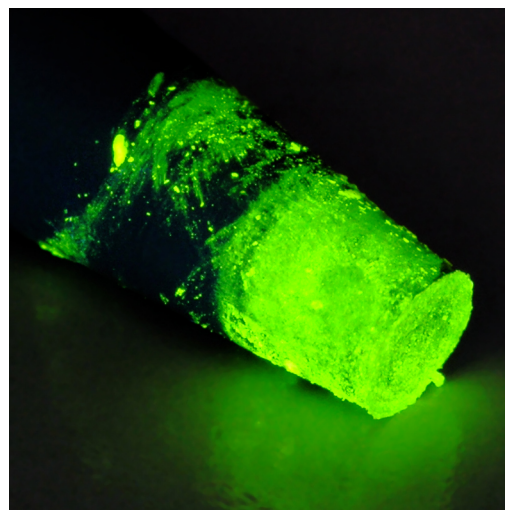
Fig. 6 Solid-state emission of **17b** in air with irradiation at 350 nm. Photograph provided courtesy of Profs. M. Wagner and F. Jäkle.

The polycondensation of 9,10-dibromo-9,10-diboraanthracene with 1,4-bis(tributylstannyl)benzene affords diboraanthracene macromolecule **18** (Scheme 12). Due to the poor air-stability of **18,** GPC data was not obtained. However, end group analysis using ^{1}H NMR spectroscopy permitted a degree of polymerization of ca. 24 to be estimated.[68] The Stille cross-coupling of 2,5-bis(trimethylstannyl)thiophene with a mixture of 2,6- and 2,7-dibromo-9,10-boraanthracene provides access to polymer **19**, an air- and moisture-stable material (M_n = 2 730 g mol^{-1}, PDI = 2.17).[69] In this example the diboraanthracene linkage is made through the carbon atoms of the aryl ring rather than boron.
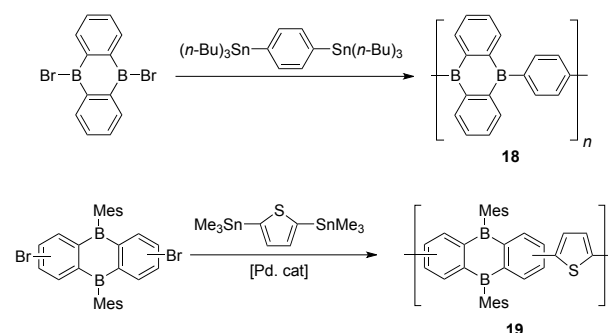
Scheme 12 Condensation polymerization routes to 9,10-diboraanthracene macromolecules.

2.17 Borole-containing macromolecules

Boroles incorporate boron atoms in a rigid π-conjugated framework and are attractive due to their intriguing electronic properties combined with their chemical functionality as Lewis acids.[70] Despite this fact, borole-containing macromolecules are exceedingly rare. The random borole-containing copolymer **20** was synthesized by a Yamamoto-type polycondensation of 2,7-dibromo-9,9-di-*n*-octylfluorene with a dibrominated 9-borafluorene species (9:1 ratio) (**20**: M_n = 22 900 g mol^{-1}, PDI = 1.78, Scheme 13).[71] Thin films of copolymer **20** were made by drop-casting from a dilute toluene solution. Solutions of **20** show luminescence quenching in the presence of certain anions (e.g. F$^-$, CN$^-$, I$^-$, H$_2$PO$_4^-$) but no response towards others (e.g. Br$^-$, Cl$^-$, BF$_4^-$, HSO$_4^-$, NO$_3^-$). It was postulated that the presence of a *para*-cyano group on the 9-phenyl substituent electronically stabilizes the polymer towards air oxidation.
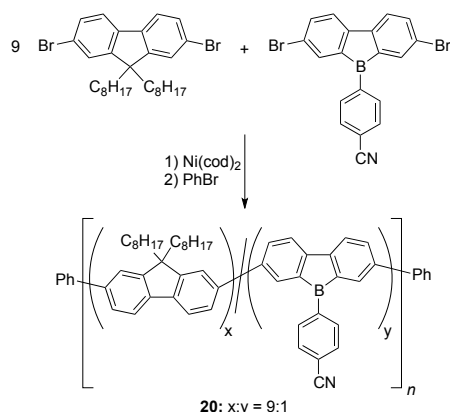
**Scheme 13** Synthesis of borole-containing polymer by nickel(0)-mediated cross-coupling.

Poly(dioxaborole)s with reasonable molecular weights (e.g. M_n = 10 400 g mol^{-1}, PDI = 2.4) have been prepared from the condensation of 9,9-dihexylfluorene-2,7-diboronic acid and 1,2,4,5-tetrahydroxybenzene.[72] Photophysical and theoretical investigations of the resultant material were consistent with a significant degree of π-conjugation within the blue-emitting material.

The preparation of a poly(9-borafluorene) homopolymer using the Yamamoto coupling of a triisopropylphenyl substituted borafluorene has appeared recently (M_n = 6 300 g mol^{-1}, PDI = 2.54).[73] To limit the molecular weight and enable solubility, bromobenzene was added to the reaction mixture. A poly(9-borafluorene vinylene) has been made by Stille coupling (M_n = 7 200 g mol^{-1}, PDI = 4.17). As expected, both polymers show significant red shifts in their absorption maxima in comparison to the monomer and show reasonable quantum yields (λ_{max} = 586nm, Φ = 0.50 and 614nm, Φ = 0.28). Interestingly, the emissive properties are highly sensitive towards ammonia vapour suggesting potential sensing applications for these novel macromolecules.

### 2.18 Linear macromolecules with boron in the side-chain

The controlled polymerization of 4-trimethylsilylstyrene by atom transfer radical polymerization (ATRP) followed by boron-silicon exchange by BBr$_3$ provides a facile route to

boron-substituted polymer **21a** (Scheme 14).[74] The B-Br bonds are readily substituted, thereby providing access to a variety of organoborane macromolecules. For example, polymer **21a** can be treated with nucleophiles (such as organocopper or organotin reagents) to produce poly(organoborane)s **21b** (R = ferrocenyl,[75] thienyl,[76, 77] pentafluorophenyl,[77] and polyaryl[78]). Additionally, alkoxide addition to polymer **21a** will produce boronic esters.[74] Asymmetric triarylboranes (i.e. **21b** bearing two different R groups) have also been synthesized.[75, 78] Polymers synthesized bearing a variety of pendant fluorescing groups show strong emissive properties in solution and solid state. These materials undergo "turn off" fluorescence upon addition of F$^-$ or CN$^-$ anions but no response is observed with Cl$^-$, Br$^-$ or NO$_3^-$ anions.
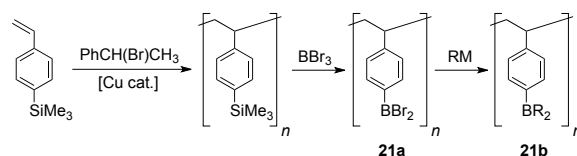
Scheme 14 A route to polystyrene polymers with pendant borane moieties.

Cationic boron polymers have been prepared by treating polymer **21a** with either (4-*t*-butylphenyl)trimethyltin or mesitylcopper(I) to afford **22a** and **22b**, respectively (Scheme 15). The subsequent addition of 2,2'-bipyridine gives the tetracoordinate organoboronium ionomers **23a** and **23b**.[79, 80] Following a different synthetic protocol, the dibromoborane polymer **21a** can be converted to triphenylborate-functionalized polystyrene **24**.[81] In the same report, a similar procedure was adopted to afford the analogous tris(pentafluorophenyl)borate-functionalized polystyrene. Borane-functionalized polyethylene[82] and polynorbornene[83] have also been prepared by polymerization of the respective triarylborane-substituted alkene.
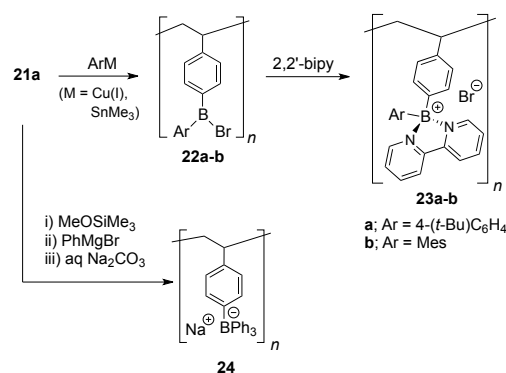
Scheme 15 Boronium- and borate-substituted polystyrene.

2.2 Gallium and indium

To our knowledge, no long chain macromolecules have been reported with aluminium atoms in the main chain and those incorporating heavier group 13 elements are very limited. This is due, in part, to the inherent moisture and air instability of these elements. Recently the first example of an organogallium polymer has been reported (Scheme 16).[84]

Nickel(0)-mediated reductive homocoupling of a dibrominated monomer provided the gallium-containing macromolecule **25** (M_n = 3 500 g mol^{-1}, PDI = 1.54). Alternatively, the palladium(0)-catalyzed cross-coupling of the same dibrominated monomer with bis(pinacolborane)s can be used to afford main chain gallium polymer **26** (M_n = 8 800 g mol^{-1}, PDI = 1.48). The bulky substituent on the gallium combined with the pendant amine-gallane functionality serves to enhance stability of the resultant polymer. It is particularly striking that the four-coordinate gallium center possesses a near-planar geometry. This was further investigated by X-ray structure determinations and DFT calculations of model compounds which suggest that there is significant π-conjugation through gallium.
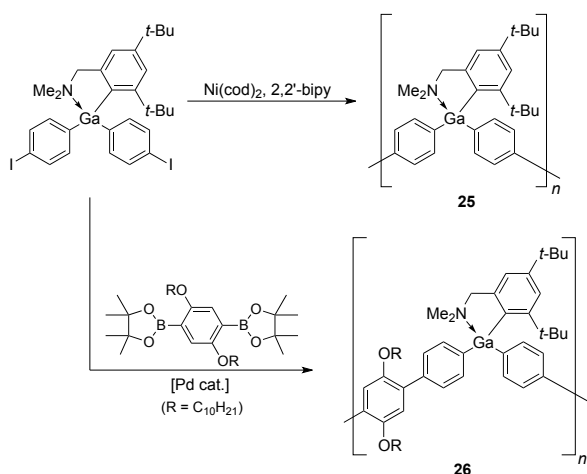
Scheme 16   Gallium-containing polymers from nickel-mediated homocoupling or palladium-catalyzed Suzuki cross-coupling.

It is noteworthy that macromolecules containing 9-gallafluorene moieties bridged by aryl spacers have been synthesized using Suzuki, Sonogashira, and Stille coupling methodologies.[85] The identity of the aryl comonomer gives rise to a variety of vivid colour emissions through the whole visible spectrum, with high quantum yield (Φ = 0.69).

The ROP of a gallium-bridged [1]ferrocenophane has been reported (Scheme 17).[86] The amorphous poly(ferrocenylgallane) **27** posseses modest molecular weight and broad polydispersity (M_n = 15 000 g mol^{-1}, PDI = 3.3, T_g = 205 °C). Interestingly, the analysis of this novel gallium polymer using thermogravimetric analysis (TGA) showed that **27** possessed high thermal stability, with 98 % of its mass being retained at 340 °C.
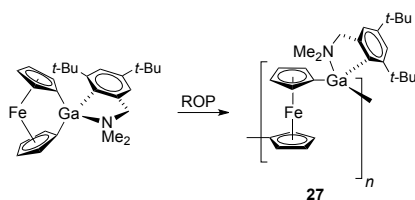
Scheme 17   ROP of a gallium-bridged [1]ferrocenophane.

At the present time there are no examples of organoindium polymers. The closest approach thus far involved the synthesis of the fascinating polyindane oligomer **28** (Fig. 7), a catenated chain containing six covalently bound indium atoms.[87]
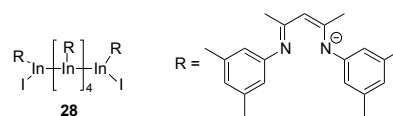

**Fig. 7**   Molecular structure of hexaindium chain determined by X-ray crystallography.

3 Group 14 elements

Polymers featuring the tetraels in the main chain are of great academic and commercial importance. Instantly recognizable are the silicones, or polysiloxanes, which constitute a multi-billion dollar industry. Silicones are used in many aspects of modern life, from lubricants to adhesives to biomedical implants and beyond. Polysilanes represent a unique class of semi-conductive linear polymers that have commercial relevance as precursors to silicon carbide fibres. Polymers containing catenated germanium and tin, the polygermanes and polystannanes, possess attractive electronic properties like their silicon congeners. In this section, emphasis will be placed on the most recent advances in the field with the foundational concepts being outlined to place this work in context. We have not covered the broad field of silole-containing materials and the reader is referred to a comprehensive recent review.[88] For more details on Group 14-element polymers the reader is referred to the following excellent books and reviews.[89]

3.1 Silicon

3.11 Polysiloxanes and related derivatives

The ubiquitous polysiloxanes, containing an inorganic backbone of silicon and oxygen atoms, are used in many facets of everyday life due to their excellent chemical, physical, and electrical properties. The study of these polymers has produced thousands of papers and patents since their first discovery by Kipping in the early 1900s.[90] Industrially, *ca.* 850 kilotonnes per year[91] of polysiloxanes are produced from R_2SiCl_2 (R is most commonly Me) and water following either a polycondensation or ROP as outlined in Scheme 18 (R = Me: poly(dimethylsiloxane, PDMS). When high molecular weights are required, the ROP of cyclic oligosiloxanes (x = 3 and 4) using cationic or anionic methods of initiation provides the optimal method of synthesis. Recently, it has been shown that *N*-heterocyclic carbenes are excellent initiators for the ROP of cyclic oligosiloxanes.[92] The ROP of cyclic monomers containing silicon, oxygen, and carbon have been reported as a route to polycarbosiloxanes.[93, 94]

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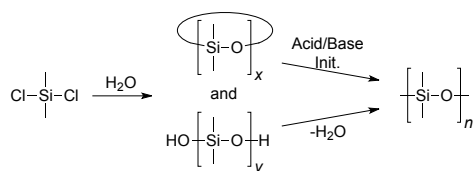
Scheme 18   Methods for the commercial production of silicones (polysiloxanes).

Despite these well-established methodologies, the incorporation of specific functionalities such as acidic or basic moieties still poses a considerable challenge. Post-polymerization hydrosilylation using metal catalysts offers a means to overcome this obstacle and integrate a variety of functional groups (Scheme 19).[95-101] This methodology enables the incorporation of more sensitive moieties such as ethers, esters and amides and permits crosslinking. A noteworthy example illustrating the broad applicability of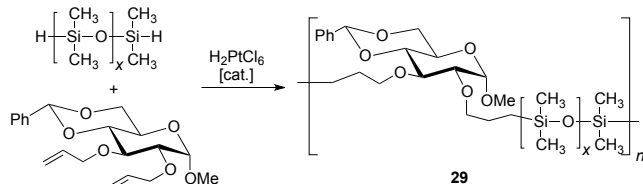 hydrosilylation is the copolymerization of α,ω-dihydro-functional polysiloxane with dienes to afford a sophisticated carbohydrate-segmented PDMS (**29**, Scheme 20).[102]
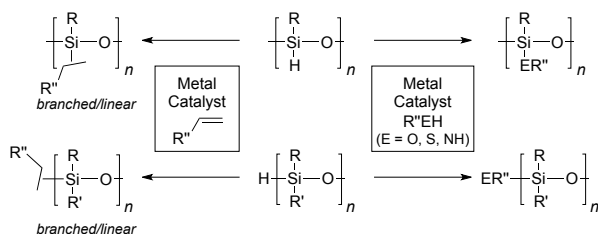
Scheme 19   Hydrosilylation as a strategy for modifying polysiloxanes either at the terminus or in the main chain.

Scheme 20   Synthesis of poly(silalkylene siloxane)s by hydrosilylation.

Alternatively, dehydrogenative coupling can be used to create silicon-heteroatom linkages leading to thio-,[103] amino-, and alkoxy-polysiloxanes.[104-106] A recent report detailed a simple route to poly(methylalkoxy siloxane)s (Scheme 21).[107] Using either Karstedt's or Speier's catalyst, a mixture of low molecular weight poly(methylhydrosiloxane) (**30**: M_n = 750 g mol^{-1}) was treated with a variety of alcohols affording poly(alkoxy siloxane) **31**. It is noteworthy that, in contrast to most hydrosilylation chemistry, Karstedt's catalyst was effective at ambient temperature and under aerobic conditions. In addition, alcohols substituted with reactive functional groups (e.g. R = epoxides, ethers, and halogens) could be incorporated into the silicone side-chain in high yields.
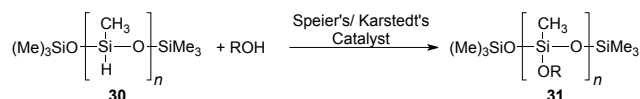
Scheme 21   Hydrosilylation modification of poly(methylhydrosiloxane) to afford poly(alkoxy siloxane)s.

Substituted poly(silalkylene siloxane)s or poly(silalkylene silazane)s can be synthesized via metal-catalyzed cross-dehydrocoupling of bis(hydrosilane)s with water or ammonia (Scheme 22).[108, 109] In particular, 1,4-bis(dimethylsilyl)benzene was shown to be a versatile monomer for the synthesis of oxygen- (**32a**: M_n = 16 000 g mol^{-1}, PDI = 2.2) or nitrogen-containing (**32b**: M_n = 8 500 g mol^{-1}, PDI = 1.4) polymers. This methodology was expanded to different aryl spacers and more complex diols as coupling partners to give a variety of diverse poly(silalkylene siloxane)s.[110-113]

32a; E = O
32b; E = NH
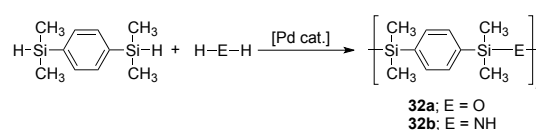
Scheme 22   Routes to poly(silalkylene siloxane)s by metal-catalyzed cross-dehydrogenative coupling polymerization.

Rhodium(I)-catalyzed dehydrocoupling has been used to copolymerize two optically active siloxane monomers to afford highly syndiotactic polysiloxane **33** (M_n = 2 400 g mol^{-1}, PDI = 1.7, syndiotactic: 60%, heterotactic: 32%, isotactic: 8%, Scheme 23)[114] Surprisingly, little change in physical properties were observed for **33** when compared to the analogous atactic polymer. This investigation serves as a rare example of stereoselective polysiloxane synthesis.

33
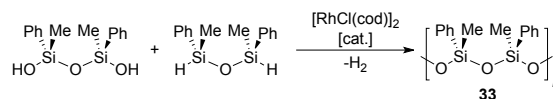
Scheme 23   Rhodium(I)-catalyzed dehydropolymerization to highly syndiotactic polysiloxanes.

Metal-catalyzed hydrosilylation polymerization of silanes with ketones provides a unique strategy to incorporate silicon, oxygen, and aryl groups into a polymer backbone. For example, the ruthenium-catalyzed hydrosilylation of dimethyl siloxy ketones gives poly(silyl ether)s **34a-c** (**34a**: M_n = 4 400 g mol^{-1}, PDI: 1.09; **34b**: M_n = 5 900 g mol^{-1}, PDI: 1.7; **34c**: M_n = 57 800 g mol^{-1}, PDI: 2.1, Scheme 24).[115, 116] Poly(silyl ether)s have also been made by the copolymerization of dihydrosilanes and p-quinones.[117, 118] These polymers are difficult to prepare by classical methods due to their poor acid and base stability.

34a-c

R =
a   **b**   **c**
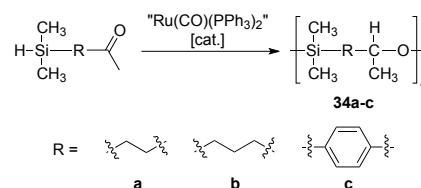
Scheme 24   Hydrosilylation polymerization of siloxy ketones to afford poly(silyl ether)s.

3.12 Polysilanes

The discovery of the first solution-processable polysilanes by West and co-workers[119] marked the beginning of the rapidly growing area of catenated tetrael macromolecules. In contrast to polyolefins, the heavier element polymers possess fascinating electronic properties resulting from their σ-conjugated structures. The classical synthetic approaches to polysilanes are outlined in Scheme 25 and this shall not be covered in detail here.

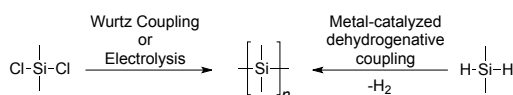**Scheme 25**   General synthetic methodologies to polysilanes.

Despite its success and widespread use, the harsh conditions of the Wurtz coupling route renders this procedure incompatible with functional substituents. Moreover, this method offers poor molecular weight control often leading to polymodal distributions and large quantities of undesirable short chain or cyclic by-products. Likewise, both electrolysis and dehydrogenative coupling give mainly low to moderate molecular weight materials. Thus, recent efforts have been directed towards opening up chain growth methods to catenated silanes.

The development of ROP methods to polysilanes is particularly challenging due to the requirement of finding suitable cyclic precursors. Nevertheless, the ROP of cyclotetrasilanes[120, 121] and cyclopentasilanes[122] has been accomplished using anionic methods of initiation. In both cases, the substitution around the silicon was limited to small substituents (e.g. Me, Ph). More recently, the ROP of the 4-membered octachlorocyclotetrasilane has been reported to afford the moisture sensitive perchloropolysilane (**35**: M_n = 3 500 g mol^{-1}, Scheme 26,).[123, 124] Treatment of chlorinated **35** with a variety of alcohols afforded moisture stable alkoxy-or amino-substituted polysilanes (**36a**: M_n = 3 000 – 62 000 g mol^{-1}, PDI = 1.5 – 2.3; **36b**: M_w = 4 200 g mol^{-1}).[124, 125] It is noteworthy that poly(alkoxy silane)s (**36a**) are not accessible using Wurtz coupling strategies. Moreover, this post-polymerization substitution method permits vinyl moieties to be incorporated into the side chain (i.e. substitution of **35** with 5-hexen-1-ol). An alternative method to incorporate heteroatoms (e.g. S) into polysilanes employs Si-H bond activation. Recently, the B(C$_6$F$_5$)$_3$-catalyzed addition of thiols to poly(phenylhydrosilane) was demonstrated to provide access to a collection of polysilanes with thiolato substituents.[126]
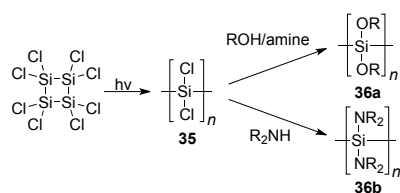
Scheme 26   Reactions of perchloropolysilane to give heteroatom-functionalized polysilanes.

Given that disilenes (R$_2$Si=SiR$_2$) are only isolable with large polymerization-inhibiting substituents (e.g. R = Mes), the polymerization of so-called "masked disilenes" has been investigated.[127] These strained cyclic monomers undergo anion-initiated ROP with concomitant release of biphenyl (Scheme 27). Polysilane **37** prepared from "masked disilene" was of higher molecular weight and narrower polydispersity (M_n = 530 000 g mol^{-1}, PDI = 1.5) than the identical material prepared by Wurtz coupling (M_n = 97 000 g mol^{-1}, PDI = 2.6).
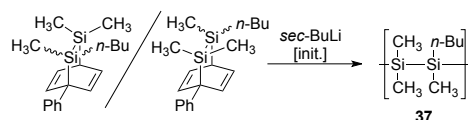
Scheme 27   ROP of "masked disilenes" as a route to alternating polysilanes.

An amino-functionalized "masked disilene" has been shown to undergo regioselective ROP to give poly(amino silane) **38** with a highly ordered alternating structure (Scheme 28).[128] Poly(amino silane) **38** can be converted to the chloro derivative **39** by reaction with acetyl chloride.[129] Substitution of the chlorine was then performed using a variety of nucleophiles (alcohols, Grignard, or organolithium reagents). This procedure provides a simple method to polysilanes (**40**) having functional groups that would otherwise be inaccessible.
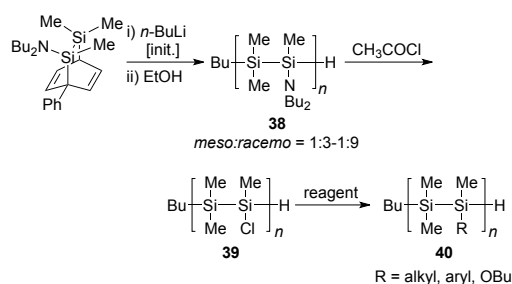
Scheme 28   Polymerization of an amino-containing "masked disilene" and further elaboration to functionalized polysilanes.

The influence that substituents can have over the degree of σ-conjugation, backbone conformation, and photophysical characteristics in polysilanes is a fascinating area of investigation.[130, 131] In general, polysilanes adopt a helical conformation in solution at room temperature as a mixture of both *P*- and *M*-type helices. However, when the substituents on silicon are chiral the polymer (i.e. R*) may adopt a one-handed *M*- or *P*-type helical-screw conformation as evidenced by circular dichroism (CD) spectroscopy (Fig. 8). Typically, these polymers are prepared by Wurtz coupling.

Mixture of ***M***- and ***P***-type helices

Predominate ***M***- or ***P***-type helix

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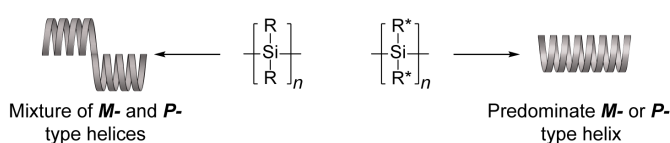
Fig. 8   Selected examples of chiroptical polysilanes.

One of the earliest examples where rod-like formation was observed for a polysilane was in (*S*)-2-methylbutyl-substituted **41a**.[132] The inclusion of an oligo(ethylene oxide) side chain in **41b** imparts alcohol solubility and this material maintains a helical sense in polar protic solvents.[133] In contrast, the addition of a non-solvent (MeOH or EtOH) to THF solutions of helical **41c** led to the remarkable observation of screw sense switching as evidenced by the change in sign of the CD spectra.[134] Striking shape-like formations have been observed when CF_3-containing **41d** adheres to silicon surfaces, with AFM analysis revealing that short chains form rods and longer chains form semi- and fu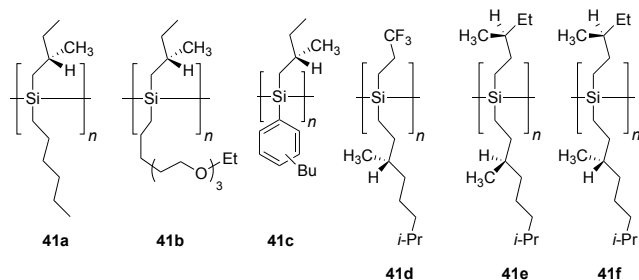ll-circles.[135] The subtle inversion of configuration of one stereocenter between **41e** and **41f** results in strikingly different temperature dependence of helicity.[136] In particular, a solution of **41e** in *n*-octane switches chirality upon heating from −80 to >10 °C whilst **41f** shows no temperature dependency. The authors postulate that this results from a lower potential energy difference between *P*- and *M*-type helices for **41e** compared to **41f**. A further example of the profound helical nature of polysilanes is the higher molecular weight observed when $MePhSiCl_2$ was polymerized in a chiral solvent when compared to a racemic solvent [(+)-limonene: 80 000 g mol^{-1}, (+/-)-limonene: 39 200 g mol^{-1}].[137]

The ROP of "masked disilenes" provides a convenient route to block copolymers with control of the polysilane secondary structure. For example, poly(1,1-dimethyl-2,2-dihexylsilane), prepared by the ROP of a masked disilene, was copolymerized with triphenylmethyl methacrylate in the presence of (−)-sparteine to give block copolymer **42** (M_n = 10 000 g mol^{-1}, PDI = 1.5, Scheme 29).[138] The triphenylmethyl methacrylate block adopts a persistent right-handed helix due to the chiral structure of (−)-sparteine. At low temperatures (< -20 °C) the initially random polysilane block adopts a complimentary helical screw, as measured by CD spectroscopy. This helical-sense programming is lost as the sample is warmed above -20 °C, but returns upon cooling.
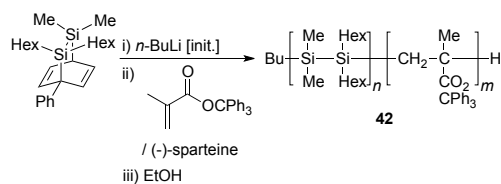
Scheme 29   Synthesis of chiral poly(silane-*b*-methacrylate) from a "masked disilene".

Another example of chiral induction by chemical manipulation of the secondary structure of polysilanes has recently been reported.[139] For example, the deprotonation of poly[methyl(*p*-tolyl)silane] **43** in the presence of a chiral diamine catalyst [e.g. (−)-sparteine] induced helical chirality within the polymer (**44**, Scheme 30). After protonation with ammonium chloride, the CD spectrum of the resultant polysilane **43*** shows that it retains the imparted chiral information.
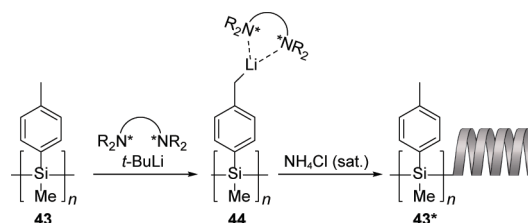
Scheme 30   Chiral induction of poly(methyl(*p*-tolyl)silane) using *t*-BuLi in the presence of a chiral diamine catalyst.

In a recent report, phenylsilane was polymerized using $B(C_6F_5)_3$ as an initiator to afford branched polymer **45** (M_n = 1 100 − 1 900 g mol^{-1}, PDI = 1.3 − 2.1, Scheme 31).[140] Although the molecular weights were low, this represents a novel metal-free approach to polysilyne and offers the possibility of future developments involving catalyst optimization.
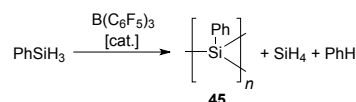
Scheme 31   Metal-free synthesis of a branched poly(phenylsilyne).

3.13 Polycarbosilanes

Macromolecules containing alternating carbon and silicon atoms in the main chain is a mature field that began in the late 1940's with the sodium-mediated coupling of (chloromethyl)chlorosilanes.[141] Importantly, the pyrolysis of polycarbosilane fibres affords the tough ceramic silicon carbide in fibrous form which has high thermo-oxidative stability.[142] Historically, a successful approach to polycarbosilanes involves the metal-catalyzed ROP of strained 1,3-disilacyclobutanes at elevated temperatures. A convenient ambient temperature route to polycarbodimethylsilane **46** from 1,1,3,3-tetramethyl-1,3-disilacyclobutane has been developed using platinum(II) photocatalysis (Scheme 32).[143] This improved methodology showed high monomer conversion (> 90%) giving high molecular weight material (**46**: M_w *ca.* 100 000 g mol^{-1}) after only 15 min irradiation at room temperature.
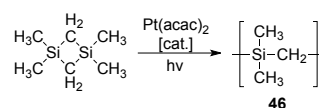
Scheme 32   Platinum(II) photocatalyzed ROP of 1,3-disilacyclobutane to afford polycarbosilane.

In addition to 1,3-disilacyclobutanes, silacyclobutanes undergo anion-initiated ROP to produce polycarbosilanes **47** (R = alkyl, aryl, etc., Scheme 33).[144-147] Under certain conditions living polymerization can be achieved.[148, 149] Platinum(0) catalysts will also initiate the ROP of silacyclobutanes.[150, 151] The anionic ROP of silacyclopent-3-enes,[152-156] and 2,3-benzo-1-silacyclobut-2-enes[157-159] has also been reported.

Scheme 33   Synthesis of polycarbosilanes by ROP of silacyclobutanes.

The ROP of strained silacyclopropanes represents an alternative route to polycarbosilanes (Scheme 34). In an early report, the intermediacy of a silacyclopropane was postulated in reactions of bis(chloromethyl)diorganosilanes with magnesium to produce polycarbosilane.[160] Subsequently, silacyclopropane monomers were isolated and deliberately subjected to *n*-BuLi-initiated ROP there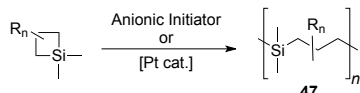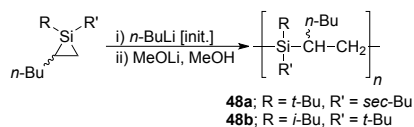by affording polycarbosilanes **48**.[161] The resultant hydrophobic materials were formed in low molecular weight (**48a**: M_n = 2 100 g mol^{-1}, PDI = 1.5; **48b**: M_n = 1 800 g mol^{-1}, PDI = 1.6).

48a; R = *t*-Bu, R' = *sec*-Bu
48b; R = *i*-Bu, R' = *t*-Bu

**Scheme 34**   Anion-initiated ROP of silacyclopropanes to polcarbosilanes.

Polycarbosilane **49** has recently been synthesized by the addition polymerization of kinetically stabilized silenes (Scheme 35).[162] Specifically, the polymerization of 1,1-dimesitylneopentylsilene, initiated by *t*-BuLi, afforded high molecular weight **49** (M_n = 280 000 g mol^{-1}, PDI = 1.2). Precipitation of the polymer from MeOH afforded **49** as an air-stable white solid, characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy, differential scanning calorimetry (DSC: T_g = 153 °C) and TGA (weight loss 325–525 °C, ceramic yield = 12% at 800 °C).
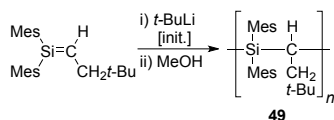
Scheme 35   Addition polymerization of an isolable silene.

The fascinating polymerization of the silene (Me$_3$Si)$_2$Si=Ad (Scheme 36, Ad = 2-adamantylidene) has been reported.[163] (Me$_3$Si)$_2$Si=Ad, produced by thermal dissociation of the head-to-tail dimer, was polymerized either thermally or in the presence of a radical to give polycarbosilane **50** (M_w *ca.* 110 000 g mol^{-1}). Detailed ^{29}Si NMR and experimental analyses revealed the unexpected microstructure shown in Scheme 36. Thus, the mechanism of polymerization does not follow a

simple addition across the Si=C bond nor does it involve ROP of the aforementioned Si$_2$C$_2$ dimer.
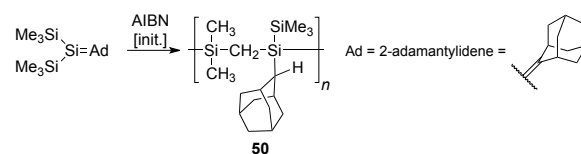
Scheme 36   The unexpected isomerization during the polymerization of a silene.

3.2 Germanium and tin

3.21 Polygermanes

Polygermanes (Scheme 37), first synthesized by Wurtz coupling of Bu$_2$GeCl$_2$ in 1985,[164] possess similar attractive electronic properties as their silicon congeners.[165] The main routes to catenated germanium macromolecules are the Wurtz coupling or electrolysis of dichlorogermanes and the metal-catalyzed dehydrogenative coupling of dihydrogermanes. An alternate route unique to polygermanes involves the demethanative coupling of methylhydrogermanes.[166-168]
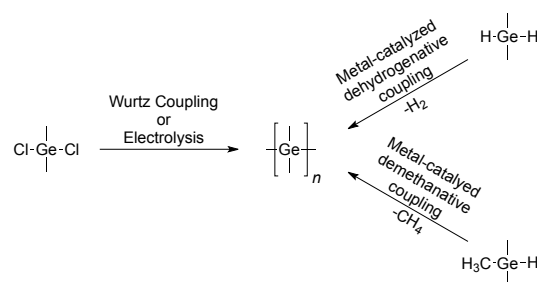
Scheme 37   Synthetic strategies towards polygermanes.

As an alternative to the alkali metals used in Wurtz coupling, the mild one-electron reducing agent SmI$_2$ facilitates the formation of a series of polygermanes (**51a**: R = Me, Et) and polystannanes (**51b**: R = Me, Et, Bu) (Scheme 38).[169, 170] For example, refluxing Et$_2$GeCl$_2$ with SmI$_2$ affords polydiethylgermane **51a** (M_n = 4 300 g mol^{-1}, PDI = 1.1), albeit in lower molecular weight than standard Wurtz conditions.

51a; E = Ge
51b; E = Sn
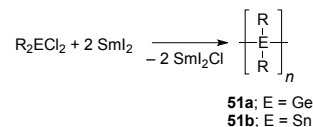
Scheme 38   Samarium diiodide-promoted polymerization of organogermanium and organotin dichlorides.

A unique photochemical route to polygermanes has been developed.[171] Irradiation of dibenzoyldiethylgermane with a 400 nm light source affords polydiethylgermane **52** (M_n = 2 800 g mol^{-1}, PDI = 1.1, Scheme 39). Presently, this route only gives lower molecular weight polygermanes, but it negates the use of alkali metals.
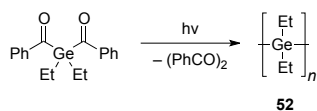
Scheme 39 Photopolymerization of dibenzoylgermanes.

Synthetic routes to polycarbogermanes are more limited than those for polycarbosilanes, however these unique polymers are of interest as precursors to GeC ceramics.[172] The first anion-initiated addition polymerization of a kinetically stable germene, 1,1-dimesitylneopentylgermene, was reported recently to give polycarbogermane **53** (Scheme 40).[173] GPC analysis of the resultant air-stable polymer suggested a bimodal molecular weight distribution (M_n = 7 100 and 36 000 g mol^{-1}, PDI = 1.1 and 1.5, respectively). Interestingly, the *in situ* preparation of the germene from a fluorovinylgermane and *t*-BuLi (1 equiv), followed by initiation with *t*-BuLi (10 mol%) gave a polymer with monomodal distribution (M_n = 39 000 g mol^{-1}, PDI = 2.0). Although this two-step route gives a broader PDI, it is a more convenient method for the synthesis of **53** since the monomodal higher molecular weight polymer was isolated in higher yield with fewer experimental manipulations.
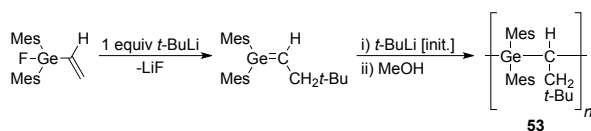
Scheme 40 Addition polymerization of a germene

3.22 Polystannanes

Polystannanes (Scheme 41), polymers that consist of a backbone of σ-bonded tin atoms, are the only example of characterized polymers containing covalently bound metal atoms. The large size of tin increases the delocalization of electrons along the polymer backbone (*cf.* polysilanes and polygermanes).[174, 175] As with polysilanes and polygermanes, Wurtz coupling and electrolysis of dichlorostannanes provides access to high molecular weight polystannanes. Unfortunately, the yields are low and often accompanied by unwanted cyclic oligomers. The metal-catalyzed dehydrogenative coupling of secondary stannanes presents a more desirable route that is still capable of achieving high molecular weights but offers significantly fewer byproducts.[176-180] The poor thermal and light stability of these polymers in solution makes characterization difficult. Degradation to five- and six-membered oligostannanes is common.[181, 182]
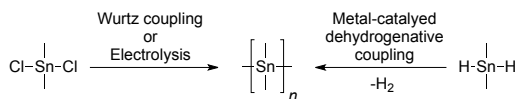
Scheme 41 Synthetic strategies towards polystannanes.

Catalytic dehydrocoupling of a dihydrostannane, prepared in two steps from triphenylstannane, was performed using Wilkinson's catalyst to give polystannane **54** (M_n = 7 700 g mol$^-$

[1], PDI = 1.3, Scheme 42).[183] The resulting polymer showed much improved stability compared to other polystannanes, as in sealed flasks there was no sign of degradation of the solid polymer **54** for several weeks, and solutions in C_6D_6 were stable for over a week in the dark. Although no direct evidence was observed, it was postulated that a Sn···O dative interaction from the flexible oxypropyl linked phenyl rings may play a role in the enhanced light stability.
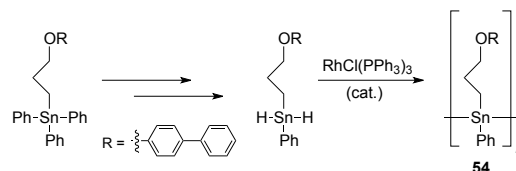
Scheme 42 Synthesis of ether-stabilized polystannanes.

The mechanism of metal-catalyzed dehydrocoupling of secondary stannanes has been rigorously investigated.[184, 185] Interestingly, detailed NMR spectroscopic studies suggest that the Sn-Sn bond-forming step may involve direct insertion of free stannylene (R_2Sn:) into a M-Sn bond. This is in contrast to the classic Chalk-Harrod mechanism proposed for the catalytic dehydrocoupling of silanes.

A modification to Wurtz coupling has been reported using sodium in liquid ammonia.[186] Another route to polystannanes involves treatment Et_2O solutions of diorganostannanes with TMEDA (tetramethylethylenediamine).[187] The effectiveness and limits of the Na/NH_3 Wurtz coupling, the TMEDA-mediated dehydrocoupling and the dehydrocoupling using Wilkinson's catalyst were evaluated with a variety of different stannane monomers (Fig. 9).[187] Dehydrogenative coupling appears to be the most general approach, while the other methods appear more substrate dependant.

Sodium in liquid ammonia	✗	✗	—	✓
TMEDA	✓	✓	✓	✗
Wilkinson's Catalyst	✓	✓	—	—

Fig. 9 Polymerization methods for the preparation of polystannanes. Symbols: (✓): M_w above 8×10^3 g mol^{-1}, (—): M_w below 8×10^3 g mol^{-1} or cyclic byproducts, (✗): very slow reaction or absence of polymeric product.

A recent communication highlights an interesting strategy for alternating polystannanes **55** that cannot be prepared by the previously discussed routes (Scheme 43).[188] Tin dihydrides were reacted with tin diamides, followed by concentration under vacuum to remove volatile byproducts. Isolated yields were generally high with excellent M_n values considering the synthetic ease of the polymerization (**55**: M_n = 19 000 – 240 000 g mol^{-1}, PDI *ca.* 2.5). This new polycondensation strategy

details a route to homo- or alternating polystannanes that show remarkable light-stability (Fig. 10).
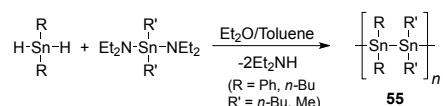
Scheme 43   A route to alternating polystannanes via polycondensation.
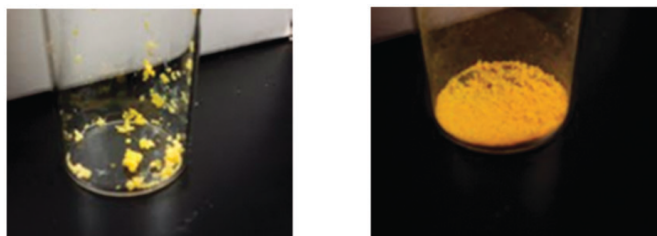
Fig. 10   Polystannanes $[Ph_2Sn\text{-}alt\text{-}Sn(n\text{-}Bu)_2]_n$ and $[Ph_2Sn\text{-}alt\text{-}SnMe_2]_n$ after exposure to ambient light for 7 days. Reproduced from Ref. 188.

3.23 Polygermoles and polystannoles

In contrast to the well-established polysiloles, examples of non-annulated polygermoles and polystannoles are comparatively few. Nevertheless, polymers containing germanium or tin metalloles are attractive synthetic targets due to their increasing metallic character when compared to their silicon analogues.[189] Examples of germole-containing polymers have been obtained by incorporating germoles into annulated frameworks (e.g. dithienogermoles, diselenogermoles, and dithienogermolocarbozoles). This has led to investigations into germole-containing polymers for use in photovoltaics[190-199] or as sensors for explosives.[200]

Analogous to poly(1,1-silole)s, Wurtz coupling[201, 202] and metal-catalyzed dehydrocoupling polymerization[203] represent the most popular routes to poly(1,1-germole)s (**56**, Scheme 44). In general, the M_n and PDI values for **56** obtained from either methods are modest (*ca.* 4 000 g mol^{-1} and <1.9, respectively), although catalytic dehydrocoupling gives higher isolated yields.[202]
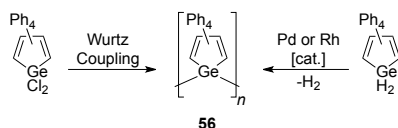
Scheme 44   Synthetic strategies towards poly(1,1-stannole)s.

Higher molecular weight non-annulated germole-containing polymers have been synthesized by the nickel(0)-promoted homocoupling of a 2,5-bis(4-bromophenyl)germole derivative (Scheme 45).[204] The resulting poly(*p*-biphenylene-2,5-germole) **57** (M_n = 20 000 g mol^{-1}, PDI = 2.9) was isolated as a bright yellow solid. The optical properties of polymer **57** (λ_{max} = 442 nm) indicate considerable π-conjugation compared to molecular models (λ_{max} = 360 − 380 nm). The conjugation length was estimated to be greater than seven monomer units (or 21 rings). Additionally, poly(2,5-diaryl)germoles have been

prepared from titanocene-containing polymers,[205] and highly branched poly(phenylenegermolene)s are accessible from 1,1-diethynyl-2,3,4,5-tetraphenylgermole.[206]
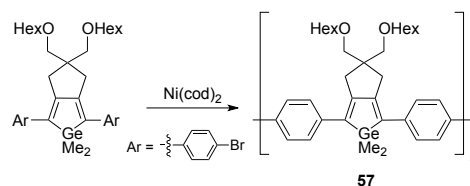
Scheme 45   Synthesis of poly(*p*-biphenylene-2,5-germole).

Despite an earlier report of oligomeric poly(2,5-diaryl)stannoles,[207] the first structurally well-defined polystannole was prepared by the palladium(0)-catalyzed cross-coupling of a bis(iodothienyl)stannole derivative with 2,5-bis(trimethylstannyl)thiophene (Scheme 46).[208] The resulting weakly fluorescent purple-black polystannole **58** (M_n = 6 800 g mol^{-1}, PDI = 2.5) was thermally stable to weight loss up to 300 °C and was characterized by ^{119}Sn, ^{1}H and ^{13}C NMR and IR spectroscopy. The use of Stille coupling is especially interesting because stannoles, such as stannafluorenes,[209] can function as nucleophiles in cross-coupling reactions. There has been a singular report of a poly(1,1-stannole), synthesized by treatment of tetraphenylstannole dianion with 1,2-dibromo-ethane.[210]
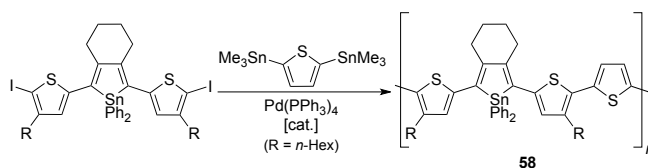
Scheme 46   Synthesis of a polystannole via Stille coupling polymerization.

4 Group 15 elements

The chemistry of pnictogen-containing macromolecules is of immense interest due to the diverse oxidation states and bonding environments possible for group 15 elements. Moreover, the Lewis basicity of the Pn(III) oxidation state and the Lewis acidity of the Pn(V) oxidation state confers unique chemical functionality to the resultant polymers. Despite the fact that the P-containing "inorganic rubber" is amongst the earliest synthetic polymers, it is only in the last quarter century that massive growth has occurred. For example, considerable advances have been made in the development of organophosphorus macromolecules possessing π-conjugation. In the case of the heavier pnictogens, exciting macromolecules containing arsenic, antimony, or bismuth atoms in the main chain have surfaced only in the last decade. The reader is referred to several important books and reviews in the field of group 15 polymers.[211] It is worth noting that significant developments have been made in the field of P-containing dendrimers,[212, 213] but this topic is beyond the scope of this review.

4.1 Phosphorus

4.11 Polyphosphazenes and related polymers

Since the discovery of "inorganic rubber" in the late 19th century, polyphosphazenes have become one of the most well studied classes of inorganic polymers.[214] They have found use in diverse applications including biomedical implants, as flame retardants, and as solid state polyelectrolytes. After a brief introduction, this section will focus on recent developments in P-N-containing macromolecules.

The thermal ROP of the cyclic phosphonitrilic chloride trimer ($N_3P_3Cl_6$) at 250 °C, pioneered by Allcock and Kugel,[215] represents the most well-established route to soluble linear poly(dichlorophosphazene). The facile replacement of chlorine substituents by nucleophilic substitution has led to the generation of an enormous library of polyphosphazene derivatives. Other classical routes to polyphosphazenes include the thermal[216-218] or anionic[219] polymerization of phosphoranimines, the thermal condensation of phosphorus azides,[220] or direct synthesis from PCl_5 and NH_4Cl (Scheme 47).[221]
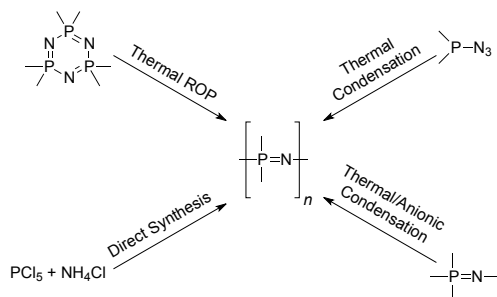
Scheme 47 Classical (pre-1995) synthetic routes to polyphosphazenes.

General drawbacks for these classical methods are the high temperatures, lack of molecular weight control, and low yields. A major breakthrough was the ambient temperature living cationic polymerization of $Cl_3P=N(SiMe_3)$ using PCl_5 as an initiator to afford poly(dichlorophosphazene) (**59**, Scheme 48).[222, 223] Since polymer **59** is moisture-sensitive, molecular weight determination was performed on the bis(trifluoroethoxy) derivative **60a** (R = CH_2CF_3: M_n = 5 800 − 66 400 g mol^{-1}, PDI = 1.04 − 1.32). This development permitted the subsequent synthesis of polyphosphazene block copolymers (e.g. **60a**-*b*-**60c**).[224] Employing an end-functional polymeric initiator permits access to organopolymer polyphosphazene block copolymers.[225]
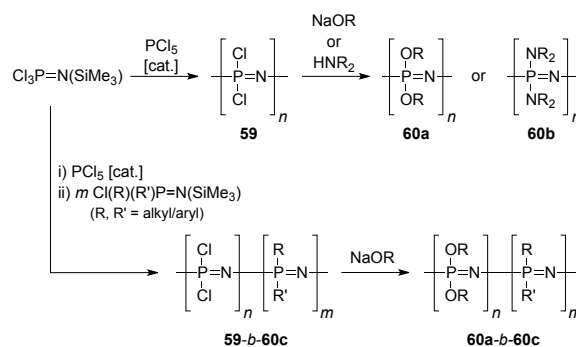
Scheme 48 PCl_5-initiated living condensation polymerization of the phosphoranimines to afford polyphosphazene homo- and block copolymers.

Poly(organophosphazene)s (**60c**) are not generally accessible by substitution of **59** due to its incompatibility with Grignard or organolithium reagents. In addition, hexa-alkyl or aryl derivatives of the cyclic trimer are unable to undergo thermal ROP; one or more halogen substituents are necessary for the polymerization (vide infra). Alternative pathways through phosphoranimines[217] or phosphorus azides[220] exist, however these routes generally require high temperatures.

More recently, the living cationic polymerization of phosphoranimines has been adapted to synthesize **60c** in low to moderate molecular weight and low PDIs (Scheme 49).[226] The polymerization was performed both in solution (M_n = 2 800 − 16 300 g mol^{-1}, PDI = 1.01 − 1.14) and in the solid state (M_n = 5 300 − 71 100 g mol^{-1}, PDI = 1.02 − 1.40). Continued mechanistic studies led to the development of a phosphite-mediated polymerization of organo-substituted *N*-silylbromophosphoranimines (Scheme 49).[227, 228] This reaction proceeds at ambient temperatures to give high molecular weight polymers with a wide range of PDI values (M_w = 106 000 − 534 000 g mol^{-1}, PDI = 1.23 − 5.20).
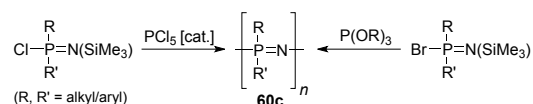
Scheme 49 Synthesis of organo-substituted polyphosphazenes from phosphoranimines.

An unprecedented P-H functionalized polyphosphazene **61** has recently been prepared from the reaction of bis(dimethylamino)chlorophosphine with ammonia (M_w = 41 000 g mol^{-1} by static light scattering, Scheme 50).[229] ^{31}P and ^{1}H NMR spectroscopic analysis of the polymer showed signals assigned to $Me_2N(HN=)P(H)–$ and $–N=P(H)-(NMe_2)_2$ end groups in a polymer with about 500 repeating units. *Ab initio* calculations provided insight into the mechanism of the polymerization, postulated to involve an equilibrium between aminophosphine [e.g. $R_2P–NH_2$] and phosphazene [e.g. $R_2P(H)=NH$] tautomers.

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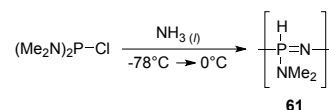
Scheme 50 Synthesis of a *P*-hydrido polyphosphazene.

A longstanding question in the thermal ROP of N$_3$P$_3$Cl$_6$ regards the mechanism of initiation and propagation. It has always been postulated to involve heterolytic dissociation of the P–Cl bond supported by the fact that the presence of Lewis acids (e.g. BCl$_3$) permit the ROP to occur at lower temperatures.[230] Definitive support for a cationic mechanism was provided with the solution polymerization of N$_3$P$_3$Cl$_6$ using a well-defined silylium carborane catalyst (Scheme 51).[231] This new system is notable for proceeding quickly at ambient temperatures to give **59** of moderate molecular weight and PDI (M_n = 61 000 g mol^{-1}, PDI = 1.83 for the trifluoroethoxide derivative, e.g. **60a**).
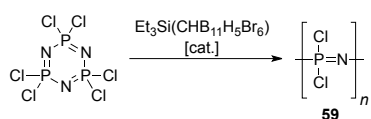
Scheme 51 Silylium carborane-catalyzed polymerization of N$_3$P$_3$Cl$_6$ to yield poly(dichlorophosphazene).

Inspired by the rich chemistry of polyphosphazenes, compounds in which the phosphorus has been substituted for other heteroatoms have also been investigated. A poly(carbophosphazene), which incorporates an sp^2-hybridized carbon atom, has been synthesized from the thermal ROP of a cyclic carbophosphazene to afford linear polymer **62a** (Scheme 52).[232-234] Another class of poly(heterophosphazene)s incorporates sulfur(IV) moieties into the main chain. Poly(thiophosphazene) **62b** can be prepared from the thermal ROP of the cyclic precursor at 90 °C (Scheme 52).[235] Similar to that of polydichlorophosphazene **59**, the carbo- and thio-polymers (**62a-b**) can undergo post-polymerization substitution chemistry of the chloro moieties with amine or alkoxy nucleophi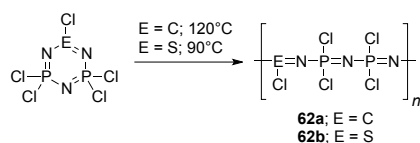les. In the case of poly(thiophosphazene), substitution occurs preferentially at the sulfur centre, however the polymers show minimal long term stability.[236]

Scheme 52 Thermal ROP of cyclic heterophosphazenes in which a phosphorus has formally been replaced by another element (E = C, S) to afford their linear polymers.

Closely related are poly(thionylphosphazene)s (**63**) which contain a four-coordinate sulfur(VI) and are prepared by the thermal ROP of the cyclic *S*-chloro or *S*-fluoro thionylphosphazene (Scheme 53).[237, 238] Interestingly, substitution occurs preferentially at the phosphorus atoms to afford air- and moisture-stable polymers after nucleophilic substitution.[239-241] GaCl$_3$ has been found to be an effective initiator for the ambient temperature ROP of the cyclic monomer, giving **63a** in comparable molecular weight and PDI as those synthesized by thermal ROP (M_n = 25 000 − 52 000 g mol^{-1}, PDI = 1.26 − 2.18).[242, 243] The authors also reported the

existence of a critical concentration (ca. 0.15 M) below which polymerization did not occur. This implies that the polymerization has a low ΔH_{ROP}, and thus is primarily entropy-driven.
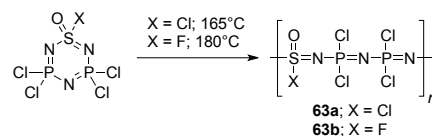
Scheme 53 Thermal ROP of cyclic thionylphosphazenes to yield their linear polymers.

A second type of poly(thionylphosphazene)s contains alternating P=N and S(VI)=N moieties in the backbone. The thermal condensation polymerization of thionylphosphazene monomers afforded **64** with a modest molecular weight (Scheme 54, M_n = 8 000 g mol^{-1}).[244] These represent the first examples of poly(thionylphosphazene)s that are fully organo-substituted.
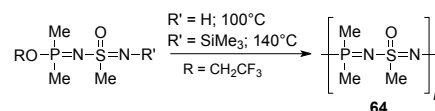
Scheme 54 Condensation of a linear thionylphosphazene monomer to yield poly(thionylphosphazene).

4.12 Poly(methylenephosphine)s

The most important method of producing commodity polymers is through the addition polymerization of the C=C bond of olefins. The addition polymerization of a P=C bond in a phosphaalkene was accomplished in 2003.[245] Specifically, the polymerization of MesP=CPh$_2$ afforded poly(methylenephosphine) (PMP, **65**). Polymer **65** was first isolated from the residue that remained after the distillation of the phosphaalkene monomer. In the same report, the radical- and anion-initiated polymerizations afforded samples of **65** with near-identical spectroscopic properties (Scheme 55). Shortly after, the radical-initiated polymerization was amenable to the random copolymerization of MesP=CPh$_2$ and styrene (**66**, Scheme 55).[246]
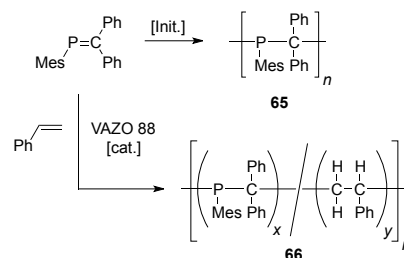
Scheme 55 Addition homo- and copolymerization of MesP=CPh$_2$ to yield poly(methylenephosphine) and poly(methylenephosphine)-*co*-polystyrene

Mass spectrometric investigations of oligomers prepared by treating MesP=CPh$_2$ with MeLi as initiator (25 mol%) provided the first evidence for chain growth in solution at

ambient temperature.[247] Subsequently, the room temperature polymerization of phosphaalkenes using *n*-BuLi was shown to follow a living mechanism. PMPs **67a-b** were prepared with controlled molecular weights and low PDIs (M/I = 25:1-100:1, M_n = 8 900 − 29 600 g mol^{-1}, PDI = 1.04 − 1.15).[248] In addition, employing living polystyrene as the radical initiator afforded polystyrene-block-poly(methylenephosphine) copolymers (**68**, Scheme 57). These novel copolymers possess interesting film-forming properties (Fig. 11). Detailed studies of the kinetics of the living anionic polymerization of MesP=CPh$_2$ allowed for the determination of the activation energy for propagation (E_a = 14.0 ± 0.9 kcal mol^{-1}), one of the largest recorded for an addition polymerization.[249]
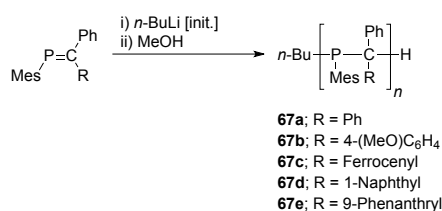
Scheme 56   Anionic polymerization of substituted phosphaalkenes.

67a; R = Ph
67b; R = 4-(MeO)C$_6$H$_4$
67c; R = Ferrocenyl
67d; R = 1-Naphthyl
67e; R = 9-Phenanthryl

Scheme 57   Preparation of polystyrene-block-poly(methylenephosphine) by living anionic polymerization.

Fig. 11   Film cast from a block copolymer of phosphaalkene and styrene. Photograph provided courtesy of Dr. E. Conrad.

As long as the P=C bond is kinetically stabilized with sterically encumbering substituents, phosphaalkenes bearing a variety of functional substituents can be polymerized. To this end, the ferrocene-containing monomer, MesP=C(Fc)Ph, has been anionically polymerized to afford the novel redox-active PMP **67c** (M_n = 9 500 g mol^{-1}, PDI = 1.21, $\Delta E_{1/2}$ = 0.41 V vs. SCE).[250] Phosphaalkenes bearing polyaromatic chromophores (e.g. 1-naphthyl, 9-phenanthryl) have been synthesized and polymerized using anionic initiators to afford the PMPs **67d-e** (M_n = 15 100 − 27 100 g mol^{-1}, PDI = 1.14 − 1.37).[251] These polymers demonstrate turn-on fluorescent emission

selectively when oxidized, making them attractive for sensor applications.

Another example illustrating the structural diversity possible for PMPs is the polymerization of enantiomerically pure phosphaalkenes. Specifically, the chiral phosphaalkene-oxazoline[252] was copolymerized with styrene to give a phosphine-containing polymer bearing enantiomerically pure substituents (**69**: M_w = 7 400 g mol^{-1}, PDI = 1.15) (Scheme 58).[253] The phosphaalkene incorporation in copolymer **69** was estimated by elemental analysis to be 13 mol % and the optical rotation found to be −14.0°.
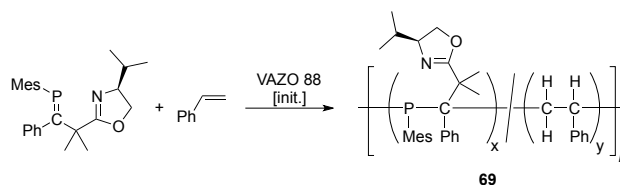
Scheme 58   Copolymerization of an enantiomerically pure phosphaalkene-oxazoline and styrene.

A unique feature of PMPs is their chemical functionality through the phosphorus lone pairs. Homopolymer **65** can be oxidized with either H$_2$O$_2$ or S$_8$ (**70a** and **70b**),[245] coordinated to either borane (**70c**)[254] or gold(I) (**70d**)[255], and alkylated to yield an iono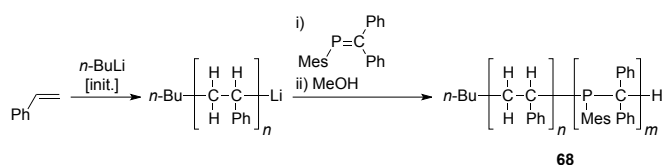mer (**70e**) (Scheme 59).[254] In the case of borane and gold(I), uncoordinated phosphorus moieties could not be observed by ^{31}P NMR spectroscopy indicating complete conversion to the phosphine-borane or phosphine-gold adducts. In contrast, the phosphonium ionomer **70e** could not be obtained in higher than 50% conversion, possibly due to ionic repulsion. In all cases, molecular weight analysis by GPC of the resulting polymers showed no degradation of the polymer chain, but only the expected increase in molecular weight. For example, gold(I) complex **70d**, synthesized from a sample of polymer **65** (M_n = 38 900 g mol^{-1}), was found to have an M_n of 71 600 g mol^{-1}.
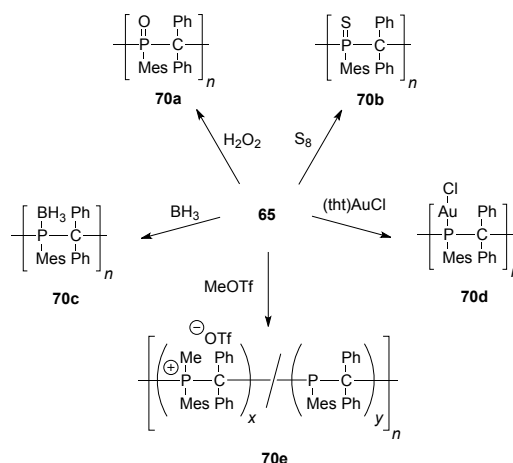
Scheme 59   The functionalization of poly(methylenephosphine)s.

When coordinated to gold(I), amphiphilic phosphaalkene-isoprene block copolymers, [PI]$_{404}$-*b*-[PMP]$_{35}$ formed self-

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assembled nanostructures in a block-selective solvent [R_h = 5 nm (THF), 82 nm (*n*-heptane)].[256] Transmission electron microscopy (TEM) analysis of samples obtained from dilute *n*-heptane revealed spherical nanostructures (28-32 nm) that were attributed to micelles with a PMP·AuCl core and polyisoprene corona. Remarkably, increasing the PMP block length in the copolymer afforded worm-like gold nanostructures with high aspect ratio.

The use of phosphaalkene/styrene random copolymers in polymer-supported palladium catalysis has been demonstrated.[246] Specifically, the copolymer **68** (9 mol% P; M_w = 7000 g mol^{-1}, PDI = 1.7) has been employed in combination with Pd$_2$(dba)$_3$ as a catalyst for the Suzuki coupling of phenylboronic acid and bromobenzene. The biphenyl product was isolated in high yield (90 %) and purity without the need for chromatography and the polymer was recovered by simple precipitation.

The use of poly(methylenephosphine)s as flame retardants has been reported recently (Fig. 12).[257] Paper samples were treated with homopolymer **67a** and its oxide **70a** and subjected to flame testing and both were found to be competent flame retardants (limiting oxygen index = 25.9 %), with the oxidized homopolymer performing slightly better. Importantly, after leaching with water no loss of flame retardancy was observed.

Fig. 12 Top: Dynamic sheet formed (DSF) paper made from thermomechanical pulp (TMP) was coated with poly(methylenephosphine oxide) **70a** (0.8 mmol P / g) and ignited with a lighter in air. This flame retardant paper is self-extinguishing. Bottom: An untreated DSF TMP sheet was ignited in air and burns completely.

Recently, detailed spectroscopic analysis of homopolymer previously formulated as **65** synthesized by radical-initiated polymerization revealed the presence of an unexpected microstructure **71** resulting from an isomerization polymerization (Scheme 60).[258] It was speculated that after the addition of the radical species to the P in MesP=CPh$_2$ affording a C-based radical, a hyd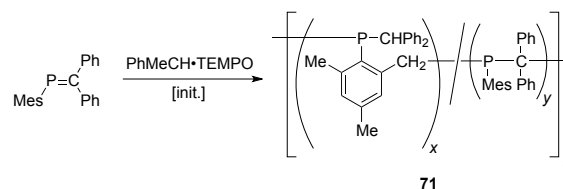rogen atom migrates from the *o*-Me of mesityl to this carbon radical. Thus, a benzylic radical is formed at the *o*-Me position that functions as the propagating species and accounts for the microstructure **71** (*x* >> *y*). The same microstructure has since been observed in PMPs synthesized by anionic polymerization (e.g. **67d-e**).[251]

Scheme 60 Alternative microstructure of poly(methylenephosphine) using a nitroxide-mediated radical polymerization initiator.

4.13 Poly(arylene/vinylene/ethynylene phosphine)s

Polymer **72**, the first well-characterized example of a poly(arylenephosphine), was prepared using nickel-catalyzed homocoupling (Scheme 61, M_n = 15 300 g mol^{-1}, PDI = 1.65).[259] An unoxidized *P*-alkyl derivative was synthesized by the palladium(0)-catalyzed coupling of 4,4'-diiodobiphenyl and a primary alkylphosphine, albeit in lower molecular weight (M_n = 3 100 g mol^{-1}).[260] Similar polymers have been synthesized by nucleophilic aromatic substitution reactions.[261, 262]
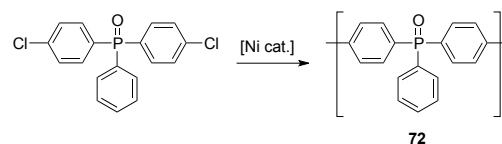
Scheme 61 Nickel-catalyzed cross-coupling of bis(4-chlorophenyl)phenylphosphine oxide to afford a poly(arylenephosphine oxide).

The first true phosphorus analogue of polyaniline, poly(*p*-phenylenephosphine) (**73**), was synthesized by palladium(0)-catalyzed cross-coupling of 1,4-diiodobenzene and a primary phosphine to afford low molecular weight materials (Scheme 62, M_n = 1 300 − 3 100 g mol^{-1}, PDI = 1.3 − 1.5).[263] This approach was extended to the synthesis of a series of poly(*p*-phenylenephosphine)/polyaniline copolymers.[264] Interestingly, photophysical measurements suggested significant conjugation through the phosphine moiety. Transition metal-catalyzed hydrophosphorylation has been used to prepare polymers with both arylenephosphine and vinylenephosphine moieties in the main chain.[265]

R = iBu, Ph, 2,4,4-trimethylpentyl
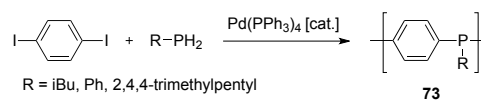
Scheme 62 Synthesis of poly(*p*-phenylenephosphine)s by palladium-catalyzed cross-coupling.

Related macromolecules that incorporate unsaturated organic moieties next to phosphorus include macromolecules composed of alkenyl- or alkynyl-phosphine backbones. The anionic ROP of a phosphirene affords poly(vinylenephosphine) **74**, the first example of a polymer containing only vinylene and phosphine units in the main chain (Scheme 63, M_n = 1 700 − 18 000 g mol^{-1}, PDI = 1.23 − 1.58).[266] Some molecular weight control was demonstrated by varying the monomer to initiator ratio.
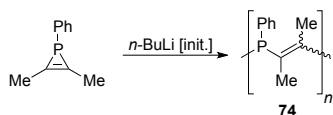
Scheme 63 Anion-initiated ROP of a phosphirene to yield a poly(vinylenephosphine).

Subsequently, an alternate methodology has been developed to produce poly(vinylenephosphine)s. In particular, treatment of *cyclo*-(PMe)$_5$ with phenylacetylene in the presence of the radical initiator AIBN results in polymer **75** with low molecular weight (Scheme 64, M_n = 2 500 g mol^{-1}, PDI = 1.25).[267] This strategy was adapted from earlier work on the synthesis of polymers containing heavier group 15 congeners (vide infra), however lower molecular weights were observed for phosphorus.
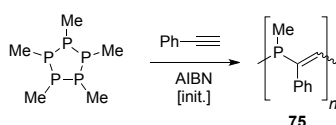
Scheme 64 Radical copolymerization of a cyclo-pentaphosphine with a primary alkyne to generate a poly(vinylenephosphine).

Recently, the first example of a poly(*p*-phenylenediethynylene phosphine) (PPYP) was reported.[268] PPYP **76** was synthesized by nickel-catalyzed cross-coupling between a diethynylbenzene derivatives and dichlorophenylphosphine (M_n = 10 000 − 12 000 g mol^{-1}, PDI = 1.8 − 2.0, Scheme 65). Interestingly, this conjugated polymer shows blue fluorescence selectively upon oxidation of the phosphorus atoms (Fig. 13) despite that fact that both the unoxidized and oxidized polymers show similar features in their absorbance spectra (**76**: λ_{abs} = 289, 305, 317, 330 nm; **76**·O: λ_{abs} = 288, 298, 317, 329).
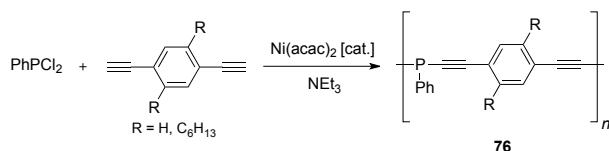
Scheme 65 Synthesis of poly(*p*-phenylenediethynylene phosphine)s by nickel-catalyzed cross-coupling.

Fig. 13 A photograph showing (left) a THF solution of poly(p-phenylenediethynylene phosphine) **76** (R = C$_6$H$_{13}$) and (right) an analogous solution of the phosphine oxide **76**·O. Both samples are being irradiated with a UV lamp.

4.14 phospha-PPVs

The first example of a linear polymer containing multiple bonds involving a low-valent heavier main group element was **77a**, a phosphorus analogue of poly(*p*-phenylenevinylene) (PPV) (Scheme 66).[269] Heating together 1,4-bis(disilylphosphino)benzene and tetramethyl terephthaloyl chloride afforded **77a** with approximately equal ratio of *E*- to *Z*-isomers for the P=C bonds. Employing a bulkier phosphorus monomer allowed for significantly greater stereoselectivity, such that polymer **77b** is in exclusively the *Z*-configuration.[270] The air-sensitivity of **77a-b** precluded determination of the absolute molecular weight by GPC analysis, however estimation by end-group analysis revealed modest molecular weights (M_n = 2 900 − 10 500 g mol^{-1}).
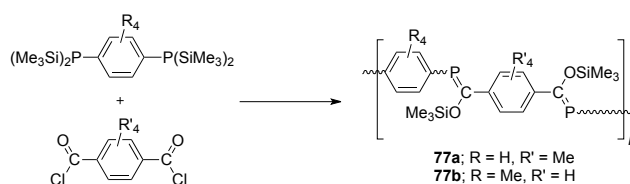
Scheme 66 Synthesis of poly(*p*-phenylenephosphaalkene)s employing the Becker reaction of a bis(disilylphosphine) and a bis(acyl chloride).

Phosphaalkene-containing PPV analogues have also been accessed by employing the phospha-Wittig reaction as the P=C bond forming step (Scheme 67).[271] In this approach, a bis(dichlorophosphine) was first treated with PMe$_3$ in the presence of zinc to generate a phospha-Wittig reagent. Subsequent addition of a dialdehyde afforded polymer **78** in predominantly the *E*-configuration. The molecular weights were estimated by end-group analysis (M_n = 6 500 g mol^{-1}).
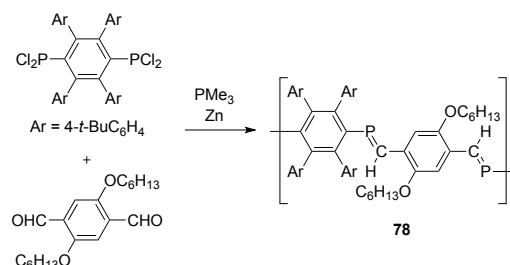
Scheme 67 Synthesis of a poly(*p*-phenylenephosphaalkene) by the phospha-Wittig reaction.

This strategy has been extended to the fascinating diphosphene-containing polymer **79**, the first example of a polymer containing a multiple bond between heavy main group elements in the backbone.[272] In this case, the phospha-Wittig intermediate was either photolyzed of thermolyzed to afford **79** (Scheme 68, M_n = 5900 g mol^{-1}, PDI = 2.1). Photophysical measurements revealed that the red polymer was not fluorescent in solution.
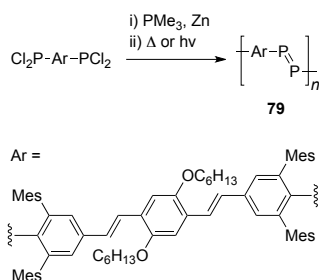
Scheme 68   Synthesis of a diphosphene-contaning polymer by a phospha-Wittig reaction.

4.15 Poly(phosphole)s

The incorporation of phosphole moieties into extended π-conjugated structures is a growing area of interest due to the fascinating photophysical properties of this P-heterocycle. The first phosphole-containing polymer (**80**) was synthesized by oxidative coupling using zirconocenes (Scheme 69).[273] The resulting metallacycle-containing polymer was then treated with dichlorophenylphosphine to generate the phosphole-containing macromolecule with moderate regioselectivity (M_n = 6200 g mol^{-1}, PDI = 2.6). Polymer **80** was found to be fluorescent (λ_{max} = 308 nm, λ_{em} = 470 nm), albeit with moderate quantum yield (Φ = 0.09).
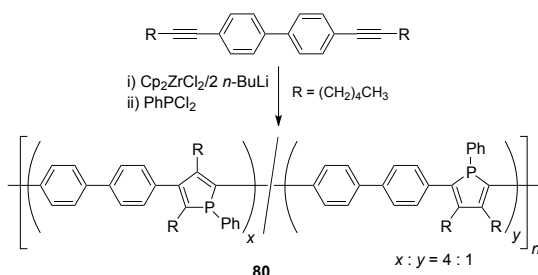
Scheme 69   Synthesis of a phosphole-containing polymer by zirconocene-mediated oxidative coupling.

A more common strategy is to first synthesize a phosphole-containing monomer using zirconocene coupling. This route was used in combination with Sonogashira coupling to synthesize a series of arylenephosphole-alkynylarene polymers (**81**: M_n = 6 800 − 10 200 g mol^{-1}, PDI = 1.3 − 1.5, Scheme 70).[274]
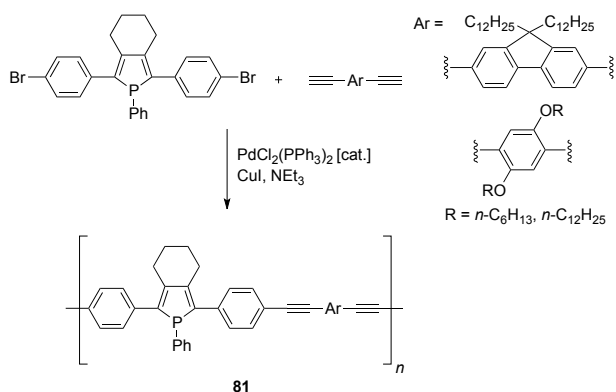
Scheme 70   Synthesis of a phosphole-containing polymer by Sonogashira coupling.

Classic synthetic routes to polythiophenes such as electropolymerization are not compatible with phosphole functionalities. Thus, researchers have turned their attention towards hybrid systems that combine the properties of phospholes with the well-developed chemistry of thiophenes. This has been demonstrated by synthesizing 2,5-bis(2-thienyl)phospholes followed by electropolymerization to yield insoluble polymeric films (**82**) (Scheme 71).[275, 276] The polymer bearing σ^3,λ^3-phosphole moieties was initially only accessible by the decomplexation of gold(I)-coordinated polymer **82e**,[277] however in a subsequent report, it was found a 2,5-bis(3,4-ethylenedioxythiophene)phosphole derivative could successfully be electropolymerized.[278] Poly[2,5-bis(2-thienyl)phosphole]s have also been prepared with sulfur-functionalized phospholes, bearing an additional site of reactivity for electronic tuning.[279] In all cases the insolubility of the films precluded molecular weight determination, however bathochromic shifts in the electronic absorption spectra relative to the monomer or model oligomers confirmed the presence of an extended conjugated system.
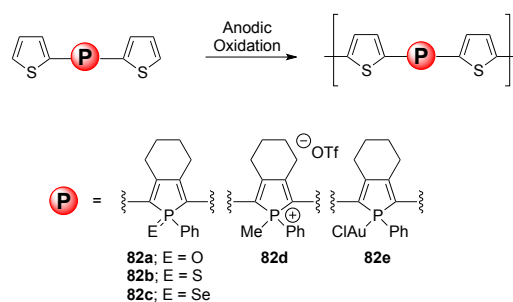
Scheme 71   Electropolymerization of 2,5-bis(2-thienyl)phospholes.

Polymers containing bis(thienyl)phosphole moieties have also been synthesized using Stille coupling.[280] Rather than coupling a pre-formed bis(thienyl)phosphole monomer, a phosphole and dithiophene can be directly coupled to afford similar materials to those described above with moderate molecular weight (M_n = 11 500 − 13 800 g mol^{-1}, PDI = 2.3 − 3.7). The electronic transition energies observed in the UV-Vis spectra were found to be affected by the substitution on phosphorus as well as whether the copolymer was in solution or a film.

Dithienophospholes, in which two thiophene rings are annulated to a phosphole core, can be incorporated into polymers to provide novel fluorescent materials (**83**, Fig. 14). This rigid tricyclic system offers greater conjugation, excellent fluorescence quantum yields and high molecular weights. Vinyl-functionalized dithienophospholes were first incorporated into the side chain of a polymer by copolymerization with styrene.[281, 282]

R_1 = TBDMS; R_2 = 4-(NMe$_2$)C$_6$H$_4$

83
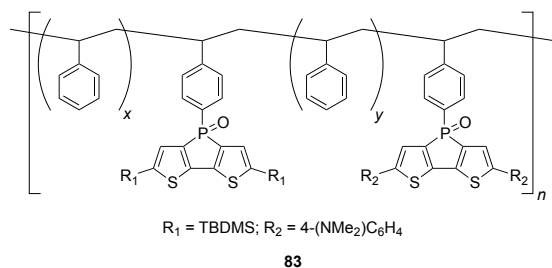
Fig. 14 White light emitting styrene-dithienophosphole copolymer.

Main-chain dithienophosphole polymers **84**-**86** have been synthesized using a series of transition metal cross-coupling strategies including Stille coupling,[283] platinum-catalyzed dehydrocoupling,[284] and Suzuki coupling[285] (Scheme 72). In some cases poor solubility precluded extensive molecular weight analysis of the polymers, however the Suzuki coupling route afforded **86** in moderate molecular weight and PDI (M_w = 9 800 g mol^{-1}, PDI = 1.7).
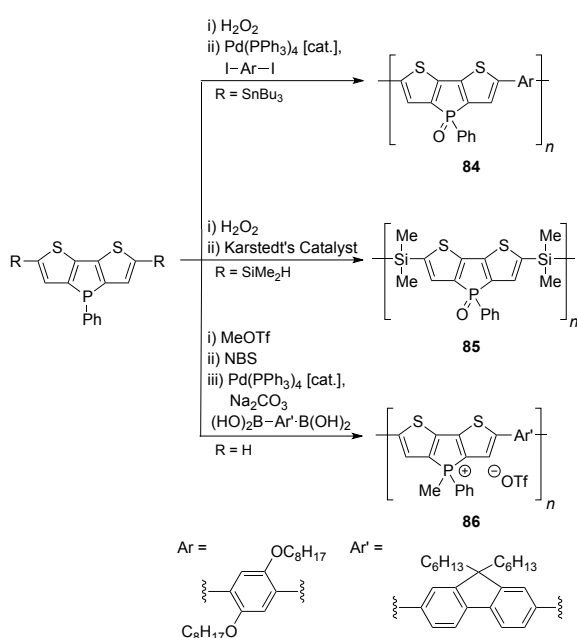
Scheme 72 Synthetic routes to polymers containing the dithienophosphole motif.

The phosphorus analogue of fluorene, dibenzophosphole, remains an underexplored motif in main-group polymer chemistry. In a singular study, dibenzophosphole/fluorene copolymers were synthesized by Suzuki coupling (M_n = 9 500 – 15 400 g mol^{-1}, PDI = 1.1 – 2.3).[286]

Recently, the first example of a homopolymer containing only *P*-oxide phosphole rings (**87**) was reported.[287, 288] This material was prepared by Stille-type cross-coupling of phosphole comonomers affording the moderate molecular weight polyphosphole (M_n = 13 000 g mol^{-1}, PDI = 2.3, Scheme 73). Efforts to reduce the phosphorus(V) moiety to the P(III) oxidation state were unsuccessful. In a related study, the analogous homopolymerization of *P*-alkanesulfonylimide phosphole provided access to poly(phosphole)s with P=NR rather than P=O moieties.[288]

Ar = OC$_{12}$H$_{25}$
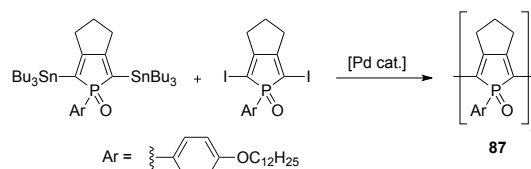
Scheme 73 Synthesis of a poly(phosphole) by Stille-type cross-coupling.

4.16 Miscellaneous phosphorus polymers

Enantiomerically pure *P*-chiral compounds are well established as ligands for asymmetric catalysis, but are relatively unexplored in macromolecular chemistry. Several novel optically active polymers (**88**) containing stereogenic phosphorus centers in the main chain have been isolated (Fig. 15).[289] Starting from known bifunctional chiral bisphosphines monomers the macromolecules were obtained via substitution,[289, 290] Sonogashira cross-coupling,[291, 292] or copper-catalyzed "click" reactions.[293]
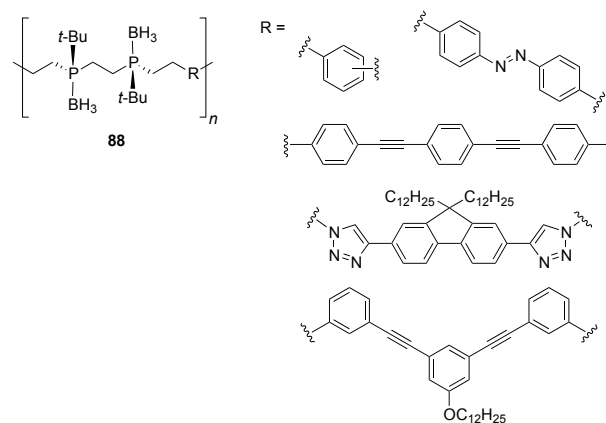
Fig. 15 Examples of P-chiral polymers.

Using a unique "migration insertion polymerization", an exciting new class of organophosphorus macromolecule has been synthesized using a carbonyl(phosphinoalkyl)iron(II) complex monomer (Scheme 74).[294] Upon heating, carbonyl insertion into the metal-carbon bond, followed by coordination of the pendant phosphine moiety, generated the linear iron and phosphorus-containing polymer **89** (M_n = 3 320 – 12 100 g mol^{-1}, PDI = 1.09 – 1.33).
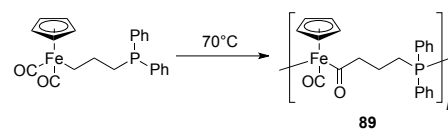
Scheme 74 Synthesis of a phosphino-iron containing polymer by migration insertion polymerization

4.2 Arsenic, antimony and bismuth

The first examples of heavier group 15-containing polymers, poly(vinylene arsine)s (**90**), were synthesized using a ring-collapsed radical alternating copolymerization (RCRAC).[295] Five- or six-membered cyclic oligoarsines and phenylacetylene

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were polymerized using either AIBN as a radical initiator or by irradiation with a xenon lamp (M_n = 5 000 – 11 500 g mol^{-1}, PDI = 1.4 – 4.3, Scheme 75). This interesting methodology is amenable to various acetylenic systems,[296, 297] and in some cases no initiator is necessary.[298] This strategy has been extended to the synthesis of poly(vinylene stibine)s[299] (M_n = 3 000 – 4 600 g mol^{-1}, PDI = 1.4 – 2.0) and poly(vinylene stibene)/poly(vinylene arsine) copolymers.[300]
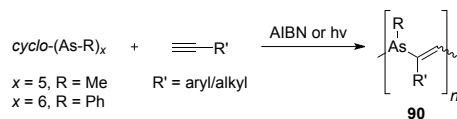
Scheme 75 Preparation of poly(vinylenearsine)s by copolymerizing cyclic oligoarsines and primary alkynes.

In a separate study, the five-membered cyclic oligoarsine $(AsMe)_5$ was first treated with 2,3-dimethyl-1,3-butadiene to afford a 1,2-diarsacyclohex-4-ene monomer.[301] Reaction of the cyclic monomer with styrene in the presence of AIBN, promotes the homolytic cleavage of the As-As bonds to afford a linear arsine/styrene copolymer (M_n = 12 000 – 16 400 g mol^{-1}, PDI = 1.2).

More recently, arsenic-containing polymer **91** has been obtained through condensation polymerization.[302] First, a diarsa-cyclohexadiene derivative with two acid anhydride moieties is synthesized followed by a dehydrating imidation with diamines to give the arsenic containing polyimide **91** (Scheme 76).
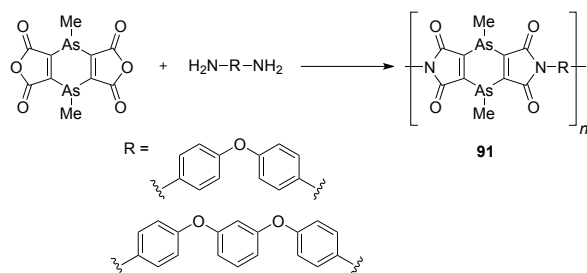
Scheme 76 Synthesis of an arsenic-containing polymer by dehydrating imidation.

To our knowledge, only one example exists of a linear polymer incorporating bismuth atoms in the main chain.[303] Using a modification of the zirconocene oxidative coupling strategy, a vinyl iodide-containing polymer was synthesized. Treatment of this polymer with *n*-BuLi followed by addition of PhBiBr$_2$ afforded the conjugated bismole-containing polymer **92** (M_n = 3 400 g mol^{-1}, PDI = 3.6, Scheme 77). The dark green polymer exhibited blue fluorescence (λ_{abs} = 311 nm, λ_{em} = 440 nm, Φ = 0.13).
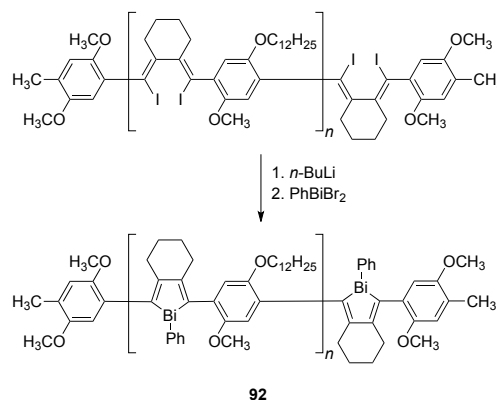
Scheme 77 Synthesis of a bismole-containing macromolecule.

5 Group 16 elements

Polymers featuring chalcogens in the main chain have a long history and continue to be of substantial academic and industrial importance.[304, 305] The vulcanization of rubber using elemental sulfur, first established in the early 19th century, continues to be of commercial importance in the manufacture of materials such as tires, hoses and hockey pucks. Polysulfones and poly(*p*-phenylene sulfide)s are used commercially in thermoplastics due to their rigidity, high strength and chemical inertness. The fascinating and structurally complex poly(sulfur nitride), $(SN)_x$, is widely known for its superconductive properties. The poly(thiophene)s are gaining increasing recognition as organic semiconducting materials of the future. Materials incorporating these functionalities have found use in photovoltaic cells, organic light-emitting diodes, organic field effect transistors and chemical sensors. In this section, we will focus on the developments of new synthetic methodologies aspects of group 16 element-containing macromolecules with emphasis on recent developments. The broad and mature areas of poly(sulfur nitride)[306] and poly(thiophene)[307] will not be discussed and the reader is referred to recent reviews.

5.1 Sulfur

5.11 Polysulfur

The thermal ROP of elemental sulfur is a fascinating demonstration used in undergraduate chemistry classes. The multistep polymerization process is well understood (Scheme 78),[308] with the first step occurring at 95.3 °C where S_8 is converted from its α- to β-form. Upon melting at 119.6 °C, S_8 equilibrates with other rings (e.g. S_6-S_9) and at 159.4 °C, the λ temperature, a large increase in viscosity is observed as polysulfur **93** is formed. Rapid cooling and/or precipitation affords sulfur rubber. Remarkably, the molecular weight of sulfur rubber can be as high as 2 000 000 g mol^{-1}. Continued heating of the polymer is accompanied by a decrease in viscosity and a color change to dark red, at which point the composition consists of a mixture of S_x (x = 2-8), including S_2 in

the vapour. Polymeric sulfur **93** is metastable and at room temperature will slowly depolymerize to α-sulfur (S_8).
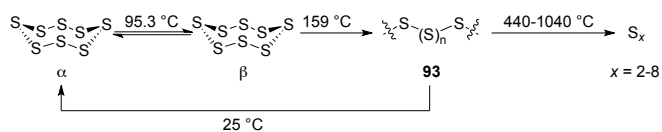
Scheme 78 The thermal ROP of elemental S_8 to afford sulfur rubber.

The prospect of commercializing polymers derived from elemental sulfur is tantalizing due to its ready availability as a by-product of the petrochemical industry. A key challenge is to find methods that inhibit the long-term depolymerization of long chains consisting solely of sulfur-sulfur linkages. The anionic copolymerization of sulfur and propylene sulfide to produce materials with (up to) an S_9 linear chain that do not depolymerize represents a key early development.[309] Despite this early advance, the development of stable catenated sulfur macromolecules remained largely unexplored until recently. A significant advance came with the incorporation of a high proportion of sulfur into a polymer chain using an "inverse vulcanization" strategy (Scheme 79).[310] Namely, treating S_8 with 1,3-diisopropenylbenzene at 185 °C results in a chemically stable material (**94**) with very high sulfur content (up to 90 wt%) and deep red colour. Significantly, this exciting technology is amenable to scale-up to kilogram quantities.[311]
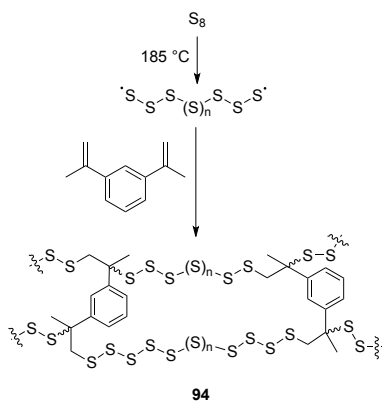
Scheme 79 Synthesis of polysulfur by inverse vulcanization of sulfur by using 1,3-diisopropenylbenzene.

Varying the feed ratio of the reactants using this "inverse vulcanization" strategy provides access to materials with diverse thermo-mechanical and optical properties (Fig. 16). For example, these high refractive index (n = 1.8) infrared transparent polysulfur materials[312] have been employed as polymeric electrodes for Li-S batteries,[313-315] and visible-light-active photoelectrocatalysts for water splitting.[316] Composites of polymer **94** with CdS, PbS, Fe_3O_4, CoO, InP/ZnS quantum dots and gold nanoparticles have been reported.[317-319] In related work, treating S_8 with aqueous Na_2S followed by reaction with 1,2,3 trichloropropane has been shown to make sulfur rich nanoparticles in an interfacial polymerization.[320]

Fig. 16 Film of inverse vulcanized polysulfur **94**. Image provided courtesey of Prof. J. Pyun.

5.12 Poly(oxothiazene)s

The synthesis of poly(oxothiazene)s (**95**, R = alkyl, aryl) bears a resemblance to both polyphosphazenes and poly(thionylphosphazene)s (see Section 4.11). The first well-characterized examples were synthesized by the thermal condensation of sulfonimidates (Scheme 80),[321, 322] analogous to the phosphoranimine route to polyphosphazenes. More recently, the synthesis of poly(oxothiazene)s using an ambient temperature PCl_5-catalyzed polymerization of sulfonimidates was reported (Scheme 80).[323] This affords poly(oxothiazene)s of high molecular weight and low PDIs (**95**: M_w = 67 000 − 3 300 000 g mol^{-1}, PDI = 1.2 − 1.6).
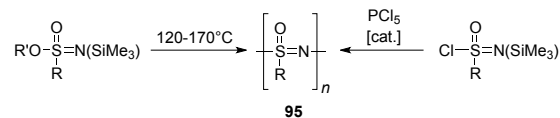
Scheme 80 Synthetic routes to poly(oxothiazene)s.

5.13 Poly(arylene sulfide)s

Poly(p-phenylene sulfide) (Ryton®) is a commercial organosulfur polymer produced from 1,4-dichlorobenzene and sodium sulfide. A variety of related sulfide-containing macromolecules have been prepared from the thermal ROP of cyclic aryl disulfides.[324-326] The radical-initiated copolymerization of cyclic disulfides with elemental sulfur at 200 °C affords insoluble polysulfanes, **96a**, with up to 7 S–S linkages (Scheme 81).[327] The thermal ring-opening of cyclic disulfides leads to radical products that react with a variety of dihaloarylenes in the presence of KI at high temperature to give **96b**.[325] Similar cyclic aromatic disulfides with oxygen linkers have been seen to undergo similar reactivity (Scheme 81).[328]
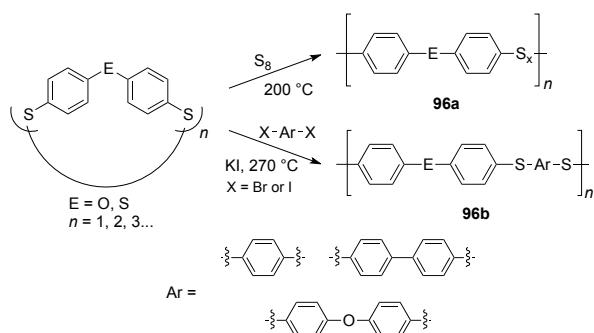
Scheme 81   ROP of cyclic sulfides to afford poly(*p*-phenylene sulfide)s.

5.2 Selenium

5.21 Poly(selenophene)s

The selenium analogue of thiophene, selenophene, is the most important functional group in selenium-containing polymers.[329] Due to the decreased electronegativity and larger size of selenium compared to sulfur, selenophenes are more polarizable than thiophenes and thus are better at stabilizing charge upon doping. Theoretical[330, 331] and experimental[332] studies have demonstrated that poly(selenophene)s have lower band gaps than polythiophenes, even approaching those of commonly used inorganic thin film semiconductors (e.g CdTe: E_g = 1.5 eV). Given these potential properties, the study of poly(selenophene)s has recently entered a significant growth phase.

Initial efforts to synthesize poly(selenophene) **97** by electrochemical methods produced dark coloured films which were difficult to characterize (Scheme 82).[333-340] Electrical conductivity measurements of polymers made by this method were highly dependant on the quality of the films produced.[338, 341, 342] Classical routes to **97** also include oxidative chemical polymerization using FeCl₃[343, 344] and Kumada coupling (Scheme 82).[332, 345] More recently, poly(3-hexylselenophene) and poly (3-hexylselenophene-alt-3-hexylthiophene) were synthesized by C-H arylation polymerization using a palladium catalyst with N-heterocyclic carbene ligands.[346]
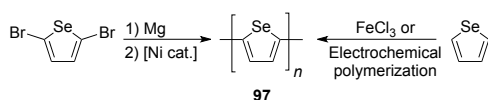
Scheme 82   Classical Routes to Insoluble Polyselenophenes.

Due to the commercial success of poly(3,4-ethylenedioxythiophene) (PEDOT),[347] the selenium analogue poly(3,4-ethylenedioxyselenophene) (PEDOS, **98**) is of considerable current interest and, thus, has been comprehensively reviewed.[348, 349] Despite the challenging synthesis of the EDOS monomer,[350, 351] its polymerization has been accomplished either by electrochemical reduction or by employing FeCl₃ (Scheme 83).[351] Alternatively, bromination of EDOS afforded the 2,5-dibromo monomer that undergoes

nickel(0)-mediated homocoupling. The solid-state reaction of 2,5-dibromo or 2,5-diiodo-3,4-ethylenedioxyselenophene provided an additional method to PEDOS.
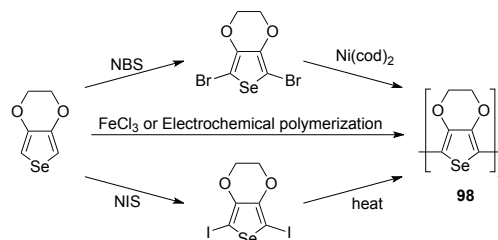
Scheme 83   Synthetic routes to poly(3,4-ethylenedioxyselenophene) (PEDOS).

In related work, the Suzuki coupling of 2,5-bis(pinacol borane)selenophene with a diiodofluorene derivative permitted access to a selenophene-fluorene copolymer.[352] MALDI-TOF mass spectrometry suggested modest molecular weight (≤ 5 000 g mol⁻¹) for this blue-fluorescent material that is attractive for PLED applications (λ_{abs} = 389 nm, λ_{em} = 458 nm, Φ = 0.012).

Kumada coupling has been used to make block[353] and gradient[354] copolymers of selenophenes and thiophenes. Random copolymers have been made by electrochemical polymerization.[355] A variety of polyselenophenes with large aromatic co-monomers[356-361] and alternating selenophene-vinylene macromolecules[362] have been synthesized via Stille cross-coupling.

Group 16 heteroles have been incorporated into poly(*p*-phenylene vinylene) using a Wittig reaction (Scheme 84).[363] In contrast to insoluble poly(selenophane)s **97** and **98**, the molecular weights of the solution-processable sulfur-, selenium- or tellurium-containing materials **99a-c** can be obtained (**99a**: M_n = 12 000 g mol⁻¹; **99b**: M_n = 11 000 g mol⁻¹; **99c**: M_n = 7 000 g mol⁻¹) in moderate molecular weights. An alternating copolymer of selenophene and aniline has been reported by chemical oxidation using FeCl₃.[364]
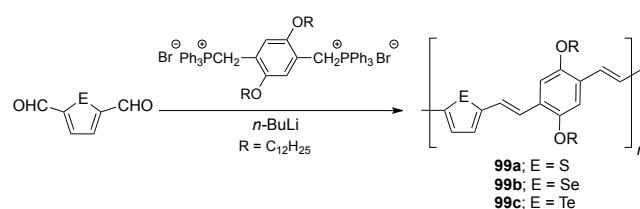
Scheme 84   A Wittig polymerization to afford soluble vinylene-macromolecules containing thiophene, selenophene and tellurophene.

A recent report detailed an alternative synthesis of selenophene-phenylene copolymers following a titanacyclopentadiene oxidative coupling strategy (Scheme 85).[365] Addition of Se₂Cl₂ to titanium polymer **100** in the presence of ambient light afforded selenophene polymer **101** in moderate molecular weight (M_n = 5 700 g mol⁻¹). This soluble material was fluorescent in solution (λ_{abs} = 434 nm, λ_{em} = 540 nm).
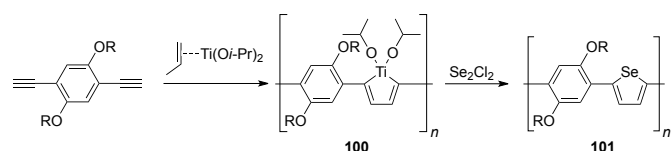
Scheme 85 A route to poly(phenylene selenophene) using the Fagan-Nugent reaction.

5.22 Other Selenium-Containing Polymers

The incorporation of selenides and diselenides into polymer backbones has garnered recent attention as potential biomaterials for drug release (Fig. 17).[366, 367] Selenium atoms were incorporated between two large polymer blocks, typically polyethylene glycol, to give novel materials **102**.[368, 369] These amphiphilic macromolecules and their supramolecular structures undergo significant change in response to different mediums. The selenium environment plays a pivotal role in the supramolecular structure. For example, oxidation of selenium atoms with hydrogen peroxide leads to disassembly of the micelles in aqueous solution.
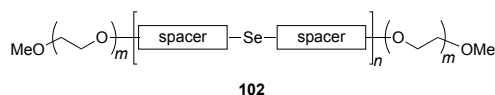
Fig. 17 Amphiphilic selenium-containing macromolecule containing polyethylene glycol. The spacer is a polyurethane incorporating long alkylene (C-11) units adjacent to Se.

5.3 Tellurium

5.31 Poly(tellurophene)s

The heaviest stable group 16 element has only been incorporated into polymers in the form of tellurophene. Despite being the least studied chalcogen heterocycle, they have great potential as semiconducting materials.[370] Tellurophenes have a lower band gap, are more polarizable than thiophenes or selenophenes, and exhibit Te-Te interactions, potentially aiding charge transport throughout a polymeric structure.[371]

Poly(tellurophene) was first obtained by the oxidative polymerization of tellurophene vapour with a $FeCl_3$ catalyst to yield an insoluble film.[372] Despite various reports of poly(tellurophene)s as powders or films over the next few years, characterization of these materials was limited due to their insolubility.[373-375]

A key breakthrough in this field came with the synthesis of a solution-processable poly(3-alkyltellurophene)s using a Kumada-type coupling (Scheme 86).[376] Specifically, the nickel(II)-catalyzed homocoupling of *in situ* formed Grignard reagents derived from 2,5-diiodo-3-alkyltellurophenes affords soluble tellurophene macromolecules **103a-c** ($M_n = 5\,400 - 11\,300$ g mol^{-1}). Analysis of the materials using ^{1}H NMR spectroscopy confirmed that the polymerization reaction was highly regioselective. In a separate study, regioregular poly(3-dodecyltellurophene) **103c** was obtained in substantially

higher molecular weight ($M_n = 20\,000$ g mol^{-1}) utilizing a polycondensation Suzuki-coupling reaction.[377]
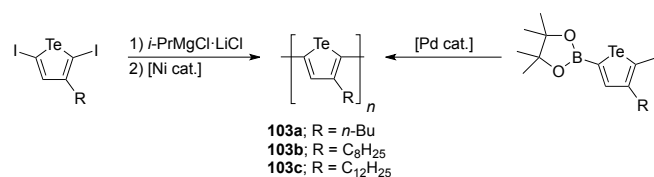
Scheme 86 Routes to solution-processible poly(tellurophene)s using Kumada and Suzuki catalysts.

Several tellurophene-containing copolymers have been synthesized using Stille coupling (Scheme 87) or Suzuki coupling (Scheme 88). This methology permitted the preparation of copolymers featuring tellurophene and cyclopentadithiophene (**104a**),[361] diketopyrrolopyrrole (**104b** and **106**),[378, 379] isoindigo (**104c**),[360] or fluorene (**105**).[380] Copolymer **104b** has recently been prepared using a novel palladium-catalyzed arylative polymerization of the dibromo-functionalized ketopyrole precursor and tellurophene bearing diphenyl(hydroxy)methyl groups in the 2- and 5-positions.[381] Polymers **104b** and **105** undergo distinct colour changes when oxidized at Te with elemental bromine and have been investigated as sensory materials.
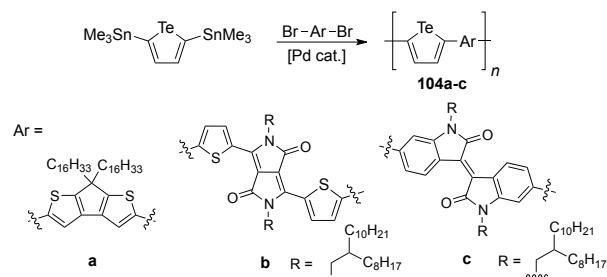
Scheme 87 π-Conjugated tellurophene-containing macromolecules prepared using Stille coupling.
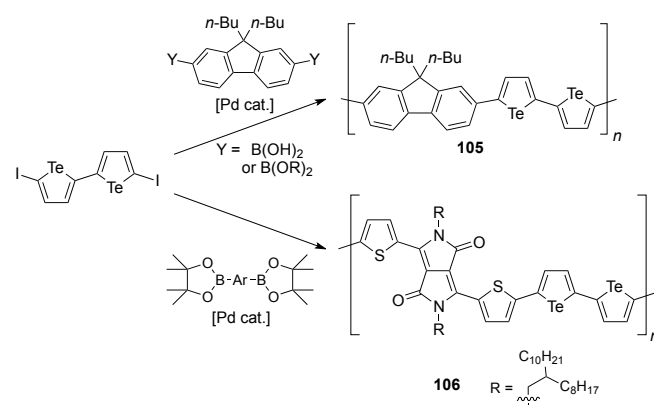
Scheme 88 Suzuki-catalyzed routes to tellurophene-containing copolymers.

The fascinating macromolecule **107** containing the group 16 trifecta of thiophene, selenophene, and tellurophene has been developed (Scheme 89).[352] This modest molecular weight material ($M_n = 4\,300$ g mol^{-1}, PDI = 1.62) does not luminesce

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either in solution or the solid state. Interestingly, films of **107** absorb at significantly lower energy than in solution ($\Delta\lambda \approx 80$ nm), consistent with an increase in conjugation length in the solid state.
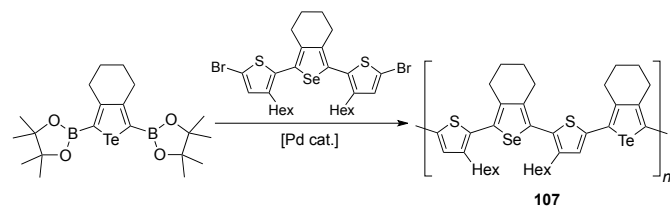
Scheme 89 A copolymer containing thiophene, selenophene and tellurophene moieties accessed by Suzuki coupling.

6 Conclusions

Main group element-containing macromolecules are now more accessible than ever due to the tremendous advances in synthetic metholodies for inorganic elements that have emerged over the last two decades. Once dominated by three main classes of polymer (polysiloxanes, polyphosphazenes and polysilanes), the field has grown to include the majority of the elements of groups 13-16. The relative ease with which previously unknown inorganic monomers can be isolated, combined with the advent of novel techniques to link monomers into long chains, has resulted in unimagined structural diversity for polymers of the p-block elements.

The next two decades, and indeed even further in the future, will undoubtedly see even more exciting progress in the field. There is a great likelihood that, due to their unique physical, chemical and electronic properties, p-block element-containing macromolecules will evolve from purely being academic curiosities to being commercially relevant materials.

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Notes and references

‡ The authors (Priegert, Rawe and Serin) each contributed equally to the writing of this manuscript. Their names are listed in alphabetical order.

1   See, for example: (*a*) G. R. Wittell, M. D. Hager, U. S. Schubert, and I. Manners, *Nat. Chem.* 2011, **10**, 176; (*b*) T. Chivers and I. Manners, *Inorganic rings and polymers of the p-block elements: from fundamentals to applications*, RSC Publishing, Cambridge, 2009; (*c*) J. E.

Mark, H. R. Allcock, and R. West, *Inorganic polymers*, Oxford University Press, New York, 2nd Edn., 2005; (*d*) V. Chandrasekhar, *Inorganic and organometallic polymers*, Springer, Berlin, 2005; (*e*) I. Manners, *Synthetic metal-containing polymers*, Wiley-VCH, Weinheim, 2004; (*f*) I. Manners, *Science*, 2001, **294**, 5547; (*g*) R. D. Archer, *Inorganic and organometallic polymers*, Wiley, New York, 2001; (*h*) P. Nguyen, P. Gomez-Elipe, and I. Manners, *Chem. Rev.*, 1999, **99**, 1515; (*i*) I. Manners, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 1603; (*j*) J. E. Mark, H. R. Allcock, and R. West, *Inorganic polymers*, Prentice Hall, New Jersey, 1992.

2   See, for example: (*a*) F. Jäkle, *Top. Organometal. Chem.*, 2015, **49**, 297; (*b*) K. Tanaka and Y. Chujo, *Macromol. Rapid Commun.*, 2012, **33**, 1235; (*c*) F. Jäkle, *Chem. Rev.*, 2010, **110**, 3985; (d) F. Jäkle, *Coord. Chem. Rev.*, 2006, **250**, 1107.

3   R. T. Paine and C. K. Narula, *Chem. Rev.*, 1990, **90**, 73.

4   L. G. Sneddon, M. G. L. Mirabelli, A. T. Lynch, P. J. Fazen, K. Su, and J. S. Beck, *Pure Appl. Chem.*, 1991, **63**, 407.

5   K. Su, E. E. Remsen, H. M. Thompson, and L. G. Sneddon, *Macromolecules*, 1991, **24**, 3760.

6   Y. Chujo, I. Tomita, N. Murata, H. Mauermann, and T. Saegusa, *Macromolecules*, 1992, **25**, 27.

7   F. Matsumoto and Y. Chujo, *J. Organomet. Chem.*, 2003, **680**, 27.

8   N. Matsumi, T. Umeyama, and Y. Chujo, *Macromolecules*, 2001, **34**, 3510.

9   M. Miyata, N. Matsumi, and Y. Chujo, *Macromolecules*, 2001, **34**, 7331.

10   Y. Nagata and Y. Chujo, *Macromolecules*, 2007, **40**, 6.

11   Y. Nagata and Y. Chujo, *Macromolecules*, 2008, **41**, 2809.

12   Y. Tokoro, A. Nagai, and Y. Chujo, *Macromolecules*, 2010, **43**, 6229.

13   Y. Nagata and Y. Chujo, *Macromolecules*, 2008, **41**, 3488.

14   Y. Tokoro, A. Nagai, and Y. Chujo, *J. Polym. Sci. Part A: Polym. Chem.*, 2010, **48**, 3693.

15   Y. Tokoro, A. Nagai, K. Kokado, and Y. Chujo, *Macromolecules*, 2009, **42**, 2988.

16   A. Nagai, K. Kokado, Y. Nagata, and Y. Chujo, *Macromolecules*, 2008, **41**, 8295.

17   H. Li and F. Jäkle, *Macromolecules*, 2009, **42**, 3448.

18   A. Nagai, S. Kobayashi, Y. Nagata, K. Kokado, H. Taka, H. Kita, Y. Suzuri, and Y. Chujo, *J. Mater. Chem.*, 2010, **20**, 5196.

19   H. Li and F. Jäkle, *Angew. Chem., Int. Ed.*, 2009, **48**, 2313.

20   M. Benstead, G. H. Mehl, and R. W. Boyle, *Tetrahedron*, 2011, **67**, 3573.

21   M. Zhu, L. Jiang, M. Yuan, X. Liu, C. Ouyang, H. Zheng, X. Yin, Z. Zuo, H. Liu, and Y. Li, *J. Polym. Sci. Part A: Polym. Chem.*, 2008, **46**, 7401.

22   V. R. Donuru, G. K. Vegesna, S. Velayudham, S. Green, and H. Liu, *Chem. Mater.*, 2009, **21**, 2130.

23   V. R. Donuru, G. K. Vegesna, S. Velayudham, G. Meng, and H. Liu, *J. Polym. Sci. Part A: Polym. Chem.*, 2009, **47**, 5354.

24   B. C. Popere, A. M. Della Pelle, and S. Thayumanavan, *Macromolecules*, 2011, **44**, 4767.

25   A. Nagai and Y. Chujo, *Macromolecules*, 2010, **43**, 193.

26   Y. Cakmak and E. U. Akkaya, *Org. Lett.*, 2009, **11**, 85.

27   S. Zhu, J. Zhang, J. Janjanam, J. Bi, G. Vegesna, A. Tiwari, F.-T. Luo, J. Wei, and H. Liu, *Anal. Chim. Acta*, 2013, **758**, 138.

28   H. Chong, C. Nie, C. Zhu, Q. Yang, L. Liu, F. Lv, and S. Wang, *Langmuir*, 2012, **28**, 2091.

29   Y. Zhou, Z. Zhou, Y. Li, and W. Yang, *Catal. Commun.*, 2015, **64**, 96.

30   R. Yoshii, H. Yamane, A. Nagai, K. Tanaka, H. Taka, H. Kita, and Y. Chujo, *Macromolecules*, 2014, **47**, 2316.

31   R. Yoshii, A. Nagai, K. Tanaka, and Y. Chujo, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, **51**, 1726.

32   S. P. Economopoulos, C. L. Chochos, H. A. Ioannidou, M. Neophytou, C. Charilaou, G. A. Zissimou, J. M. Frost, T. Sachetan, M. Shahid, J. Nelson, M. Heeney, D. D. C. Bradley, G. Itskos, P. A. Koutentis, and S. A. Choulis, *RSC Adv.*, 2013, **3**, 10221.

33   F. Matsumoto and Y. Chujo, *Macromolecules*, 2003, **36**, 5516.

34   F. Matsumoto, Y. Nagata, and Y. Chujo, *Polym. Bull.*, 2005, **53**, 155.

35   A. W. Baggett, F. Guo, B. Li, S.-Y. Liu, and F. Jäkle, *Angew. Chem., Int. Ed.*, 2015, **54**, 11191.

36   T. B. Marder, *Angew. Chem., Int. Ed.*, 2007, **46**, 8116.

37   C. W. Hamilton, R. T. Baker, A. Staubitz, and I. Manners, *Chem. Soc. Rev.*, 2009, **38**, 279.

38   C. A. Jaska, K. Temple, A. J. Lough, and I. Manners, *Chem. Commun.*, 2001, 962.

39   C. A. Jaska, K. Temple, A. J. Lough, and I. Manners, *J. Am. Chem. Soc.*, 2003, **125**, 9424.

40   A. Staubitz, A. Presa Soto, and I. Manners, *Angew. Chem., Int. Ed.*, 2008, **47**, 6212.

41   A. Staubitz, M. E. Sloan, A. P. M. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. S. a. d. Günne, and I. Manners, *J. Am. Chem. Soc.*, 2010, **132**, 13332.

42   N. E. Stubbs, A. P. M. Robertson, E. M. Leitao, and I. Manners, *J. Organomet. Chem.*, 2013, **730**, 84.

43   H. C. Johnson, A. P. M. Robertson, A. B. Chaplin, L. J. Sewell, A. L. Thompson, M. F. Haddow, I. Manners, and A. S. Weller, *J. Am. Chem. Soc.*, 2011, **133**, 11076.

44   R. T. Baker, J. C. Gordon, C. W. Hamilton, N. J. Henson, P.-H. Lin, S. Maguire, M. Murugesu, B. L. Scott, and N. C. Smythe, *J. Am. Chem. Soc.*, 2012, **134**, 5598.

45   H. C. Johnson, E. M. Leitao, G. R. Whitten, I. Manners, G. C. Lloyd-Jones, and A. S. Weller, *J. Am. Chem. Soc.*, 2014, **136**, 9078.

46   S. Bhunya, T. Malakar, and A. Paul, *Chem. Commun.*, 2014, **50**, 5919.

47   T. Malakar, L. Roy, and A. Paul, *Chem. Eur. J.*, 2013, **19**, 5812.

48   O. J. Metters, A. M. Chapman, A. P. M. Robertson, C. H. Woodall, P. J. Gates, D. F. Wass, and I. Manners, *Chem. Commun.*, 2014, **50**, 12146.

49   H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough, and I. Manners, *J. Am. Chem. Soc.*, 2000, **122**, 6669.

50   H. Dorn, J. M. Rodezno, B. Brunnhöfer, E. Rivard, J. A. Massey, and I. Manners, *Macromolecules*, 2003, **36**, 291.

51   T. J. Clark, J. M. Rodezno, S. B. Clendenning, S. Aouba, P. M. Brodersen, A. J. Lough, H. E. Ruda, and I. Manners, *Chem. Eur. J.*, 2005, **11**, 4526.

52   A. Schäfer, T. Jurca, J. Turner, J. R. Vance, K. Lee, D. Van An, M. F. Haddow, G. R. Whittell, and I. Manners, *Angew. Chem., Int. Ed.*, 2015, **54**, 4836.

53   C. Thoms, C. Marquardt, A. Y. Timoshkin, M. Bodensteiner, and M. Scheer, *Angew. Chem., Int. Ed.*, 2013, **52**, 5150.

54   C. Marquardt, T. Jurca, K.-C. Schwan, A. Stauber, A. V. Virovets, G. R. Whittal, I. Manners, M. Scheer, *Angew. Chem. Int. Ed.* 2015, **54**, DOI: 10.1002/ange.201507084.

55   Y. Chujo, I. Tomita, and T. Saegusa, *Macromolecules*, 1990, **23**, 687.

56   Y. Chujo, I. Tomita, Y. Hashiguchi, H. Tanigawa, E. Ihara, and T. Saegusa, *Macromolecules*, 1991, **24**, 345.

57   R. J.-P. Corriu, T. Deforth, W. E. Douglas, G. Guerrero, T. Deforth, and W. S. Siebert, *Chem. Commun.*, 1998, 963.

58   N. Matsumi, K. Naka, and Y. Chujo, *J. Am. Chem. Soc.*, 1998, **120**, 5112.

59   N. Matsumi, M. Miyata, and Y. Chujo, *Macromolecules*, 1999, **32**, 4467.

60   Y. Chujo, Y. Sasaki, N. Kinomura, and N. Matsumi, *Polymer*, 2000, **41**, 5047.

61   A. Nagai, T. Murakami, Y. Nagata, K. Kokado, and Y. Chujo, *Macromolecules*, 2009, **42**, 7217.

62   N. Sato, H. Ogawa, F. Matsumoto, Y. Chujo, and T. Matsuyama, *Synth. Met.*, 2005, **154**, 113.

63   M. Miyata, N. Matsumi, and Y. Chujo, *Polym. Bull.*, 1999, **42**, 505.

64   N. Matsumi, T. Umeyama, and Y. Chujo, *Polym. Bull.*, 2000, **44**, 431.

65   N. Matsumi, K. Naka, and Y. Chujo, *J. Am. Chem. Soc.*, 1998, **120**, 10776.

66   A. Sundararaman, M. Victor, R. Varughese, and F. Jäkle, *J. Am. Chem. Soc.*, 2005, **127**, 13748.

67   A. Lorbach, M. Bolte, H. Li, H.-W. Lerner, M. C. Holthausen, F. Jäkle, and M. Wagner, *Angew. Chem., Int. Ed.*, 2009, **48**, 4584.

68   J. Chai, C. Wang, L. Jia, Y. Pang, M. Graham, and S. Z. D. Cheng, *Synth. Met.*, 2009, **159**, 1443.

69   C. Reus, F. Guo, A. John, M. Winhold, H.-W. Lerner, F. Jäkle, and M. Wagner, *Macromolecules*, 2014, **47**, 3727.

70   C. J. Berger, G. He, C. Merten, R. McDonald, M. J. Ferguson, and E. Rivard, *Inorg. Chem.*, 2014, **53**, 1475.

71   V. D. B. Bonifácio, J. Morgado, and U. Scherf, *J. Polym. Sci. Part A: Polym. Chem.*, 2008, **46**, 2878.

This journal is © The Royal Society of Chemistry 2015

Chem. Soc. Rev. 2015, **00**, 1-3 | **27**

72   W. J. Niu, M. D. Smith, and J. J. Lavigne, *J. Am. Chem. Soc.*, 2006, **128**, 16466.

73   I. A. Adams and P. A. Rupar, *Macromol. Rapid Commun.*, 2015, **36**, 1336.

74   Y. Qin, G. L. Cheng, A. Sundararaman, and F. Jäkle, *J. Am. Chem. Soc.*, 2002, **124**, 12672.

75   K. Parab and F. Jäkle, *Macromolecules*, 2009, **42**, 4002.

76   K. Parab, K. Venkatasubbaiah, and F. Jäkle, *J. Am. Chem. Soc.*, 2006, **128**, 12879.

77   Y. Qin, G. Cheng, O. Achara, K. Parab, and F. Jäkle, *Macromolecules*, 2004, **37**, 7123.

78   K. Parab, A. Doshi, F. Cheng, and F. Jäkle, *Macromolecules*, 2011, **44**, 5961.

79   C. Z. Cui, E. M. Bonder, and F. Jäkle, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 6612.

80   C. Cui and F. Jäkle, *Chem. Commun.*, 2009, 2744.

81   C. Z. Cui, E. M. Bonder, and F. Jäkle, *J. Am. Chem. Soc.*, 2010, **132**, 1810.

82   M. H. Park, T. Kim, J. O. Huh, Y. Do, and M. H. Lee, *Polymer*, 2011, **52**, 1510.

83   W. Y. Sung, M. H. Park, J. H. Park, M. Eo, M. S. Yu, Y. Do, and M. H. Lee, *Polymer*, 2012, **53**, 1857.

84   T. Matsumoto, Y. Onishi, K. Tanaka, H. Fueno, K. Tanaka, and Y. Chujo, *Chem. Commun.*, 2014, **50**, 15740.

85   T. Matsumoto, K. Tanaka, and Y. Chujo, *Macromolecules*, 2015, **48**, 1343.

86   B. Bagh, J. B. Gilroy, A. Staubitz, and J. Müller, *J. Am. Chem. Soc.*, 2010, **132**, 1794.

87   M. S. Hill, P. B. Hitchcock, and R. Pongtavornpinyo, *Science*, 2006, **311**, 1904.

88   J. Chen and Y. Cao, *Macromol. Rapid Commun.*, 2007, **28**, 1714.

89   See, for example: (*a*) J. E. Mark, D. W. Schaefer and G. Lin, *The Polysiloxanes*, Oxford University Press, New York, 2015; (*b*) A. Watanabe in *Encyclopedia of polymeric nanomaterials*; S. Kobayashi and K. Müllen (Eds.); Springer, Berlin, 2015, p. 848; (*c*) A. M. Muzafarov (Ed.), *Silicon polymers*, Advances in Polymer Science Series 235; Springer, Berlin, 2011; (*d*) Y. Abe and T. Gunji, *Prog. Polym. Sci.*, 2004, **29**, 149; (*e*) R. Jones, W. Ando and J. Chojnowski (Eds.), *Silicon-containing polymers*, Springer Netherlands, 2000; (*f*) S. J. Clarson, J. J. Fitzgerald, M. J. Owen, S. D. Smith (Eds.), *Silicones and silicone-modified materials*, ACS Symposium Series 729; ACS, Washington, 2000; (*g*) L. V. Interrante, Q. Liu, I. Rushkin and Q. Shen, *J. Organomet. Chem.*, 1996, **521**, 1; (*h*) J. M. Zeigler and F. W. G. Fearon (Eds.), *Silicon-based polymer science: a comprehensive review*, ACS Symposium Series 224; ACS, Washington, 1990; (*i*) R. D. Miller and J. Michl, *Chem. Rev.*, 1989, **89**, 1359; (*j*) G. Fritz, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1111; (*k*) R. West, *J. Organomet. Chem.*, 1986, **300**, 327.

90   N. R. Thomas, *Silicon*, 2010, **2**, 187.

91   *See: Silicones: Preparation, Properties and Performance*, Dow Corning Corporation, Midland, MI, 2005 (Form No. 01-3077-01), based on an earlier publication: A. Colas, *Chimie Nouvelle*, 1990, **8**, 847.

92   M. Rodriguez, S. Marrot, T. Kato, S. Stérin, E. Fleury, and A. Baceiredo, *J. Organomet. Chem.*, 2007, **692**, 705.

93   L. V. Interrante, Q. Shen, and J. Li, *Macromolecules*, 2001, **34**, 1545.

94   B. G. G. Lohmeijer, G. Dubois, F. Leibfarth, R. C. Pratt, F. Nederberg, A. Nelson, R. M. Waymouth, C. Wade, and J. L. Hedrick, *Org. Lett.*, 2006, **8**, 4683.

95   B. Marciniec, *Silicon Chem.*, 2002, **1**, 155.

96   S. Putzien, O. Nuyken, and F. E. Kühn, *Prog. Polym. Sci.*, 2010, **35**, 687.

97   P. J. Miller and K. Matyjaszewski, *Macromolecules*, 1999, **32**, 8760.

98   E. M. Maya, A. W. Snow, and L. J. Buckley, *Macromolecules*, 2002, **35**, 460.

99   P. Boehm, M. Mondeshki, and H. Frey, *Macromol. Rapid Commun.*, 2012, **33**, 1861.

100   Z. Zhang, D. Sherlock, R. West, R. West, K. Amine, and L. J. Lyons, *Macromolecules*, 2003, **36**, 9176.

101   Y. Wu, Y. Huang, and H. Ma, *J. Am. Chem. Soc.*, 2007, **129**, 7226.

102   D. Henkensmeier, B. C. Abele, A. Candussio, and J. Thiem, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 3814.

103   B. P. S. Chauhan and P. Boudjouk, *Tetrahedron Lett.*, 2000, **41**, 1127.

104   See, for example: B. Marciniec (Ed.), "Hydrosilylation" in *Advances in silicon science,* Vol. 1; Springer, New York, 2009.

105   C. Kim, K. Kwark, and C.-G. Song, *Appl. Organomet. Chem.*, 2005, **19**, 108.

106   B. P. S. Chauhan and P. Boudjouk, *Tetrahedron Lett.*, 1999, **40**, 4123.

107   K. D. Safa, S. Tofangdarzadeh, and A. Hassanpour, *J. Organomet. Chem.*, 2009, **694**, 4107.

108   Y. Li and Y. Kawakami, *Macromolecules*, 1999, **32**, 3540.

109   Y. Li and Y. Kawakami, *Macromolecules*, 1999, **32**, 8768.

110   Y. Kawakami, Y. Li, Y. Liu, M. Seino, C. Pakjamsai, M. Oishi, Y. Cho, and I. Imae, *Macromol. Res.*, 2004, **12**, 156.

111   J.-Y. Moon, T. Miura, I. Imae, D.-W. Park, and Y. Kawakami, *Silicon Chem.*, 2002, **1**, 139.

112   Y. Li, M. Seino, and Y. Kawakami, *Macromolecules*, 2000, **33**, 5311.

113   Y. Li and Y. Kawakami, *Macromolecules*, 1999, **32**, 6871.

114   M. Oishi, J.-Y. Moon, W. Janvikul, and Y. Kawakami, *Polym. Int.*, 2001, **50**, 135.

115   J. M. Mabry, J. K. Paulasaari, and W. P. Weber, *Polymer*, 2000, **41**, 4423.

116   J. M. Mabry, M. K. Runyon, and W. P. Weber, *Macromolecules*, 2002, **35**, 2207.

117   P. N. Reddy, B. P. S. Chauhan, T. Hayashi, and M. Tanaka, *Chem. Lett.*, 2000, **29**, 250.

118   J. M. Mabry, M. K. Runyon, and W. P. Weber, *Macromolecules*, 2001, **34**, 7264.

119   R. West, L. D. David, P. I. Djurovich, K. L. Stearley, K. S. V. Srinivasan, and H. Yu, *J. Am. Chem. Soc.*, 1981, **103**, 7352.

120   M. Cypryk, Y. Gupta, and K. Matyjaszewski, *J. Am. Chem. Soc.*, 1991, **113**, 1046.

121   K. Matyjaszewski, *Macromol. Symp.*, 1991, **42-43**, 269.

122   M. Suzuki, J. Kotani, S. Gyobu, T. Kaneko, and T. Saegusa, *Macromolecules*, 1994, **27**, 2360.

123   J. R. Koe, D. R. Powell, J. J. Buffy, S. Hayase, and R. West, *Angew. Chem., Int. Ed.*, 1998, **37**, 1441.

124   J. R. Koe, M. Motonaga, M. Fujiki, and R. West, *Macromolecules*, 2001, **34**, 706.

125   J. R. Koe and M. Fujiki, *Silicon Chem.*, 2002, **1**, 77.

126   P. T. K. Lee, M. K. Skjel, and L. Rosenberg, *Organometallics*, 2013, **32**, 1575.

127   K. Sakamoto, K. Obata, H. Hirata, M. Nakajima, and H. Sakurai, *J. Am. Chem. Soc.*, 1989, **111**, 7641.

128   H. Sakurai, R. Honbori, and T. Sanji, *Organometallics*, 2005, **24**, 4119.

129   T. Sanji, S. Isozaki, M. Yoshida, K. Sakamoto, and H. Sakurai, *J. Organomet. Chem.*, 2003, **685**, 65.

130   M. Fujiki, *Macromol. Rapid Commun.*, 2001, **22**, 539.

131   M. Fujiki, J. R. Koe, K. Terao, T. Sato, A. Teramoto, and J. Watanabe, *Polym J*, 2003, **35**, 297.

132   M. Fujiki, *J. Am. Chem. Soc.*, 1994, **116**, 6017.

133   M. Fujiki, S. Toyoda, C. H. Yuan, and H. Takigawa, *Chirality*, 1998, **10**, 667.

134   W. Q. Peng, M. Motonaga, and J. R. Koe, *J. Am. Chem. Soc.*, 2004, **126**, 13822.

135   A. Ohira, S. Y. Kim, M. Fujiki, Y. Kawakami, M. Naito, G. Kwak, and A. Saxena, *Chem. Commun.*, 2006, 2705.

136   M. Fujiki, J. R. Koe, M. Motonaga, H. Nakashima, K. Terao, and A. Teramoto, *J. Am. Chem. Soc.*, 2001, **123**, 6253.

137   S. J. Holder, M. Achilleos, and R. G. Jones, *J. Am. Chem. Soc.*, 2006, **128**, 12418.

138   T. Sanji, K. Takase, and H. Sakurai, *J. Am. Chem. Soc.*, 2001, **123**, 12690.

139   X. Ming Wang, R. Qing Fan, L. Sheng Qiang, W. Qi Li, P. Wang, H. Jie Zhang, and Y. Lin Yang, *Chem. Commun.*, 2014, **50**, 5023.

140   A. Feigl, I. Chiorescu, K. Deller, S. U. H. Heidsieck, M. R. Buchner, V. Karttunen, A. Bockholt, A. Genest, N. Rösch, and B. Rieger, *Chem. Eur. J.*, 2013, **19**, 12526.

141   J. T. Goodwin, W. E. Baldwin, and R. R. McGregor, *J. Am. Chem. Soc.*, 1947, **69**, 2247.

142   P. Colombo, G. Mera, R. Riedel, and G. D. Sorarù, *J. Am. Ceram. Soc.*, 2010, **93**, 1805.

143   X. Wu and D. C. Neckers, *Macromolecules*, 1999, **32**, 6003.

144   K. Matsumoto, M. Shinohata, and H. Yamaoka, *Polym. J.*, 2000, **32**, 1022.

145   K. Matsumoto, M. Shinohata, and H. Yamaoka, *Polym. J.*, 2000, **32**, 354.

146   K. Matsumoto, M. Deguchi, M. Nakano, and H. Yamaoka, *J. Polym. Sci. Part A: Polym. Chem.*, 1998, **36**, 2699.

147   C. Liao and W. Weber, *Polym. Bull.*, 1992, **28**, 281.

148   R. Knischka, H. Frey, U. Rapp, and F. J. Mayer-Posner, *Macromol. Rapid Commun.*, 1998, **19**, 455.

149   K. Matsumoto, H. Shimazu, M. Deguchi, and H. Yamaoka, *J. Polym. Sci. Part A: Polym. Chem.*, 1997, **35**, 3207.

150   K. Komuro and Y. Kawakami, *Polym. J.*, 1999, **31**, 138.

151   H. Yamashita, M. Tanaka, and K. Honda, *J. Am. Chem. Soc.*, 1995, **117**, 8873.

152   X. Zhang, Q. Zhou, W. P. Weber, R. F. Horvath, T. H. Chan, and G. Manuel, *Macromolecules*, 1988, **21**, 1563.

153   Q. Zhou, G. Manuel, and W. P. Weber, *Macromolecules*, 1990, **23**, 1583.

154   S. J. Sargeant, S. Q. Zhou, G. Manuel, and W. P. Weber, *Macromolecules*, 1992, **25**, 2832.

155   L. Wang and W. P. Weber, *Macromolecules*, 1993, **26**, 969.

156   S. J. Sargeant and W. P. Weber, *Macromolecules*, 1993, **26**, 2400.

157   M. Theurig, S. J. Sargeant, G. Manuel, and W. P. Weber, *Macromolecules*, 1992, **25**, 3834.

158   Y. Kakihana, K. Uenishi, I. Imae, and Y. Kawakami, *Macromolecules*, 2005, **38**, 6321.

159   K. Uenishi, I. Imae, E. Shirakawa, and Y. Kawakami, *Macromolecules*, 2002, **35**, 2455.

160   S. Ahn, Y. S. Cho, B. R. Yoo, and I. N. Jung, *Organometallics*, 1998, **17**, 2404.

161   K. Matsumoto and H. Matsuoka, *Macromolecules*, 2003, **36**, 1474.

162   L. C. Pavelka, K. K. Milnes, and K. M. Baines, *Chem. Mater.*, 2008, **20**, 5948.

163   D. Bravo-Zhivotovskii, S. Melamed, V. Molev, N. Sigal, B. Tumanskii, M. Botoshansky, G. Molev, and Y. Apeloig, *Angew. Chem., Int. Ed.*, 2009, **48**, 1834.

164   P. Trefonas and R. West, *J. Polym. Sci., Polym. Chem. Ed.*, 1985, **23**, 2099.

165   K. Mochida, S. Nagano, H. Kawata, M. Wakasa, and H. Hayashi, *J. Organomet. Chem.*, 1997, **542**, 75.

166   S. M. Katz, J. A. Reichl, and D. H. Berry, *J. Am. Chem. Soc.*, 1998, **120**, 9844.

167   J. A. Reichl, C. M. Popoff, L. A. Gallagher, D. H. Berry, and E. E. Remsen, *J. Am. Chem. Soc.*, 1996, **118**, 9430.

168   M. Motonaga, H. Nakashima, S. Katz, D. H. Berry, T. Imase, S. Kawauchi, J. Watanabe, M. Fujiki, and J. R. Koe, *J. Organomet. Chem.*, 2003, **685**, 44.

169   Y. Yokoyama, M. Hayakawa, T. Azemi, and K. Mochida, *J. Chem. Soc., Chem. Commun.*, 1995, 2275.

170   T. Azemi, Y. Yokoyama, and K. Mochida, *J. Organomet. Chem.*, 2005, **690**, 1588.

171   Y. Y. Durmaz, M. Kukut, N. Monszner, and Y. Yagci, *Macromolecules*, 2009, **42**, 2899.

172   J. L. Brefort, R. J. P. Corriu, C. Guerin, and B. J. L. Henner, *J. Organomet. Chem.*, 1994, **464**, 133.

This journal is © The Royal Society of Chemistry 2015

Chem. Soc. Rev. 2015, **00**, 1-3 | **29**

173 L. C. Pavelka, S. J. Holder, and K. M. Baines, *Chem. Commun.*, 2008, 2346.

174 L. R. Sita, *Organometallics*, 1992, **11**, 1442.

175 L. R. Sita, K. W. Terry, and K. Shibata, *J. Am. Chem. Soc.*, 1995, **117**, 8049.

176 T. Imori, V. Lu, H. Cai, and T. D. Tilley, *J. Am. Chem. Soc.*, 1995, **117**, 9931.

177 F. Choffat, S. Käser, P. Wolfer, D. Schmid, R. Mezzenga, P. Smith, and W. Caseri, *Macromolecules*, 2007, **40**, 7878.

178 T. Imori and T. D. Tilley, *J. Chem. Soc., Chem. Commun.*, 1993, 1607.

179 F. Choffat, P. Smith, and W. Caseri, *J. Mater. Chem.*, 2005, **15**, 1789.

180 F. Choffat, Y. Buchmüller, C. Mensing, P. Smith, and W. Caseri, *J. Inorg. Organomet. Polym. Mater.*, 2009, **19**, 166.

181 M. Trummer, F. Choffat, P. Smith, and W. Caseri, *Macromol. Rapid Commun.*, 2012, **33**, 448.

182 M. Trummer, T. Nauser, M.-L. Lechner, F. Uhlig, and W. Caseri, *Polym. Degrad. Stabil.*, 2011, **96**, 1841.

183 A. Khan, S. Komejan, A. Patel, C. Lombardi, A. J. Lough, and D. A. Foucher, *J. Organomet. Chem.*, 2015, **776**, 180.

184 N. R. Neale and T. D. Tilley, *J. Am. Chem. Soc.*, 2002, **124**, 3802.

185 N. R. Neale and T. D. Tilley, *Tetrahedron*, 2004, **60**, 7247.

186 M. Trummer, D. Solenthaler, P. Smith, and W. Caseri, *Chimia*, 2011, **65**, 876.

187 M.-L. Lechner, M. Trummer, I. Bräunlich, P. Smith, W. Caseri, and F. Uhlig, *Appl. Organomet. Chem.*, 2011, **25**, 769.

188 S. Harrypersad and D. Foucher, *Chem. Commun.*, 2015, **51**, 7120.

189 S. Yamaguchi, Y. Itami, and K. Tamao, *Organometallics*, 1998, **17**, 4910.

190 C. M. Amb, S. Chen, K. R. Graham, J. Subbiah, C. E. Small, F. So, and J. R. Reynolds, *J. Am. Chem. Soc.*, 2011, **133**, 10062.

191 D. Gendron, P.-O. Morin, P. Berrouard, N. Allard, B. R. Aïch, C. N. Garon, Y. Tao, and M. Leclerc, *Macromolecules*, 2011, **44**, 7188.

192 N. Allard, R. B. Aïch, D. Gendron, P.-L. T. Boudreault, C. Tessier, S. Alem, S.-C. Tse, Y. Tao, and M. Leclerc, *Macromolecules*, 2010, **43**, 2328.

193 J. Ohshita, Y.-M. Hwang, T. Mizumo, H. Yoshida, Y. Ooyama, Y. Harima, and Y. Kunugi, *Organometallics*, 2011, **30**, 3233.

194 Q. Wang, S. Zhang, L. Ye, Y. Cui, H. Fan, and J. Hou, *Macromolecules*, 2014, **47**, 5558.

195 H. Zhong, Z. Li, F. Deledalle, E. C. Fregoso, M. Shahid, Z. Fei, C. B. Nielsen, N. Yaacobi-Gross, S. Rossbauer, T. D. Anthopoulos, J. R. Durrant, and M. Heeney, *J. Am. Chem. Soc.*, 2013, **135**, 2040.

196 X. Guo, N. Zhou, S. J. Lou, J. W. Hennek, R. Ponce Ortiz, M. R. Butler, P.-L. T. Boudreault, J. Strzalka, P.-O. Morin, M. Leclerc, J. T. López Navarrete, M. A. Ratner, L. X. Chen, R. P. H. Chang, A. Facchetti, and T. J. Marks, *J. Am. Chem. Soc.*, 2012, **134**, 18427.

197 P. C. Jwo, Y. Y. Lai, C. E. Tsai, Y. Y. Lai, W. W. Liang, C. S. Hsu, and Y. J. Cheng, *Macromolecules*, 2014, **47**, 7386.

198 Z. P. Fei, R. S. Ashraf, Y. Han, S. Wang, C. P. Yau, P. S. Tuladhar, T. D. Anthopoulos, M. L. Chabinyc, and M. Heeney, *J. Mater. Chem. A*, 2015, **3**, 1986.

199 J. Ohshita, M. Miyazaki, M. Nakashima, D. Tanaka, Y. Ooyama, T. Sasaki, Y. Kunugi, and Y. Morihara, *RSC Adv.*, 2015, **5**, 12686.

200 S. J. Toal and W. C. Trogler, *J. Mater. Chem.*, 2006, **16**, 2871.

201 B.-H. Kim, M.-S. Cho, J.-I. Kong, H.-G. Woo, S.-W. Lee, and C. Lee, *Mol. Cryst. Liq. Cryst.*, 2004, **425**, 243.

202 H. Sohn, M. J. Sailor, D. Magde, and W. C. Trogler, *J. Am. Chem. Soc.*, 2003, **125**, 3821.

203 S. J. Toal, H. Sohn, L. N. Zakarov, W. S. Kassel, J. A. Golen, A. L. Rheingold, and W. C. Trogler, *Organometallics*, 2005, **24**, 3081.

204 B. L. Lucht, M. A. Buretea, and T. D. Tilley, *Organometallics*, 2000, **19**, 3469.

205 W.-M. Zhou and I. Tomita, *Polym. Bull.*, 2008, **61**, 603.

206 C. C. W. Law, J. Chen, J. W. Y. Lam, H. Peng, and B. Z. Tang, *J. Inorg. Organomet. Polym.*, 2004, **14**, 39.

207 W.-M. Zhou and I. Tomita, *J. Inorg. Organomet. Polym. Mater.*, 2009, **19**, 113.

208 J. Linshoeft, E. J. Baum, A. Hussain, P. J. Gates, C. Näther, and A. Staubitz, *Angew. Chem., Int. Ed.*, 2014, **53**, 12916.

209 B. Kumar, C. E. Strasser, and B. T. King, *J. Org. Chem.*, 2012, **77**, 311.

210 R. Haga, M. Saito, and M. Yoshioka, *Chem. Eur. J.*, 2008, **14**, 4068.

211 See, for example: (*a*) E. D. Conrad and D. P. Gates in *Encyclopedia of polymeric nanomaterials*; S. Kobayashi and K. Müllen (Eds.); Springer, Berlin, 2015, 1514; (*b*) H. R. Allcock, *Appl. Organomet. Chem.*, 2013, **27**, 620; (*c*) Y. Ren and T. Baumgartner, *Dalton Trans.*, 2012, **41**, 7792; (*d*) H. R. Allcock and N. L. Morozowich, *Polym. Chem.*, 2012, **3**, 578; (*e*) S. Monge, B. Canniccioni, A. Graillot, and J. J. Robin, *Biomacromolecules*, 2011, **12**, 1973; (*f*) J. I. Bates, J. Dugal-Tessier, and D. P. Gates, *Dalton Trans.*, 2010, **39**, 3151; (*g*) P. W. Siu, D. P. Gates in *Conjugated polymer synthesis*; Y. Chujo (Ed.); Wiley-VCH, Weinheim, 2010, 215; (*h*) J. Crassous and R. Réau, *Dalton Trans.*, 2008, 6865; (*i*) P. W. Dyer, R. Réau in *Functional organic materials. synthesis, strategies and applications*; T. J. J. Müller and U. H. F. Bunz (Eds.); Wiley-VCH, Weinheim, 2007, 119; (*j*) M. G. Hobbs and T. Baumgartner, *Eur. J. Inorg. Chem.*, 2007, 3611; (*k*) T. Baumgartner and R. Réau, *Chem. Rev.*, 2006, **106**, 4681; (*l*) D. P. Gates, *Top. Curr. Chem.* 2005, **250**, 107.

212 A. M. Caminade and J. P. Majoral, *New J. Chem.*, 2013, **37**, 3358.

213 A. M. Caminade and J. P. Majoral, *Acc. Chem. Res.*, 2004, **37**, 341.

214   H. R. Allcock, *Chemistry and applications of polyphosphazenes*, Wiley, Hoboken, 2003.

215   H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, 1965, **87**, 4216.

216   E. P. Flindt and H. Rose, *Z. Anorg. Allg. Chem.*, 1977, **428**, 204.

217   P. Wisian-Neilson and R. H. Neilson, *J. Am. Chem. Soc.*, 1980, **102**, 2848.

218   G. D'Halluin, R. De Jaeger, J. P. Chambrette, and P. Potin, *Macromolecules*, 1992, **25**, 1254.

219   R. A. Montague and K. Matyjaszewski, *J. Am. Chem. Soc.*, 1990, **112**, 6721.

220   U. Franz, O. Nuyken, and K. Matyjaszewski, *Macromolecules*, 1993, **26**, 3723.

221   G. Allen, C. J. Lewis, and S. M. Todd, *Polymer*, 1970, **11**, 31.

222   C. H. Honeyman, I. Manners, C. T. Morrissey, and H. R. Allcock, *J. Am. Chem. Soc.*, 1995, **117**, 7035.

223   H. R. Allcock, C. A. Crane, C. T. Morrissey, J. M. Nelson, S. D. Reeves, C. H. Honeyman, and I. Manners, *Macromolecules*, 1996, **29**, 7740.

224   H. R. Allcock, S. D. Reeves, J. M. Nelson, C. A. Crane, and I. Manners, *Macromolecules*, 1997, **30**, 2213.

225   J. M. Nelson, A. P. Primrose, T. J. Hartle, H. R. Allcock, and I. Manners, *Macromolecules*, 1998, **31**, 947.

226   H. R. Allcock, J. M. Nelson, S. D. Reeves, C. H. Honeyman, and I. Manners, *Macromolecules*, 1997, **30**, 50.

227   K. Huynh, A. J. Lough, and I. Manners, *J. Am. Chem. Soc.*, 2006, **128**, 14002.

228   T. J. Taylor, A. P. Soto, K. Huynh, A. J. Lough, A. C. Swain, N. C. Norman, C. A. Russell, and I. Manners, *Macromolecules*, 2010, **43**, 7446.

229   M. Raab, G. Schick, R. Fondermann, M. Dolg, W. Henze, U. Weynand, R. M. Gschwind, K. Fischer, M. Schmidt, and E. Niecke, *Angew. Chem., Int. Ed.*, 2006, **45**, 3083.

230   M. S. Sennett, G. L. Hagnauer, R. E. Singler, and G. Davies, *Macromolecules*, 1986, **19**, 959.

231   Y. Zhang, K. Huynh, I. Manners, and C. A. Reed, *Chem. Commun.*, 2008, 494.

232   I. Manners, H. R. Allcock, G. Renner, and O. Nuyken, *J. Am. Chem. Soc.*, 1989, **111**, 5478.

233   H. R. Allcock, S. M. Coley, I. Manners, O. Nuyken, and G. Renner, *Macromolecules*, 1991, **24**, 2024.

234   H. R. Allcock, S. M. Coley, and C. T. Morrissey, *Macromolecules*, 1994, **27**, 2904.

235   J. A. Dodge, I. Manners, H. R. Allcock, G. Renner, and O. Nuyken, *J. Am. Chem. Soc.*, 1990, **112**, 1268.

236   H. R. Allcock, J. A. Dodge, and I. Manners, *Macromolecules*, 1993, **26**, 11.

237   M. Liang and I. Manners, *J. Am. Chem. Soc.*, 1991, **113**, 4044.

238   Y. Z. Ni, A. Stammer, M. Liang, J. Massey, G. J. Vancso, and I. Manners, *Macromolecules*, 1992, **25**, 7119.

239   Y. Z. Ni, P. Park, M. Liang, J. Massey, C. Waddling, and I. Manners, *Macromolecules*, 1996, **29**, 3401.

240   D. P. Gates, A. R. McWilliams, and I. Manners, *Macromolecules*, 1998, **31**, 3494.

241   M. N. Nobis, A. R. McWilliams, O. Nuyken, and I. Manners, *Macromolecules*, 2000, **33**, 7707.

242   D. P. Gates, M. Edwards, L. M. Liable-Sands, A. L. Rheingold, and I. Manners, *J. Am. Chem. Soc.*, 1998, **120**, 3249.

243   A. R. McWilliams, D. P. Gates, M. Edwards, L. M. Liable-Sands, I. Guzei, A. L. Rheingold, and I. Manners, *J. Am. Chem. Soc.*, 2000, **122**, 8848.

244   V. Chunechom, T. E. Vidal, H. Adams, and M. L. Turner, *Angew. Chem., Int. Ed.*, 1998, **37**, 1928.

245   C. W. Tsang, M. Yam, and D. P. Gates, *J. Am. Chem. Soc.*, 2003, **125**, 1480.

246   C. W. Tsang, B. Baharloo, D. Riendl, M. Yam, and D. P. Gates, *Angew. Chem., Int. Ed.*, 2004, **43**, 5682.

247   B. H. Gillon and D. P. Gates, *Chem. Commun.*, 2004, 1868.

248   K. J. T. Noonan and D. P. Gates, *Angew. Chem., Int. Ed.*, 2006, **45**, 7271.

249   K. J. T. Noonan and D. P. Gates, *Macromolecules*, 2008, **41**, 1961.

250   K. J. T. Noonan, B. O. Patrick, and D. P. Gates, *Chem. Commun.*, 2007, 3658.

251   B. W. Rawe, C. P. Chun, and D. P. Gates, *Chem. Sci.*, 2014, **5**, 4928.

252   J. Dugal-Tessier, G. R. Dake, and D. P. Gates, *Angew. Chem., Int. Ed.*, 2008, **47**, 8064.

253   J. Dugal-Tessier, S. C. Serin, E. B. Castillo-Contreras, E. D. Conrad, G. R. Dake, and D. P. Gates, *Chem. Eur. J.*, 2012, **18**, 6349.

254   K. J. T. Noonan, B. Feldscher, J. I. Bates, J. J. Kingsley, M. Yam, and D. P. Gates, *Dalton Trans.*, 2008, 4451.

255   B. H. Gillon, B. O. Patrick, and D. P. Gates, *Chem. Commun.*, 2008, 2161.

256   K. J. T. Noonan, B. H. Gillon, V. Cappello, and D. P. Gates, *J. Am. Chem. Soc.*, 2008, **130**, 12876.

257   A. M. Priegert, P. W. Siu, T. Q. Hu, and D. P. Gates, *Fire Mater.*, 2015, **39**, 647.

258   P. W. Siu, S. C. Serin, I. Krummenacher, T. W. Hey, and D. P. Gates, *Angew. Chem., Int. Ed.*, 2013, **52**, 6967.

259   H. Ghassemi and E. McGrath, *Polymer*, 1997, **38**, 3139.

260   Z. Jin and B. L. Lucht, *J. Organomet. Chem.*, 2002, **653**, 167.

261   X. T. Chen, H. Sun, X. D. Tang, and C. Y. Wang, *J. Appl. Polym. Sci.*, 2008, **110**, 1304.

262   S. Y. Shao, J. Q. Ding, T. L. Ye, Z. Y. Xie, L. X. Wang, X. B. Jing, and F. S. Wang, *Adv. Mater.*, 2011, **23**, 3570.

263   B. L. Lucht and N. O. St Onge, *Chem. Commun.*, 2000, 2097.

264   Z. Jin and B. L. Lucht, *J. Am. Chem. Soc.*, 2005, **127**, 5586.

265   L. B. Han, Z. X. Huang, S. Matsuyama, Y. Ono, and C. Q. Zhao, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 5328.

This journal is © The Royal Society of Chemistry 2015

Chem. Soc. Rev. 2015, **00**, 1-3 | **31**

266 L. A. Vanderark, T. J. Clark, E. Rivard, I. Manners, J. C. Slootweg, and K. Lammertsma, *Chem. Commun.*, 2006, 3332.

267 K. Naka, T. Umeyama, A. Nakahashi, and Y. Chujo, *Macromolecules*, 2007, **40**, 4854.

268 B. W. Rawe and D. P. Gates, *Angew. Chem., Int. Ed.*, 2015, **54**, 11438.

269 V. A. Wright and D. P. Gates, *Angew. Chem., Int. Ed.*, 2002, **41**, 2389.

270 V. A. Wright, B. O. Patrick, C. Schneider, and D. P. Gates, *J. Am. Chem. Soc.*, 2006, **128**, 8836.

271 R. C. Smith, X. F. Chen, and J. D. Protasiewicz, *Inorg. Chem.*, 2003, **42**, 5468.

272 R. C. Smith and J. D. Protasiewicz, *J. Am. Chem. Soc.*, 2004, **126**, 2268.

273 S. S. H. Mao and T. D. Tilley, *Macromolecules*, 1997, **30**, 5566.

274 Y. Morisaki, Y. Aiki, and Y. Chujo, *Macromolecules*, 2003, **36**, 2594.

275 C. Hay, C. Fischmeister, M. Hissler, L. Toupet, and R. Réau, *Angew. Chem., Int. Ed.*, 2000, **39**, 1812.

276 C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulászi, and R. Réau, *Chem. Eur. J.*, 2001, **7**, 4222.

277 M. Sebastian, M. Hissler, C. Fave, J. Rault-Berthelot, C. Odin, and R. Réau, *Angew. Chem., Int. Ed.*, 2006, **45**, 6152.

278 V. L. de Talance, M. Hissler, L. Z. Zhang, T. Kárpáti, L. Nyulászi, D. Caras-Quintero, P. Bäuerle, and R. Réau, *Chem. Commun.*, 2008, 2200.

279 O. Fadhel, Z. Benkö, M. Gras, V. Deborde, D. Joly, C. Lescop, L. Nyulászi, M. Hissler, and R. Réau, *Chem. Eur. J.*, 2010, **16**, 11340.

280 Y. Matano, H. Ohkubo, T. Miyata, Y. Watanabe, Y. Hayashi, T. Umeyama, and H. Imahori, *Eur. J. Inorg. Chem.*, 2014, 1620.

281 T. Baumgartner, T. Neumann, and B. Wirges, *Angew. Chem., Int. Ed.*, 2004, **43**, 6197.

282 C. Romero-Nieto, S. Durben, I. M. Kormos, and T. Baumgartner, *Adv. Funct. Mater.*, 2009, **19**, 3625.

283 T. Baumgartner, W. Bergmans, T. Karpati, T. Neumann, M. Nieger, and L. Nyulászi, *Chem. Eur. J.*, 2005, **11**, 4687.

284 T. Baumgartner and W. Wilk, *Org. Lett.*, 2006, **8**, 503.

285 S. Durben, Y. Dienes, and T. Baumgartner, *Org. Lett.*, 2006, **8**, 5893.

286 R. F. Chen, R. Zhu, Q. L. Fan, and W. Huang, *Org. Lett.*, 2008, **10**, 2913.

287 A. Saito, Y. Matano, and H. Imahori, *Org. Lett.*, 2010, **12**, 2675.

288 Y. Matano, H. Ohkubo, Y. Honsho, A. Saito, S. Seki, and H. Imahori, *Org. Lett.*, 2013, **15**, 932.

289 Y. Morisaki, Y. Ouchi, K. Tsurui, and Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 866.

290 Y. Ouchi, Y. Morisaki, T. Ogoshi, and Y. Chujo, *Chem. Asian J.*, 2007, **2**, 397.

291 Y. Morisaki, Y. Ouchi, K. Tsurui, and Y. Chujo, *Polym. Bull.*, 2007, **58**, 665.

292 Y. Morisaki, K. Suzuki, H. Imoto, and Y. Chujo, *Macromol. Chem. Phys.*, 2011, **212**, 2603.

293 H. Imoto, Y. Morisaki, and Y. Chujo, *Chem. Commun.*, 2010, **46**, 7542.

294 X. S. Wang, K. Cao, Y. B. Liu, B. Tsang, and S. Liew, *J. Am. Chem. Soc.*, 2013, **135**, 3399.

295 K. Naka, T. Umeyama, and Y. Chujo, *J. Am. Chem. Soc.*, 2002, **124**, 6600.

296 T. Umeyama, K. Naka, A. Nakahashi, and Y. Chujo, *Macromolecules*, 2004, **37**, 1271.

297 T. Umeyama, K. Naka, and Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 3604.

298 T. Umeyama, K. Naka, and Y. Chujo, *Macromolecules*, 2004, **37**, 5952.

299 K. Naka, A. Nakahashi, and Y. Chujo, *Macromolecules*, 2006, **39**, 8257.

300 K. Naka, A. Nakahashi, and Y. Chujo, *Macromolecules*, 2007, **40**, 1372.

301 T. Umeyama, K. Naka, and Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 3023.

302 K. Naka, M. Arita, T. Shimamoto, Y. Morisaki, and Y. Chujo, *Polym. J.*, 2011, **43**, 358.

303 Y. Morisaki, K. Ohashi, H. S. Na, and Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 4857.

304 J. Lim, J. Pyun, and K. Char, *Angew. Chem., Int. Ed.*, 2015, **54**, 3249.

305 E. J. Goethals, *Top. Sulfur Chem.*, 1977, **3**, 3.

306 A. J. Banister and I. B. Gorrell, *Adv. Mater.*, 1998, **10**, 1415.

307 I. Osaka and R. D. McCullough, *Acc. Chem. Res.*, 2008, **41**, 1202.

308 B. Meyer, *Chem. Rev.*, 1976, **76**, 367.

309 S. Penczek, R. Slazak, and A. Duda, *Nature*, 1978, **273**, 738.

310 W. J. Chung, J. J. Griebel, E. T. Kim, H. Yoon, A. G. Simmonds, H. J. Ji, P. T. Dirlam, R. S. Glass, J. J. Wie, N. A. Nguyen, B. W. Guralnick, J. Park, Á. Somogyi, P. Theato, M. E. Mackay, Y.-E. Sung, K. Char, and J. Pyun, *Nat. Chem.*, 2013, **5**, 518.

311 J. J. Griebel, G. X. Li, R. S. Glass, K. Char, and J. Pyun, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 173.

312 J. J. Griebel, S. Namnabat, E. T. Kim, R. Himmelhuber, D. H. Moronta, W. J. Chung, A. G. Simmonds, K. J. Kim, J. van der Laan, N. A. Nguyen, E. L. Dereniak, M. E. Mackay, K. Char, R. S. Glass, R. A. Norwood, and J. Pyun, *Adv. Mater.*, 2014, **26**, 3014.

313 P. T. Dirlam, A. G. Simmonds, T. S. Kleine, N. A. Nguyen, L. E. Anderson, A. O. Klever, A. Florian, P. J. Costanzo, P. Theato, M. E. Mackay, R. S. Glass, K. Char, and J. Pyun, *RSC Adv.*, 2015, **5**, 24718.

314 H. Kim, J. Lee, H. Ahn, O. Kim, and M. J. Park, *Nat. Commun.*, 2015, **6**, 7278.

315 Z. Sun, M. Xiao, S. Wang, D. Han, S. Song, G. Chen, and Y. Meng, *J. Mater. Chem. A*, 2014, **2**, 9280.

316   S. Zhuo, Y. Huang, C. Liu, H. Wang, and B. Zhang, *Chem. Commun.*, 2014, **50**, 11208.

317   W. J. Chung, A. G. Simmonds, J. J. Griebel, E. T. Kim, H. S. Suh, I. B. Shim, R. S. Glass, D. A. Loy, P. Theato, Y. E. Sung, K. Char, and J. Pyun, *Angew. Chem., Int. Ed.*, 2011, **50**, 11409.

318   T. R. Martin, K. A. Mazzio, H. W. Hillhouse, and C. K. Luscombe, *Chem. Commun.*, 2015, **51**, 11244.

319   J. C. Bear, W. J. Peveler, P. D. McNaughter, I. P. Parkin, P. O'Brien, and C. W. Dunnill, *Chem. Commun.*, 2015, **51**, 10467.

320   J. Lim, U. Jung, W. T. Joe, E. T. Kim, J. Pyun, and K. Char, *Macromol. Rapid Commun.*, 2015, **36**, 1103.

321   A. K. Roy, *J. Am. Chem. Soc.*, 1992, **114**, 1530.

322   A. K. Roy, G. T. Burns, G. C. Lie, and S. Grigoras, *J. Am. Chem. Soc.*, 1993, **115**, 2604.

323   V. Aldeva, S. Gezahegn, B. Panahi, M. Shuoprasad, J. Ward, D. A. Foucher, R. A. Gossage, and A. R. McWilliams, *Macromolecules*, 2013, **46**, 2562.

324   Y. Ding and A. S. Hay, *Macromolecules*, 1996, **29**, 4811.

325   Y. Ding and A. S. Hay, *Macromolecules*, 1997, **30**, 2527.

326   Y. Ding and A. S. Hay, *Polymer*, 1997, **38**, 2239.

327   Y. Ding and A. S. Hay, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 2961.

328   K. Chen, Z. A. Liang, Y. Z. Meng, and A. S. Hay, *Polymer*, 2004, **45**, 1787.

329   A. Patra and M. Bendikov, *J. Mater. Chem.*, 2010, **20**, 422.

330   U. Salzner, J. B. Lagowski, P. G. Pickup, and R. A. Poirier, *Synth. Met.*, 1998, **96**, 177.

331   S. S. Zade and M. Bendikov, *Org. Lett.*, 2006, **8**, 5243.

332   M. Heeney, W. Zhang, D. J. Crouch, M. L. Chabinyc, S. Gordeyev, R. Hamilton, S. J. Higgins, I. McCulloch, P. J. Skabara, D. Sparrowe, and S. Tierney, *Chem. Commun.*, 2007, 5061.

333   K. Yoshino, Y. Kohno, T. Shiraishi, K. Kaneto, S. Inoue, and K. Tsukagoshi, *Synth. Met.*, 1985, **10**, 319.

334   N. Merlet, G. Dian, G. Barbey, F. Outurquin, and C. Paulmier, *Synth. Met.*, 1988, **24**, 77.

335   S. Inoue, H. Nakanishi, K. Takimiya, Y. Aso, and T. Otsubo, *Synth. Met.*, 1997, **84**, 341.

336   G. Dian, N. Merlet, G. Barbey, F. Outurquin, and C. Paulmier, *J. Electroanal. Chem.*, 1987, **238**, 225.

337   G. Dian, G. Barbey, and B. Decroix, *Synth. Met.*, 1986, **13**, 281.

338   S. Pu, J. Hou, J. Xu, G. Nie, S. Zhang, L. Shen, and Q. Xiao, *Mater. Lett.*, 2005, **59**, 1061.

339   S. Das and S. S. Zade, *Chem. Commun.*, 2010, **46**, 1168.

340   G. Tourillon, E. Dartyge, D. Guay, C. Mahatsekake, C. G. Andrieu, S. Bernstorff, and W. Braun, *J. Electrochem. Soc.*, 1990, **137**, 1827.

341   J. Xu, J. Hou, S. Zhang, G. Nie, S. Pu, L. Shen, and Q. Xiao, *J. Electroanal. Chem.*, 2005, **578**, 345.

342   B. Dong, Y. Xing, J. Xu, L. Zheng, J. Hou, and F. Zhao, *Electrochimica Acta*, 2008, **53**, 5745.

343   T.-T. Ong, S.-C. Ng, and H. S. O. Chan, *Polymer*, 2003, **44**, 5597.

344   S. Ryu-ichi, Y. Katsumi, I. Shigehito, and T. Kunimitsu, *Jpn. J. Appl. Phys.*, 1985, **24**, L425.

345   J. P. Montheard, T. Pascal, G. Seytre, G. Steffan-Boiteux, and A. Douillard, *Synth. Met.*, 1984, **9**, 389.

346   Y.-Y. Lai, T.-C. Tung, W.-W. Liang, and Y.-J. Cheng, *Macromolecules*, 2015, **48**, 2978.

347   S. Kirchmeyer and K. Reuter, *J. Mater. Chem.*, 2005, **15**, 2077.

348   A. Patra, M. Bendikov, and S. Chand, *Acc. Chem. Res.*, 2014, **47**, 1465.

349   A. Cihaner, *Synlett*, 2015, **26**, 449.

350   E. Aqad, M. V. Lakshmikantham, and M. P. Cava, *Org. Lett.*, 2001, **3**, 4283.

351   A. Patra, Y. H. Wijsboom, S. S. Zade, M. Li, Y. Sheynin, G. Leitus, and M. Bendikov, *J. Am. Chem. Soc.*, 2008, **130**, 6734.

352   G. He, L. Kang, W. T. Delgado, O. Shynkaruk, M. J. Ferguson, R. McDonald, and E. Rivard, *J. Am. Chem. Soc.*, 2013, **135**, 5360.

353   J. Hollinger, A. A. Jahnke, N. Coombs, and D. S. Seferos, *J. Am. Chem. Soc.*, 2010, **132**, 8546.

354   E. F. Palermo and A. J. McNeil, *Macromolecules*, 2012, **45**, 5948.

355   B. Lu, S. Chen, J. Xu, and G. Zhao, *Synth. Met.*, 2013, **183**, 8.

356   Y.-J. Hwang, G. Ren, N. M. Murari, and S. A. Jenekhe, *Macromolecules*, 2012, **45**, 9056.

357   M. Shahid, T. McCarthy-Ward, J. Labram, S. Rossbauer, E. B. Domingo, S. E. Watkins, N. Stingelin, T. D. Anthopoulos, and M. Heeney, *Chem. Sci.*, 2012, **3**, 181.

358   J. Cao, S. Chen, Z. Qi, Z. Xiao, J. Wang, and L. Ding, *RSC Adv.*, 2014, **4**, 5085.

359   Z. Fei, R. S. Ashraf, Y. Han, S. Wang, C. P. Yau, P. S. Tuladhar, T. D. Anthopoulos, M. L. Chabinyc, and M. Heeney, *J. Mater. Chem. A*, 2015, **3**, 1986.

360   E. H. Jung, S. Bae, T. W. Yoo, and W. H. Jo, *Polym. Chem.*, 2014, **5**, 6545.

361   M. Planells, B. C. Schroeder, and I. McCulloch, *Macromolecules*, 2014, **47**, 5889.

362   M. Al-Hashimi, M. A. Baklar, F. Colleaux, S. E. Watkins, T. D. Anthopoulos, N. Stingelin, and M. Heeney, *Macromolecules*, 2011, **44**, 5194.

363   H. Saito, S. Ukai, S. Iwatsuki, T. Itoh, and M. Kubo, *Macromolecules*, 1995, **28**, 8363.

364   S. C. Ng and L. G. Xu, *Adv. Mater.*, 1998, **10**, 1525.

365   H. Nishiyama, T. Kino, and I. Tomita, *Macromol. Rapid Commun.*, 2012, **33**, 545.

366   K. Kishore and K. Ganesh, *Adv. in Polym. Sci.*, 1995, **121**, 81.

367   H. Xu, W. Cao, and X. Zhang, *Acc. Chem. Res.*, 2013, **46**, 1647.

368   Y. Li, Z. Sun, and H. Xu, *J. Control. Release*, 2013, **172**, e70.

369   N. Ma, Y. Li, H. Ren, H. Xu, Z. Li, and X. Zhang, *Polym. Chem.*, 2010, **1**, 1609.

370   E. I. Carrera and D. S. Seferos, *Macromolecules*, 2015, **48**, 297.

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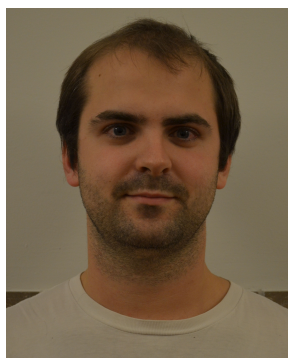
Chem. Soc. Rev. 2015, **00**, 1-3 | **33**

371 A. A. Jahnke and D. S. Seferos, *Macromol. Rapid Commun.*, 2011, **32**, 943.

372 R. Sugimoto, K. Yoshino, S. Inoue, and K. Tsukagoshi, *Jpn. J. Appl. Phys. 2*, 1985, **24**, L425.

373 T. Otsubo, S. Inoue, H. Nozoe, T. Jigami, and F. Ogura, *Synth. Met.*, 1995, **69**, 537.

374 S. Inoue, T. Jigami, H. Nozoe, T. Otsubo, and F. Ogura, *Tetrahedron Lett.*, 1994, **35**, 8009.

375 S. Inoue, T. Jigami, H. Nozoe, Y. Aso, F. Ogura, and T. Otsubo, *Heterocycles*, 2000, **52**, 159.

376 A. A. Jahnke, B. Djukic, T. M. McCormick, E. Buchaca Domingo, C. Hellmann, Y. Lee, and D. S. Seferos, *J. Am. Chem. Soc.*, 2013, **135**, 951.

377 W.-H. Lee, S. Kyu Lee, W. Suk Shin, S.-J. Moon, and I.-N. Kang, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, **51**, 2753.

378 M. Kaur, D. H. Lee, D. S. Yang, H. A. Um, M. J. Cho, J. S. Kang, and D. H. Choi, *Chem. Commun.*, 2014, **50**, 14394.

379 M. Kaur, D. Seul Yang, J. Shin, T. Wan Lee, K. Choi, M. Ju Cho, and D. Hoon Choi, *Chem. Commun.*, 2013, **49**, 5495.

380 A. A. Jahnke, G. W. Howe, and D. S. Seferos, *Angew. Chem., Int. Ed.*, 2010, **49**, 10140.

381 Y. S. Park, Q. Wu, C.-Y. Nam, and R. B. Grubbs, *Angew. Chem., Int. Ed.*, 2014, **53**, 10691.

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