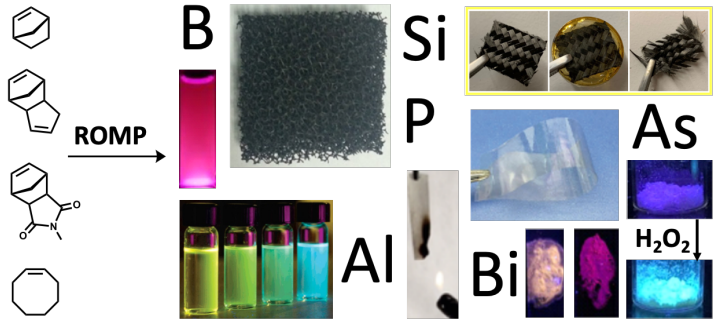
Main group functionalized polymers through ring-opening metathesis polymerization (ROMP)

James McQuade,[$] Mya I. Serrano,[$] and Frieder Jäkle*

Department of Chemistry, Rutgers University-Newark, 73 Warren St, Newark, NJ 07102, USA

[$] These authors contributed equally; * fjaekle@rutgers.edu

Abstract:



The incorporation of main group elements into polymers allows for the generation of new functional materials with hitherto-unattainable physical and chemical properties through the unique molecular geometries, electronic structures, and chemical reactivities of main group element-based functional groups. The synthesis of these novel materials requires highly controllable polymerizations which are tolerant of diverse functionalized monomers. In this review, we highlight recent developments in ring-opening metathesis polymerization (ROMP) as a versatile and advantageous method for the generation of new main group element-functionalized hybrid materials. The unique applications of ROMP-derived main group-functionalized polymers in membranes and polyelectrolytes, resins, composites, elastomers, and other engineering materials, ceramic precursors and flame retardants, polymeric ligands and metallopolymers, polymeric catalysts and reagents, and optoelectronic materials are described.

List of Abbreviations:	
AIEE: Aggregation-induced emission enhancement	ONB: Oxanorbornene
AEM: Anion-exchange membrane	PNC: poly(norbornene-COSAN)
BODIPY: boron-dipyrromethene	PDMS: Polydimethylsiloxane
DCP: Dicyclopentadiene	PMMA: Polymethylmethacrylate
FLP: Frustrated Lewis pair	POSS: Polyhedral oligomeric silsesquioxane
HOMO: Highest occupied molecular orbital	PP: Polypropylene
LUMO: Lowest unoccupied molecular orbital	RAFT: Reversible addition-fragmentation chain transfer polymerization
NBE: Norbornene	ROMP: Ring-opening metathesis polymerization
NDI: Norbornene carboximide	

1. Introduction

Main group elements, especially those from the p-block that are not typically used in organic chemistry, confer unique properties on their compounds, as a result of their varying

electronic structures, the heavy atom effect, variable coordination numbers and modes, and ability to participate in non-classical modes of bonding. Incorporating main group heteroatoms into polymers results in new combinations of properties, and thus potentially useful new materials.[1-4] Main group elements have been embedded in the polymer backbone, both in conjugated and non-conjugated materials, as well as attached as pendant groups, and the resulting polymers have shown promise in a variety of applications, including electronic materials, stimuli-responsive, degradable and smart materials, metallopolymers, and catalysts.

Living polymerizations are vital methods for the synthesis of polymers that avoid the undesired termination of polymer chain growth, allowing for greater control over molecular weight and polymer microstructure. A popular type of living polymerization that accomplishes this is ring-opening metathesis polymerization (ROMP). This technique allows not only for structural control, but also stands out for its high functional group tolerance and relatively mild conditions.[5, 6] ROMP, as the name implies, involves the polymerization of a cyclic monomer, potentially bearing a variety of substituents. The structure of this ring typically includes a double bond, with the geometry of the ring generating ring strain, the relief of which acts as a driving force for polymerization. A benefit of using a highly strained olefin is the fact that it lowers the risk of secondary metathesis of the less-strained backbone, a process which results in increased dispersities, undesired side-products, and reduced control of polymer architectures.[6] Some commonly used monomers are illustrated in **Figure 1**.

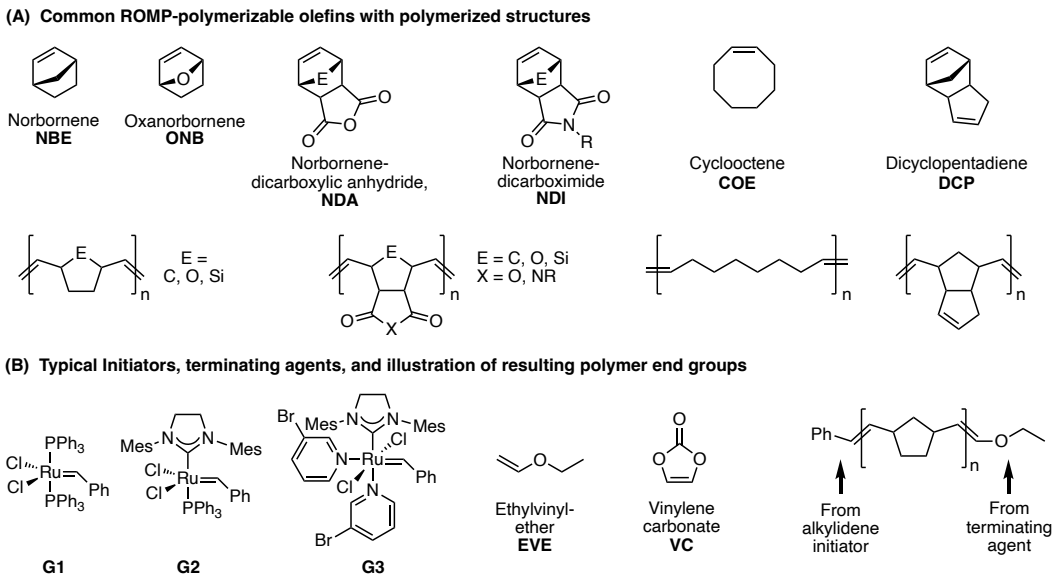


Figure 1: Common ROMP monomers, corresponding polymer structures, selected initiators, and terminating agents.

Besides the cyclic monomer, an initiator is needed to facilitate the ROMP process, usually incorporating a metal alkylidene functionality (some metal-free systems have also been

introduced[7]). In recent years, ruthenium-based initiators initially developed by the Grubbs group[8] have been heavily used in academic research, because of their more controllable polymerizations and superior functional group tolerance compared to Schrock-type initiators based on molybdenum or tungsten.[6, 9] Several initiators of relevance to this review are shown in **Figure 1B**. Grubbs 1st generation catalyst (**G1**) is used for varied applications such as pharmaceutical intermediates and different polymer composites; Grubbs 2nd generation catalyst (**G2**) can be used for low strain and/or sterically hindered ROMP substrates due to the greater electron density at the ruthenium center; Grubbs 3rd generation catalyst (**G3**) is notably faster initiating than the **G2** catalyst, enabling exceptionally low dispersities, and is thus particularly useful in the generation of advanced polymer architectures.[10]

The ROMP method is highly versatile enabling diverse applications, both in academic and industrial settings.[9] ROMP has proven useful in areas such as surface modification, grafting of polymers, preparation of brush polymers, and the realization of highly functionalized polymers.[5] Further, the use of ROMP techniques to prepare transition metal-containing polymers is well established.[11] In contrast, the development of functional polymers that incorporate main group elements is still in its infancy. In this review we seek to highlight the synthesis and unique properties of main group functionalized polymers that have been accessed by ROMP techniques. The review is organized according to the application fields of the investigated materials.

2. ROMP-Derived Engineering Materials Containing Main Group Elements

2.1 ROMP-Derived Composites and Resins

To date, the chief industrial application of ROMP polymers is in engineering materials like resins, rubbers, and elastomers, utilized for their mechanical properties in automotive, sporting, and other structural applications.[9] Main group elements can be incorporated into ROMP-derived polyolefins in the form of fillers for composites or by using functional monomers that incorporate main group elements into the polymer backbone or side chains.

Perhaps the simplest way to combine the mechanical properties of polymers with other materials is by blending them together to obtain composites. Silica-based fillers are commonly used to increase the rigidity of polymeric materials, along with related materials such as glass fibers. However, the non-polar nature of polydicyclopentadiene (PDCP) and polynorbornene (PNBE) materials results in poor adhesion between the filler and the polymer chain and thus poor mechanical performance. To address this issue, Zhang and coworkers demonstrated that olefin-functionalized silica particles allow for covalent linking of the polymer chain to the filler through metathesis of the pendant olefins, resulting in significant improvements in mechanical properties (**Figure 2a**).[12] Of note are also reports on surface-initiated ROMP;[13-17] while a variety of Si-functionalized monomers are utilized at low loadings as linkers between silicon surfaces and the polymer chains, the primary topic of these reports is the investigation of polymer behavior at

the surface rather than the preparation of functional polymers. These papers are thus not discussed in detail in this review.

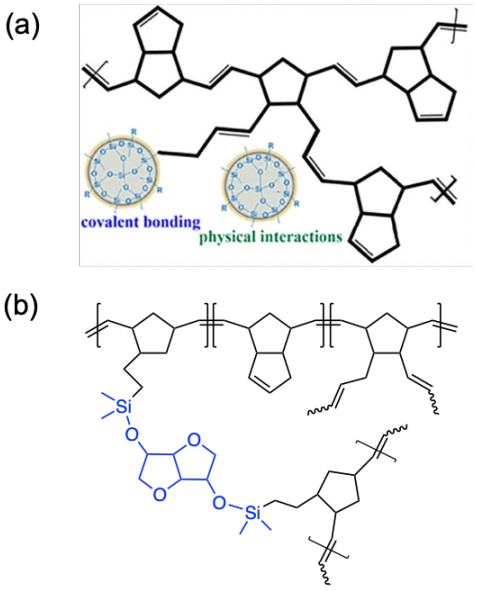


Figure 2: (a) Composites of SiO_2 with polydicyclopentadiene (PDCPD). Adapted with permission from Ref. [12]. © 2020 Wiley Periodicals, Inc.; (b) PDCPD crosslinked with silylated isosorbide bifunctional norbornene monomer.

Since their discovery in the 1930s, silicon-containing polymers have become ubiquitous commodity materials and a mature technology.[18] Beyond the familiar applications of polysiloxanes that take advantage of their high flexibility, chemical stability, and low dielectric constants, researchers have investigated diverse silicon-functionalized polymeric materials for electronic and optical materials, dynamically crosslinked materials, supramolecular assemblies, and to develop novel analogues that can mimic some of the properties of elemental silicon.[1, 19-21]

Recent fundamental studies have greatly broadened the available silicon-bearing moieties attached to ROMP monomers.[22-24] Researchers have also shown that combining ROMP polymerizable monomers with silicon-based crosslinkers can yield promising new mechanical properties. For example, in 2016, the Kessler group reported a bifunctional, silicon-linked norbornene crosslinker that incorporates a bio-based isosorbide moiety (**Figure 2b**).[25] This crosslinker was prepared by a simple condensation reaction between isosorbide and a commercial monomer decorated with a silylchloride group. The relatively flexible crosslinker enabled the formation of polydicyclopentadienes (PDCPs) at room temperature, rather than at elevated temperatures as is typical for high-melting PDCP polymers, thus simplifying the preparation of the polymers. After

curing, the resulting thermosets were found to exhibit higher crosslinking densities and lower thermal expansion coefficients than pure PDCP according to dynamic mechanical analysis measurements.

2.2 ROMP-Derived Elastomers

Elastomeric polymer networks have been obtained by crosslinking of ROMP polymer brushes with soft PDMS side chains. ROMP is ideally suited for the preparation of such materials due to the high efficiency in the preparation of brush polymer architectures. In a recent study, Sheiko, You and coworkers reported a series of ROMP polymer networks derived from PDMS-functionalized norbornenes and ditelechelic PDMS chains as crosslinkers (**Figure 3**).[26] The polymerizations were conducted under near-bulk conditions using a toluene solution of G3 as the catalyst system. The resulting elastomers exhibited desirable strain-stiffening behavior, similar to soft biological tissues. When compared with brush elastomers with a poly(methacrylate) backbone, the PMDS brush elastomers with a polynorbornene backbone were found to exhibit much lower β values, indicated less strain-stiffening behavior. An unexpected and previously unknown effect of grafting density on the elastomeric properties was observed during tensile testing: while decreasing grafting density led to lower rigidity and softer polymers as anticipated by the authors, a threshold was found below which brittle polymer films with low extensibility were observed. This indicates that, in addition to the stiff bottle-brush regime with dense interdigitation of the brush chains, and the more flexible comb-polymers with lower densities and thus more freedom of movement for the polynorbornene chains, a previously undescribed regime exists where very few brushes are present and brittle polymers are obtained, presumably because insufficient brush density exists for effective interdigitation.

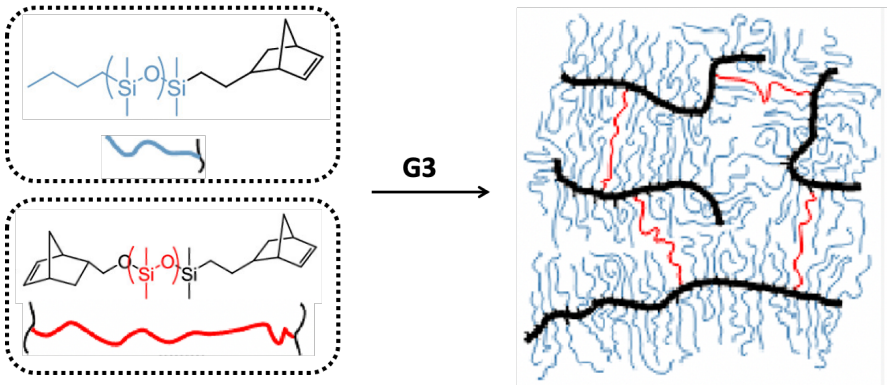


Figure 3: Brush-elastomers using PDMS-functionalized norbornene. Adapted with permission from Ref. [26]. Copyright © 2021 American Chemical Society

In pursuit of super-soft elastomers that are mouldable through 3D printing, Chabinyc, Bates and coworkers developed statistical bottlebrush copolymers based on a polynorbornene dicarboximide platform with PDMS and polyethylene oxide (PEO) side chains (**Figure 4**).[27] The 3D printing process requires excellent shear-thinning properties which is challenging to achieve for super-soft

elastomers. The requisite shear thinning properties could be realized by self-assembly of the brush polymers into well-ordered body-centered cubic (BCC) spheres even at highly asymmetric compositions (f_{PEO} = 0.04 to 0.06). Obtaining these highly asymmetric compositions requires precise control of the polymer architecture, afforded by living ROMP. Using **G3** as the catalyst, PDMS-*stat*-PEO bottlebrush polymers were synthesized in DCM via the grafting-through copolymerization of norbornene dicarboximide-terminated PEO and PDMS macromonomers on multigram scale (Đ < 1.2). The resulting materials exhibited fast and reversible yielding at room temperature in response to shear. Furthermore, the addition of telechelic PDMS with benzophenone end groups allowed the researchers to readily photocrosslink the printed materials by UV irradiation. This first reported example of solvent-free 3D printing of the elastomers was followed by their incorporation into pressure sensor devices.[28]

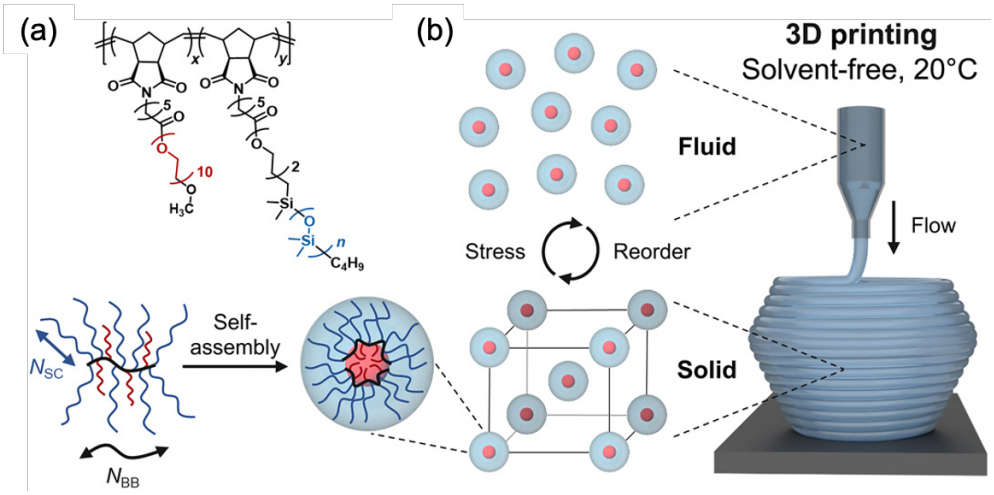


Figure 4: Super-soft bottlebrush elastomers for 3D printing. (a) Structure of statistical copolymer structure and illustration of its self-assembly; (b) schematic illustration of extrusion-based 3-D printing process enable by shear-thinning. Adapted with permission from Ref. [27]. Copyright © 2020 The Authors.

Impact-resistant materials have been designed using ROMP polymers with polyhedral oligomeric silsesquioxane (POSS) side chains. POSSs consist of a cage-like polyhedral siloxane structure bearing organic functionalities at the silica and are of the empirical formula $(RSiO_{1.5})_n$. They can be thought of as the smallest possible silica nanoparticles, 1-3 nm across. POSSs are readily functionalized with diverse R-groups for incorporation into macromolecular frameworks and confer improved mechanical, thermal, electrical, and surface properties on the resulting polymers, as well as presenting the possibility of incorporating solubilizing R groups or other desired functionalities.[29] The Yang and Yin groups functionalized POSS with a polymerizable norbornene dicarboximide group to generate reprocessable impact-resistant materials by **G3**-initiated polymerization in THF solution (**Figure 5**).[30] The steric bulk of the interdigitated isooctyl-functionalized POSS units restricts the motion of the ROMP-polymer chains, analogous to covalent crosslinking in resins, and thus termed “physical crosslinking”. Tensile tests revealed

fracture strains above 1000%, with samples showing no loss of tensile strength over three cycles of (i) tensile testing, (ii) reprocessing back into their original form, and (iii) retesting. Compressive tests using the Split-Hopkinson Pressure Bar method showed flow stresses around 20 Mpa compared to approximately 11 Mpa in polyurethanes, and impact tests using an air gun confirmed the desired high kinetic energy dissipation performance.

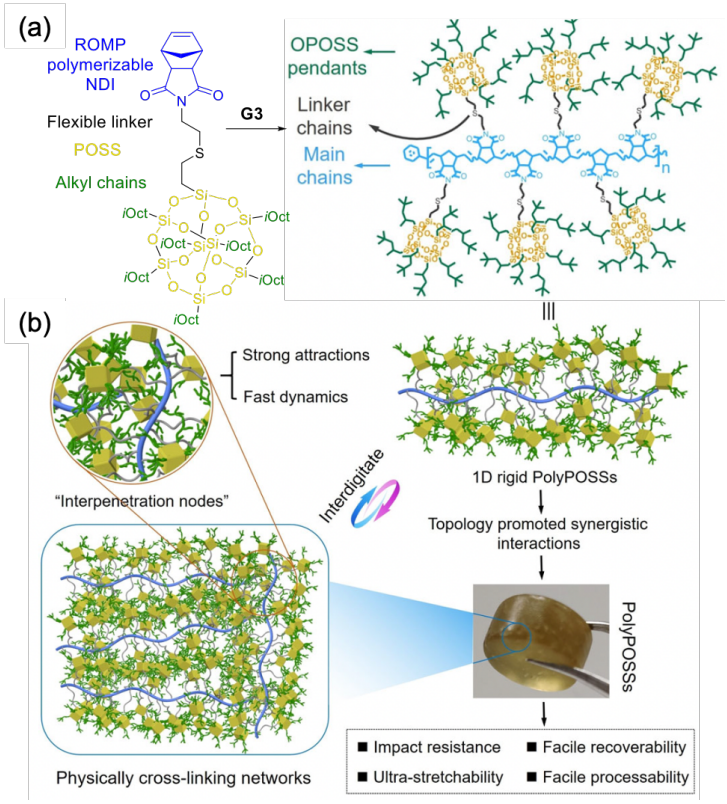


Figure 5. ROMP-derived POSS polymers as impact-resistant materials. (a) Synthetic route; (b) illustration of polymer dynamics in the material. Adapted with permission from Ref. [30]. Copyright © 2021 Wiley-VCH.

2.3 ROMP-Derived Dielectric Materials

Electronic components commonly incorporate, or are coated with, insulating materials, which are often based on silicone rubbers and resins.[31, 32] These materials tend to be difficult to process or recycle, and crosslinking is often achieved through the addition of small-molecules which may compromise other aspects of the function of the device. The development of new dielectric materials which are more easily processable, exhibit high purities, and have higher performance is therefore of considerable interest, especially given the ongoing miniaturization of electronic devices.

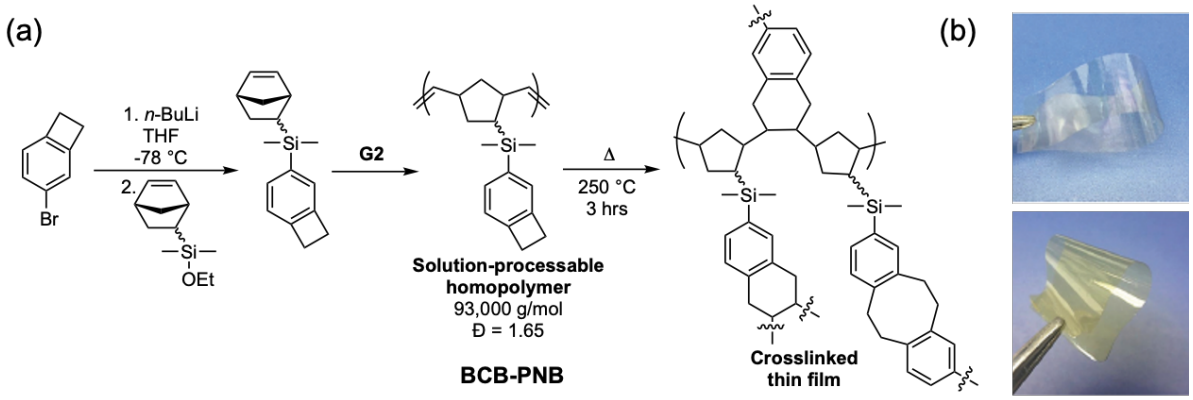


Figure 6. (a) ROMP synthesis of benzocyclobutene-functionalized polynorbornene (BCB-PNB); (b) photographs of BCB-PNB film before (top) and after (bottom) crosslinking. Adapted with permission from Ref. [33]. Copyright © 2018 Royal Society of Chemistry.

In 2018, Wang and coworkers introduced a new silyl-functionalized polynorbornene (BCB-PNB) with thermally crosslinkable benzocyclobutene side chains for dielectric materials applications (**Figure 6a**).[33] Poly-NBEs prepared by vinyl addition polymerization are suitably insulating and have the thermal stability and high glass transition temperatures necessary for this application, but they tend to be difficult to process by solution or melt processing. In comparison, ROMP-derived poly-NBEs typically have lower T_gs. The authors designed a norbornene monomer incorporating a flexible, solubilizing silane linker and a thermally crosslinkable benzocyclobutene unit, which was readily polymerized using **G2** as the initiator. The resulting homopolymer exhibited good solubility and film-forming ability when processed using simple solution techniques. Thermal crosslinking resulted in transparent films (**Figure 6b**) with a dielectric constant of 2.6, and high thermostability up to 400 °C, comparable to the commercial dielectric material CYCLOTENE (dielectric constant 2.65, thermostable up to 350 °C). Subsequently, the same authors reported an analogous system utilizing the thermal crosslinking of tetrafluorovinyl ether to yield water-resistant films with low dielectric constants, even up to gigahertz frequencies.[34]

2.4 ROMP-Derived Stimuli-Responsive and Degradable Materials

Degradable polymers are well-established in biodegradable sutures, where synthetic analogues were devised to mirror naturally degradable materials.[35] Increasingly, degradable and stimulus-responsive polymers are of interest because of the problem of plastic waste, as well as their utility in drug delivery systems, prosthetics, and other medical device applications.[36]

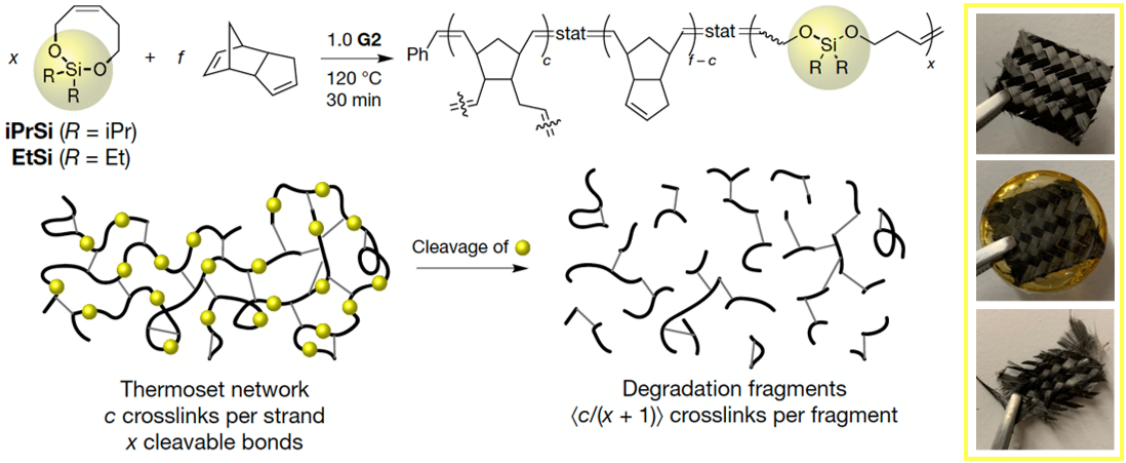


Figure 7. Degradable ROMP polymer resins based on siloxane-functionalized cyclooctenes. Inset: preparation of a carbon fiber-reinforced composite and recovery of the carbon fibers. Adapted with permission from Ref. [37]. Copyright © 2020, The Authors, under exclusive license to Springer Nature Limited.

In 2020, Johnson and coworkers reported the use of siloxane-bridged comonomers (**iPrSi**, **EtSi**; **Figure 7**) to impart triggerable degradability to PDCP resins—ROMP thermosets which, to date, are very challenging to recycle, especially when utilized in composite materials. Incorporation of the monomer at 10% loading allowed for full conversion to soluble products upon addition of tetrabutylammonium fluoride (TBAF), while having a negligible impact on the mechanical properties of the material. The degradation products, comprising linear PDCP oligomers, could be recycled by blending with virgin PDCP and cured to obtain new (though now non-degradable) PDCP resin. The degradable polymer was also used to fabricate a carbon-fiber reinforced composite and then degraded using TBAF, allowing for full recovery of the valuable carbon fiber filler (**Figure 7**, inset).[37] Other dynamic bonding motifs that involve main group elements have also been pursued. For example, phosphoramidate-based cyclic monomers can be used to produce acid-sensitive degradable ROMP polymers, as described in a 2020 communication by the Gianneschi group.[38]

2.5 ROMP-Derived Membranes and Polyelectrolyte Composites

Polymer membranes serve as selective barriers, allowing certain species to cross while preventing the transport of others. Relevant classes of membranes include gas separations, ion exchange membranes, etc. Since the 1970s, polymer membranes have become enormously commercially important, and are key to numerous processes in medical devices, water purification, fossil fuel separations, and fuel cells.[39, 40]

The synthesis of silyl-functionalized norbornenes and norbornene dicarboximides, although well established, continues to attract significant interest because of the great potential of silylated polymers for applications in gas separation membranes. Various substitution patterns have been

realized, and both vinyl addition polymerization[41-43] and ROMP methods[22, 24, 44, 45] have been explored in pursuit of new and more effective membranes. Selected ROMP polymers and their respective glass transition temperatures (T_gs)[24] are displayed in **Figure 8a**. In a recent study, Morontsev and coworkers prepared a bicyclic silacyclopentane-fused norbornene that was converted to the respective polymer with **G1** as the catalyst (**Figure 8b**).[44] The polymer was then subjected to gem-difluorocyclopropanation which increased the glass transition temperature and stability of the films, as well as their gas permeability. Upon storage for 2 months in air no discoloration was observed in contrast to the observed darkening of polynorbornene films.

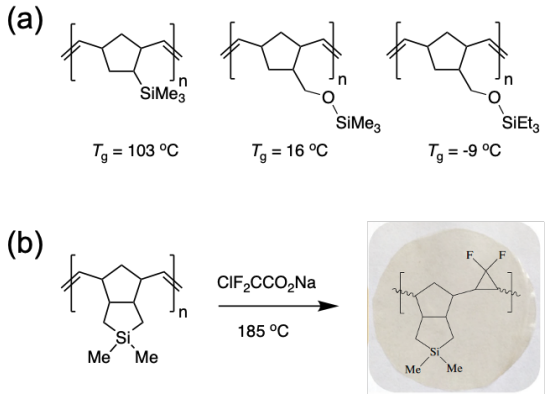


Figure 8: (a) Examples of silyl-functionalized polynorbornenes prepared by ROMP and their glass transition temperatures; (b) a bicyclic silyl-functionalized polymer and its difluoromethylation product; illustrated as thin film after exposure to air for 2 months. Adapted with permission from Ref. [44]. Copyright © 2019, Pleiades Publishing, Ltd.

In pursuit of new materials for selective ion transport, the Matějíček group synthesized anionic polyelectrolytes via **G3**-initiated ROMP of metallacarborane cluster-functionalized norbornene (**Figure 9a**).[46] The product, poly(norbornene-COSAN) (PNC) is miscible with poly(ethylene oxide), forming a nanocomposite that shows good Li^+ ion mobilities. Solid-state ^7Li magic-angle spinning (MAS) NMR data showed that Li^+ cations are strongly bound in the PNC matrix, as evidenced by a ^7Li signal in the high resonance region ($\delta \approx -0.25$ ppm), but the mixing of PNC with PEO led to a greatly improved local Li^+ mobility and enhanced dynamics of the PNC polymer chains, as shown by the ^7Li MAS NMR signal at $\delta \approx -0.75$ ppm. Conversely, in pursuit of more robust hydroxide-based anion-exchange membranes (AEMs), the Kowaleski and Noonan groups designed a tetraaminophosphonium-functionalized norbornene that is derived from organic superbases and, as such, exceptionally stable in alkaline media (**Figure 9b**).[47] Both statistical and block copolymers were prepared using Grubbs **G3** as the initiator, and the ROMP polymers were then subjected to hydrogenation to improve the mechanical properties. The statistical copolymers proved to be superior due to suppression of crystallinity, forming free-standing films.

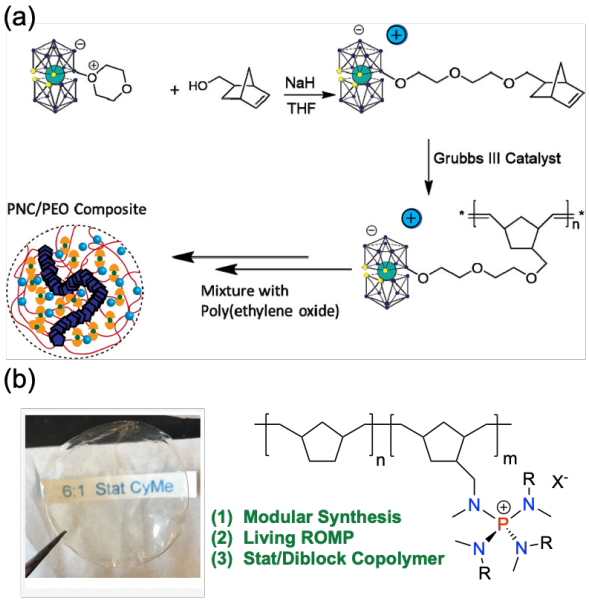


Figure 9. (a) Metallacarborane-functionalized polynorbornenes for Li ion transport. Reproduced with permission from Ref. [46]. Copyright © 2021 American Chemical Society; (b) hydrogenated tetraaminophosphonium-functionalized norbornene copolymer membranes for hydroxide ion transport. Adapted with permission from Ref. [47]. Copyright © 2020 American Chemical Society.

3 ROMP-Derived Flame Retardants and Preceramics

3.1 ROMP Polymers as Flame Retardants

Polymers containing main group elements (especially B and P) are frequently used as intumescent flame retardants, which form an inert char on the surface of a material during combustion that acts as a barrier between the source of ignition and the bulk of the material. The hydrocarbon chains in many organic polymers, including ROMP polymers, store a tremendous amount of chemical energy and can thus contribute to very damaging fires, and the automotive and elastomer applications of polynorbornenes and polydicyclopentadienes in industry tend to be ones in which fire risk is a concern. In recent years, severe toxicity, carcinogenicity, and reprotoxicity associated with halogenated small-molecule flame retardants has been of increasing concern, leading to the development of polymeric flame retardants with lower leaching, as well as the use of less toxic main group functionalities such as phosphonates. Polymeric flame retardants are also anticipated to improve material properties through more homogenous blending with the polymer.[48-51]

The Özkoç and Eren groups have reported a series of ROMP polymers incorporating flame retardant moieties, including phosphonates which contribute to the formation of fire-proof chars. Oxanorbornene dicarboximide monomers were utilized, which confer high flexibility to the

polymer backbone. A simple synthesis based on the Mitsunobu reaction allowed the phosphonate monomer to be obtained in 67% yield (**Figure 10**). Phosphonate-functionalized ROMP polymers were found to have increased char residue and lower peak heat release during combustion, indicative of flame retardancy.[52, 53] Subsequent work showed the incorporation of these polymers into polypropylene composites, resulting in substantial improvements in flame retardancy with better mechanical properties than obtainable using conventional small-molecule intumescent flame retardants.

Figure 10: Flame retardant ROMP homo- and copolymers (R = benzyl, naphthyl, anthracenyl) incorporating phosphonate groups and photographs of chars from flame testing on treated polypropylene (PP) test samples. Untreated PP test pieces were completely consumed. Adapted with permission from Ref. [53]. Copyright © 2018 Wiley-VCH.

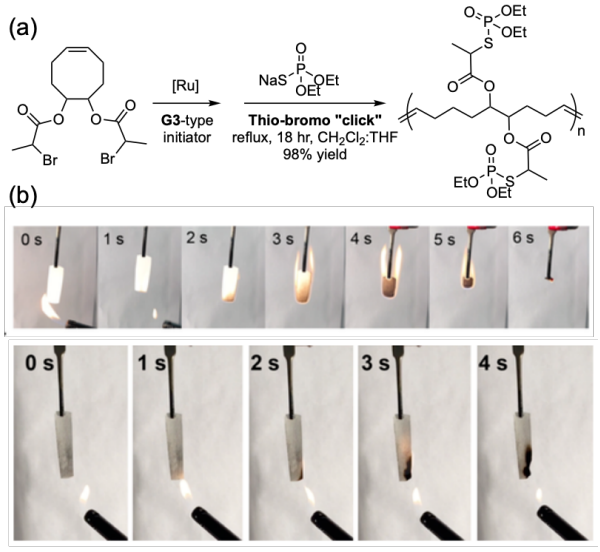


Figure 11: (a) Post-functionalization route to flame-retardant ROMP polymers; (b) flame tests on untreated filter paper (top) and on filter paper after impregnation with the flame-retardant polymer (bottom). Adapted with permission from Ref. [54]. Copyright © 2018 Wiley-VCH

Post-functionalization of ROMP polymers with phosphonates has been explored as an alternative approach to the preparation of functional monomers. A convenient route from readily available

alcohol-functionalized monomers was devised by the Hobbs group (**Figure 11a**).[54] The alcohols were esterified by simple overnight stirring at room temperature with 2-bromo-propionoic acid to furnish bromo-functionalized monomers. After ROMP, thio-bromo "click" chemistry furnished the flame-retardant functionalized polymers. These polymers proved to be highly effective flame retardants in standard tests. Treated paper samples exhibited a self-extinguishment time of 3 seconds, a limiting oxygen index of 26% (compared to 19.6% for untreated paper), and a residue mass of 94% (compared to 0% for untreated paper) in a UL 94 horizontal burn test (**Figure 11b**).

3.2 ROMP Polymers as Preceramic Materials

Ceramics are inorganic, non-metallic solids prepared by sintering of a precursor, and are among the oldest known artificially-produced materials.[55] Ceramics exhibit very high hardness, thermal resistance, and chemical stability, and often useful optical or electronic properties. Traditional ceramics use naturally-occurring inorganic precursors including powders (e.g., sand, gypsum) and colloids (e.g., clays) which are formed into the desired shape (e.g., by compression of a powder, or moulding of clays) and fused at high temperatures to form the desired products.[56] Since the 1960s, synthetic precursors have been developed to enable better control of precursor composition and thus the properties of the finished materials, but fundamental challenges remain because of the limited processability of powders and clays. A milestone in the development of ceramic precursors was the report in 1976 by Yajima and coworkers that polycarbosilane fibers could be sintered to form continuous silicon carbide fibers.[57, 58] The polymer fibers were spun by well-known polymer processing techniques, enabling previously-unattainable control over the morphology of the finished ceramic. Since this time, a wide variety of polymer-derived ceramics have been reported, enabling new morphologies, coatings, and new methods of processing.[59]

Boron in particular forms several useful ceramic materials including the ubiquitous borosilicate glass, boron nitride, and boron carbide. Boron carbides and nitrides are extremely hard, lightweight, and high melting, and are commonly used in abrasives, refractory materials, and ceramic composites. Applications taking advantage of the high neutron cross-section of boron are also well-known.[60, 61] The preparation of boron carbide from ROMP polymers was first reported by Sneddon and Allcock's groups in 2005.[62-64] They synthesized decaborane-functionalized norbornene (4:1 *exo:endo* ratio) and cyclooctene monomers (**Figure 12**), which were readily polymerized using **G1** and **G2** catalysts. ROMP methods are particularly attractive for the synthesis of these polymers because of the high reactivity of decaboranes and the good compatibility with Grubbs-type catalysts. TGA analysis of the polymers gave char yields of 72% and 70%, indicating the successful formation of boron carbide.[62] Further, electrospinning of the polynorbornene yielded fine fibers which were pyrolyzed to form ceramic material. The formation of graphite and boron carbide was confirmed by powder X-ray diffraction.[63]

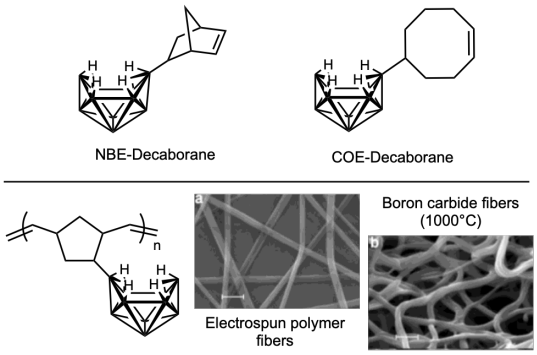


Figure 12: Top: Decaborane-functionalized ROMP monomers reported by Sneddon. Bottom: Polymer structure and micrographs of electrospun fibers (13 wt% polymer in THF, 19 kV) and ceramic fibers prepared by pyrolysis in argon at 1000 °C. Adapted with permission from Ref. [63]. Copyright © 2005 Wiley-VCH.

Building on these seminal first reports, the ROMP approach has been investigated to generate block copolymers as precursors to nanostructured ceramic materials. In 2007, Malenfant and coworkers reported a method for the formation of nano-ordered boron carbide, boron carbonitride, and boron nitride ceramics based on ROMP copolymers (**Figure 13**).[65] Block copolymers incorporating a decaborane-functionalized block along with an unfunctionalized polynorbornene block were prepared (**Figure 13a**), self-assembled into lamellar or porous architectures using simple solvent casting, and pyrolyzed to form lamellar and mesoporous ceramics (**Figure 13b**). Interestingly, varying the atmosphere during pyrolysis allowed for control over the composition of the ceramic (**Figure 13c**). Pyrolysis at 1000 °C in ammonia resulted in a boron nitride ceramic with a structure consistent with turbostratic boron nitride according to high resolution transmission electron microscopy (TEM), whereas hexagonal BN was obtained by pyrolysis at 1400 °C in ammonia. Pyrolysis in N_2 gas at 1000 °C yielded a ceramic with a lamellar structure composed of boron carbonitride and carbon layers.

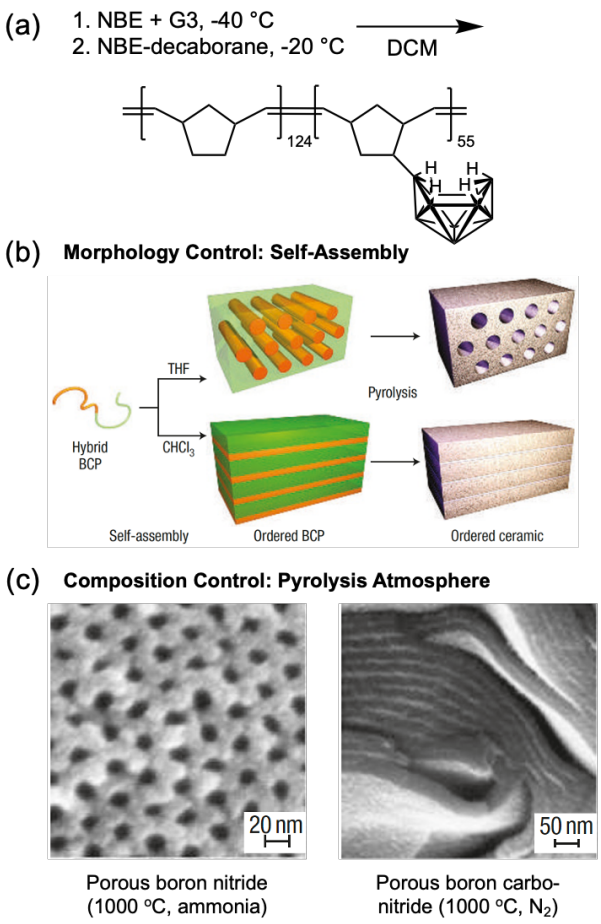


Figure 13. Boron ceramics with controllable structure and morphology derived from a decaborane-functionalized block copolymer precursor. (a) Polymer architecture; (b) schematic showing self-assembly of the polymer precursor and pyrolyzed products (polynorbornene segment orange, decaborane-functionalized polynorbornene segment green); (c) micrographs of pyrolyzed products. Adapted with permission from Ref. [65]. Copyright © 2007 Nature Publishing Group.

Other groups later used similar processes to create precursor copolymers that allowed for more specialized boron carbide products. For instance, J. Li, B. Li and coworkers prepared polymeric materials using the 6-norbornenyldecaborane monomer in combination with 1,5-hexadiene as co-monomer (**Figure 14a**).[66] These polymers were designed to have better solubility and film-forming ability than previously-reported examples. Double emulsion droplets were generated using a triple orifice droplet generator to fabricate hollow microspheres. In separate work, studying the copolymerization with unfunctionalized decaborane as a comonomer, Cao, Li and coworkers found that the **G2** Ru-alkylidene catalyst could play a dual role; promoting both ROMP of 6-norbornenyldecaborane and hydroboration of double bonds in the resulting polymer main chain with decaborane (**Figure 14b**).[67] The simultaneous ROMP and hydroboration reactions lead to an increased loading with decaborane units which resulted in increased char yields and improved

crystallinity of the polymer-derived ceramics. Finally, Gou, Wang and coworkers prepared a ROMP-derived poly(norbornenyldecaborane-*b*-cyclooctenyldecaborane) block copolymer (**Figure 14c**), which in turn was converted into a ceramic foam.[68] The foam was prepared through use of a polyurethane foam template, by immersing the foam in the decaborane polymer solution, drying under vacuum to remove solvents, and removal of the template through heat treatment in an electrical furnace under argon. Boron carbide foams have potential utility in neutron detection and as catalyst supports.

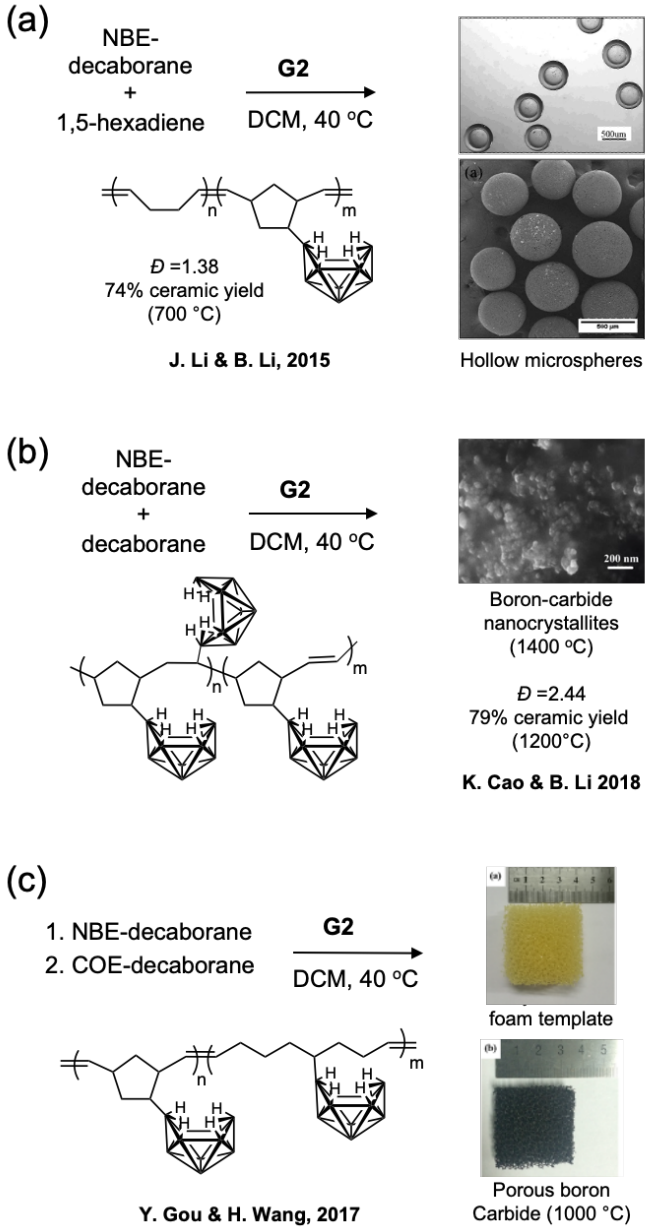


Figure 14. (a) Copolymer of norbornenyldecaborane with 1,5-hexadiene as precursor to boron carbide microspheres (top, optical image of double emulsion droplets; bottom, SEM image of microspheres). Adapted with permission from Ref. [66]. Copyright © 2015 Royal Society of

Chemistry; (b) copolymer of norbornenyldecaborane with decaborane as precursor to boron carbide with improved crystallinity and SEM image of ceramic residue at 1400 ºC. Adapted with permission from Ref. [67]; (c) poly(norbornenyldecaborane-*b*-cyclooctenyldecaborane) block copolymer (PND-*b*-PCB) as precursor of boron carbide ceramic foams (optical images). Adapted with permission from Ref. [68]. Copyright © 2017 Elsevier.

4. ROMP-Derived Supported Ligands, Reagents and Catalysts Containing Main Group Elements

4.1 Tris(pyridyl)borate Polyligands and Metallopolymers

Metallopolymers are of interest because of their mechanical, catalytic, and magnetic properties,[69, 70] including ligands and complexes supported by ROMP polymers.[71-73] However, while main group elements are useful both as ligand donor sites and for tuning ligand electronics and geometry,[74] main group ROMP polymers have not, thus far, been extensively explored for metallopolymer applications.[11] The Jäkle group have reported a tris(pyridyl)borate ligand-functionalized norbornene, prepared through a microwave-assisted Diels-Alder synthesis.[75] ROMP using **G3** furnished a variety of copolymers as well as the homopolymer. Amphiphilic micelles were prepared with pH responsive behavior (**Figure 15a**). The polyligands were found to complex metal salts, resulting in metal-induced polymer crosslinking (**Figure 15b**). Further, metal ion exchange from the Cu to the Fe complex was demonstrated.

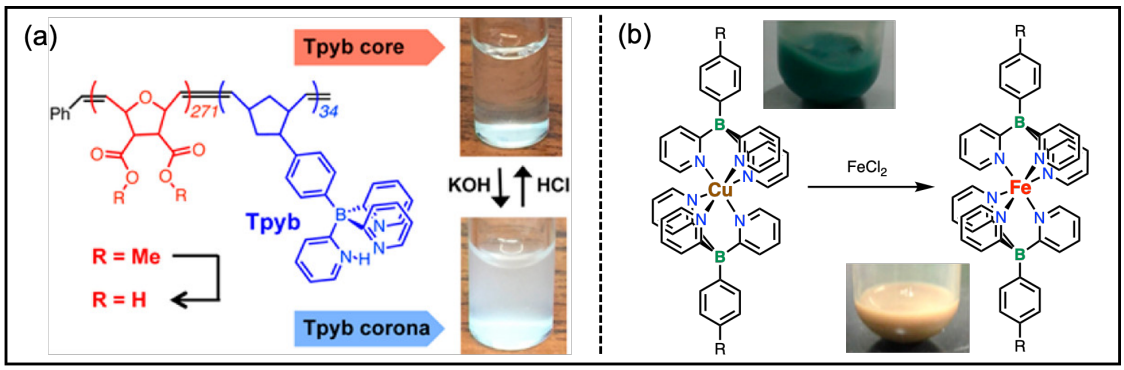


Figure 15. (a) Tris(pyridyl)borate block copolymers as pH-switchable polyligands and (b) for reversible uptake of metal ions (R = polymer chain). Adapted with permission from Ref. [75]. Copyright © 2015 American Chemical Society.

4.2 ROMP Polymer-supported Lewis Acid Catalysts

Main group species are also attracting interest as Lewis acid catalysts that enable metal-free routes to reactions that were previously only known to be promoted by transition metals. The important triarylborane class of Lewis acids[76-79] has been supported on polymers by the Jäkle group,[80]

including the first examples of ROMP-derived polymers.[81] The norbornene-functionalized triarylborane **B1** (**Figure 16a**) was readily polymerized using **G3**, and incorporated into insoluble crosslinked resins using a bifunctional crosslinker (**Figure 16b**). Frustrated Lewis pair hydrogen activation[77] was demonstrated using 1,4-diazabicyclo[2.2.2]octane (DABCO) as a Lewis base. The polymeric Lewis acids, when reversibly coordinated with acetonitrile, proved to be exceptionally stable to air yet highly active as catalysts in organic transformations even under ambient conditions. Reductive aminations of aldehydes and ketones were performed using dimethylphenylsilane[82, 83] as the reducing agent (**Figure 16c**). The resins allowed for the facile separation of the catalyst from the product mixture and its repeated use.

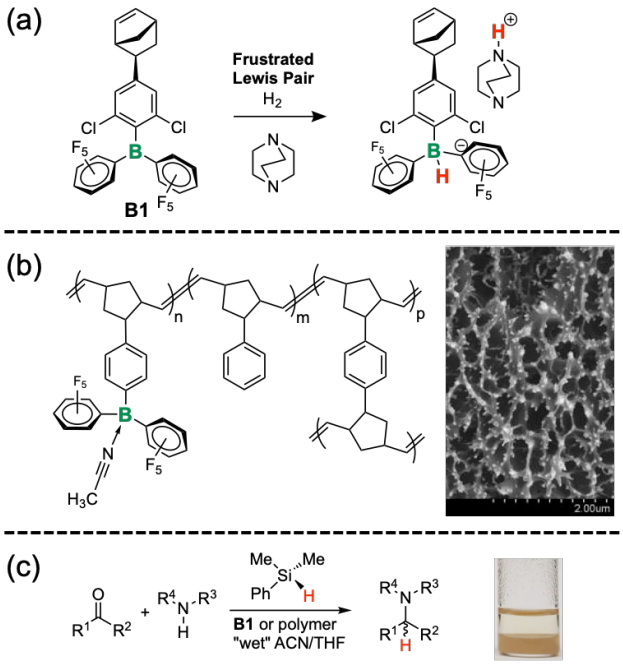


Figure 16. ROMP-derived triarylborane polymers. (a) Monomer structure and frustrated Lewis pair hydrogen activation; (b) structure of copolymer resin and its SEM micrograph; (c) reductive amination processes and photograph of reaction mixture with polymer resin. Adapted with permission from Ref. [81]. Copyright © 2020 American Chemical Society.

4.3 ROMP Polymers Incorporating Geminal Diboranes as Functional Groups

Stein, Masarwa, and coworkers reported stereoselective Diels-Alder reactions, using geminal diborylalkenes as the dienophile, to obtain diverse *gem*-diboronic ester functionalized olefins, including the norbornenes illustrated in **Figure 17**.[84] Unsymmetric alkenes bearing both pinacolato-boron (Bpin) and B-1,8-diaminonaphthalene (Bdan) moieties were incorporated stereoselectively, with the Bdan group in the *endo* position. The norbornenes were readily converted to polymers using **G2** as the catalyst. The post-functionalization chemistry of the

polymers was then explored: the backbone alkenes were hydrogenated using *p*-toluenesulfonyl hydrazide, the Bpin groups converted to BF_3K using potassium fluoride or potassium hydrogen fluoride, and palladium-catalyzed Suzuki-Miyaura coupling furnished arylated products. Reaction with methanol in the presence of cesium carbonate generated the protodeborylation or deuterodeborylation products.

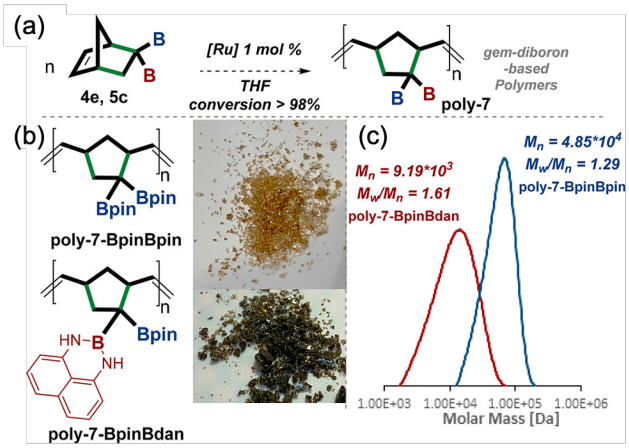


Figure 17. Geminal bis-borane-functionalized polymers (Bpin = pinacolato-boron, Bdan = B-1,8-diaminonaphthalene). (a) ROMP synthesis; (b) symmetric and unsymmetric polymer structures and photographs of the products; (c) GPC traces of symmetric and unsymmetric polymers. Reproduced with permission from Ref. [84]. Copyright © 2021 American Chemical Society.

5. ROMP-Derived Optoelectronic Materials Containing Main Group Elements

5.1 ROMP Polymers Incorporating Boron-Based Fluorophores

When embedded into or attached to π-conjugated systems, the diverse orbital configurations and structures of main group elements give rise to unique properties.[2, 85] Variation of the heteroatom enables tuning of the electronic and photophysical properties, thus the incorporation of main group chromophores and fluorophores into polymeric systems has been extensively studied.[1] ROMP has recently emerged as a convenient tool to incorporate fluorophores into well-defined positions along the polymer chain, for example, enabling the development of efficient thermally activated delayed fluorescence (TADF) materials[86] and of polymeric dyes[87] for multi-color living cell imaging.[88-90] As discussed below, much of the research on ROMP-derived main group-based optoelectronic materials has been focused on boron fluorophores, but recent studies have also tackled the incorporation of phosphorescent building blocks based on heavier Group 15 elements.

Boron fluorophores commonly take the form of BF_2 chelate complexes as seen, for example, in boron dipyrromethene (BODIPY) or boron formazanates.[91] They have characteristics that are highly desired, such as intense and narrow emission, high photo-, thermal, and oxidative stability, and low LUMO orbital levels which render them good electron acceptors for optoelectronic device

applications. Several research groups have pursued polymers which incorporate BF_2 chelates to harness the advantageous absorption, emission, and electrochemical characteristics. ROMP's functional group tolerance and utility in generating diverse polymer architectures are particularly relevant, allowing for potential applications in areas such as biomedical imaging, drug delivery, and for tracking biological processes.[92-94]

By far the most widely studied boron chelate fluorophore is boron-dipyrromethene (BODIPY).[95] In recent work, the Zimmerman group pursued BODIPY-functionalized crosslinked dendronized polyols (CDPs, **Figure 18a**) with the aim of developing water soluble, bright, photostable and biocompatible fluorophores for applications in bioimaging and intracellular delivery.[92] The crosslinked BODIPY polymer not only showed higher emission than free BODIPY, attributed to reduced self-quenching, but also favorable aqueous solubility allowing it to readily enter cells. The same group later studied linear dendronized polyols (LDPs), enabling similarly advantageous properties while simplifying the synthetic route considerably.[94] Although the BODIPY LDPs were less photostable than the CDP analogues, they were dramatically more stable than the free chromophore. The authors found a 2000-fold increase in emission intensity compared with free BODIPY after 4 hours of irradiation. The Goldsmith group developed a ROMP-polymerizable BODIPY monomer with spiro-fluorene-extended conjugation (**Figure 18b**).[93] In addition to being readily polymerizable using **G3**, the monomers were found to exhibit self-assembly behavior, forming nanoparticles with strongly enhanced emission properties that depend on their morphology. The vertically stacked assemblies shown in **Figure 18b** were found to result in a strong blueshifted emission from an upper exciton state, in violation of Kasha's rule.

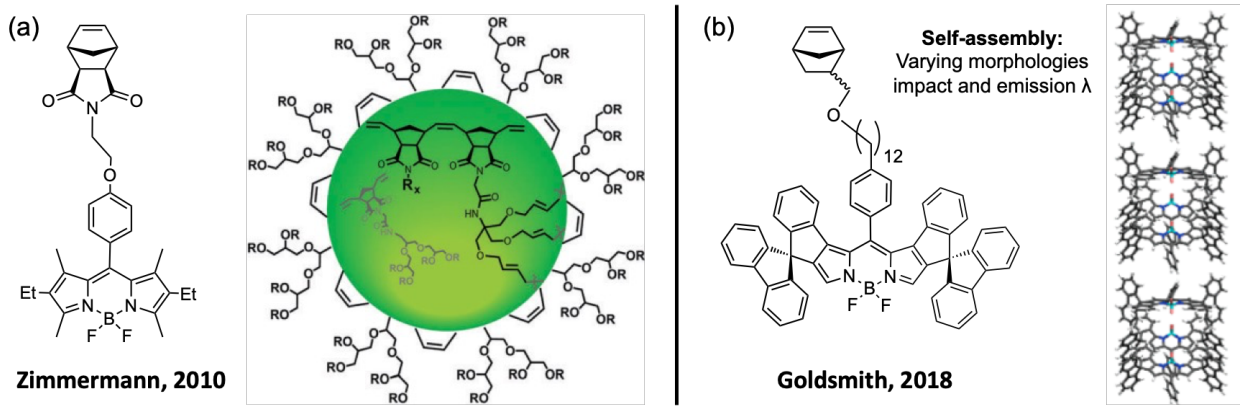


Figure 18: Examples of BODIPY-functionalized monomers and their ROMP products. (a) BODIPY monomer incorporation into crosslinked dendronized polyols (CDPs). Adapted with permission from Ref. [92]. Copyright © 2010 Royal Society of Chemistry; (b) BODIPY monomer with extended conjugation and its supramolecular assembly. Adapted with permission from Ref.[93]. Copyright © 2018 American Chemical Society.

Boron formazanate dyes have been supported on ROMP-polymer scaffolds as demonstrated in a series of papers from the Gilroy group.[96-98] In 2016, Gilroy and coworkers reported the first

ROMP polymer bearing boron formazanate sidechains. The monomer was synthesized in 3 steps from a norbornene-functionalized benzaldehyde precursor and was readily polymerized using **G3**. The emission for the homopolymer showed modest enhancement compared to the monomer (**Figure 19a**), indicating that self-quenching remained significant in the homopolymer. Cyclic voltammetry data did not show the second reduction peak observed for the monomer. Since the first peak remained reversible, precluding the reductive decomposition of the chromophore units, the authors attributed this to the high concentration of the anionic groups on the polymer chain.[96] Building on these results, the group devised a convenient "click" chemistry route to a highly emissive 3-cyanoformazanate monomer (**Figure 19b**, top). Variation of the polymer architecture had a strong impact on the emission of the polymers: homopolymers and block copolymers exhibited weak emission, while dilution of the chromophore by incorporation into random copolymers restored strong emission due to the spatial separation of the chromophores (**Figure 19b**, bottom).[97] In 2020, the Gilroy group developed a new type of ROMP monomer bearing a boron difluoride hydrazone (BODIHY) chromophore (**Figure 19c**). In this case, the chromophores exhibited aggregation-induced emission enhancement (AIEE) properties: monomer and polymer solutions exhibited minimal emission in solution, while in thin films they showed significantly higher quantum yields of Φ = 10% and 6%, respectively.[98]

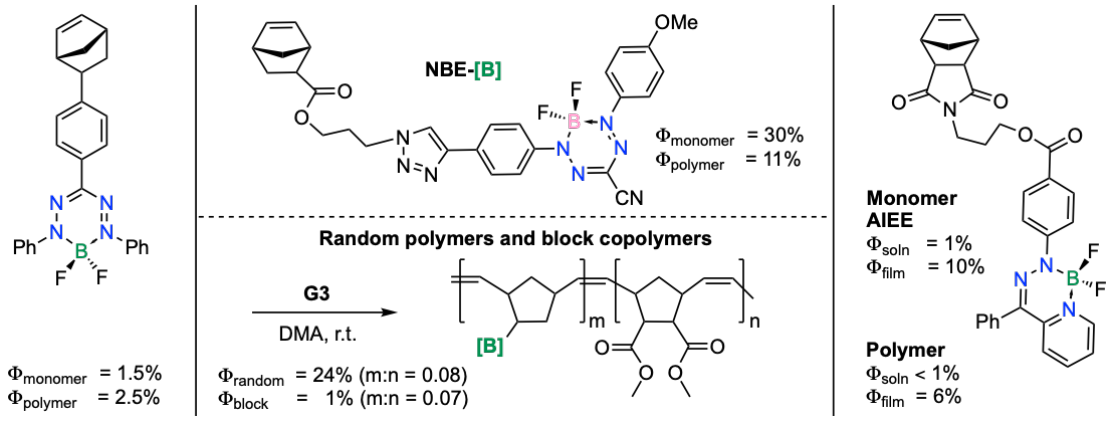


Figure 19: ROMP-polymerizable boron chromophores from the Gilroy group. (a) The first reported boron formazanate; (b) more strongly emissive boron cyanoformazanates; (c) boron difluoride hydrazone (BODIHY) monomer with AIEE property.

A family of ROMP-polymerizable boron difluoride curcuminoid-based dyes with thermally-activated delayed fluorescence (TADF) properties have been reported by Hudson and coworkers.[99] A β-diketone-functionalized monomer (**Figure 20a**), prepared in 3 steps from *exo*-5-norbornenecarboxylic acid, was reacted with boron trifluoride diethyletherate to form the boron diketonate acceptor. *n*-Butylamine-promoted condensation with donor-functionalized benzaldehydes furnished the donor-acceptor systems. These monomers were readily polymerized

in DCM at -20 °C using **G3**, yielding polymers which were highly emissive in the near-infrared (NIR) region. The materials thus obtained exhibited a desirable combination of NIR emission within the biological transparency window and TADF, which allows for the use of time-gated microscopy to image biological samples while removing background autofluorescence. Copolymers were prepared to enable solubility in aqueous media and the use of these polymeric dyes for imaging in biological media was explored. Functionalization of the copolymers with secondary goat anti-mouse IgG1 antibodies allowed for their use in immunolabeling experiments, with the polymeric dye rendering the binding sites in cells visible by fluorescence microscopy.

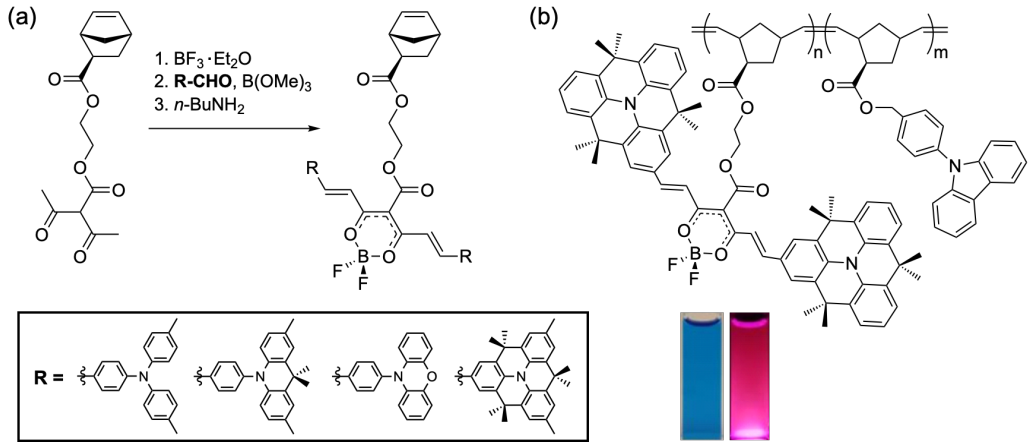


Figure 20: (a) Boron difluoride curcuminoid monomer synthesis; (b) representative structure of donor-acceptor polymer. Inset: toluene solution of polymer under room light (left) and upon excitation at 365 nm (right). Adapted with permission from Ref. [99]. Copyright © 2021 Wiley-VCH.

5.2 ROMP Polymers Incorporating Aluminum-Based Fluorophores

8-Hydroxyquinoline complexes of boron and aluminum have also attracted significant interest as fluorophores for luminescent and electroactive polymers. This research has been inspired by the discovery that aluminum tris(8-hydroxyquinolate) (Alq_3) serves as an efficient electron conduction and emissive layer in the first ever reported organic light emitting diodes (OLEDs). Most polymers that have been studied feature polystyrene as a backbone,[100-105] but a few reports on ROMP polymers have also appeared in the literature. Most notably, Weck and coworkers introduced Alq_3-functionalized polymers derived from ROMP of functional norbornene derivatives (**Figure 21**).[106] The resulting polymers are well soluble, can be spin coated onto surfaces, and show strong emission in solution and film states. The emission color can be fine-tuned by installing electron-donating or electron-withdrawing substituents on the pendant 8-hydroxyquinoline ligands. More recently, the first examples of boron quinolate-functionalized polynorbornenes were prepared by Bochkarev and coworkers and studied in OLEDs.[107]

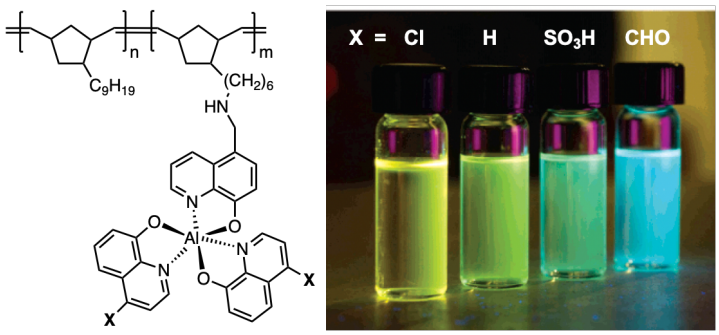
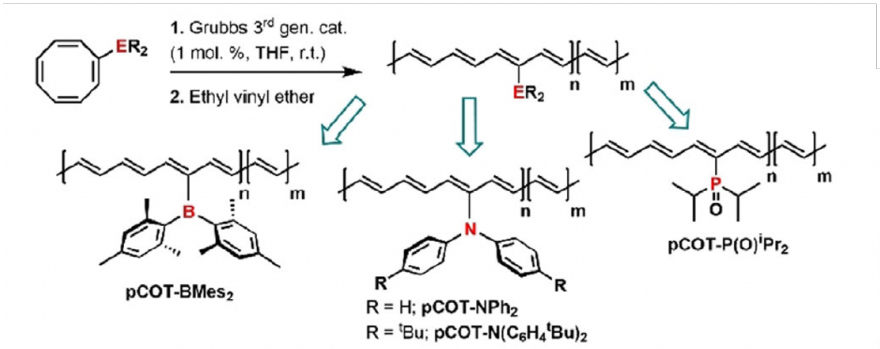


Figure 21. Aluminum tris(8-hydroxyquinolate) copolymers and photographs of solutions in $CHCl_3$ under UV light. Adapted with permission from Ref. [106] Copyright © 2004 American Chemical Society.

5.3 Functionalized Polyacetylenes Prepared Through ROMP

Very recently, Rivard and coworkers explored the ROMP polymerization of main group element-substituted cyclooctatetraenes using **G3** as a novel route to functionalized polyacetylenes, conducting polymers whose use to date has been hindered by poor solubility, processability, and air-stability (**Figure 22**).[108] Main group moieties, including Lewis acidic diarylboranes, metal-coordinating phosphines, and solubilizing trialkylsilanes were utilized to tune the optical, redox, and solubility properties of the polyacetylenes. Interestingly, phosphine monomers were found to prevent ROMP, presumably through coordination to the Ru alkylidene initiator. Thus, the phosphine-substituted polymers were prepared by polymerization of the phosphine oxide followed by reduction. Thin films of the functionalized polyacetylenes were readily obtained through simple solvent casting from THF. The polymer with $BMes_2$ side groups formed a lustrous golden film upon slow evaporation of the solvent. The phosphine oxide and amine groups led to significantly increased air stability, and the use of the redox-active pendant groups was found to enable redox-tunable near-IR absorption.



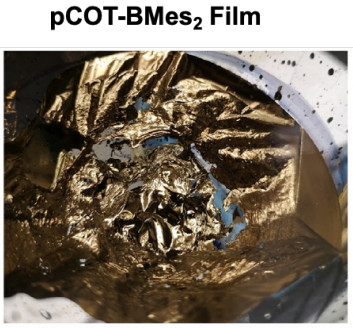


Figure 22. ROMP synthesis of functionalized polyacetylenes and photograph of a $BMes_2$-functionalized polyacetylene film obtained through solvent casting. Adapted with permission from Ref. [108]. Copyright © 2021 Wiley-VCH.

5.4 ROMP Polymers Incorporating Heavier Main Group Elements

Heavier main group elements are known to facilitate intersystem crossing (ISC) from the singlet to the triplet manifold. The opportunity to generate materials with long-lived phosphorescence makes their incorporation into polymers particularly attractive. In 2018, the Rivard group reported phosphorescent benzobismole monomers (**Figure 23a**).[109] The benzobismole ring was furnished through Cu(I)-catalyzed metallacycle transfer from a benzozirconacycle formed by Fagan-Nugent chemistry to the phenylnorbornene-functionalized bismuth compound. The phosphorescent monomers were readily polymerizable using Grubbs' **G2** or **G3** catalyst in THF at room temperature. The successful polymerization demonstrates the advantages of ROMP for polymerizing monomers containing heavier elements with relatively weak bonds. The monomers had respectable phosphorescence intensity (Φ = 0.68, 1.62% for the phenyl and pentafluorophenyl monomers respectively) and were robust to oxygen quenching in films prepared by dropcasting from hexanes. However, the polymeric derivatives exhibited weak emission, even when the rigidity of the polymer films was increased through thermal annealing, fuming with solvent vapors, or use of a trifunctional bismuth-containing crosslinker. The weak emission was attributed to the amorphous packing of the chromophores enabling increased molecular motion and thus more rapid nonradiative decay. Block copolymers that are able to form micelles in block-selective solvents were prepared by using an alkyl-functionalized comonomer. TEM analyses of the micelle solution after drop-casting indicated the formation of highly ordered films with spherical bismuth-rich regions. This approach may offer a route to novel bismuth-based nanostructures.

Rivard and coworkers utilized similar zirconacycle precursors to generate NBE-functionalized benzophospholes and benzophosphole oxides (**Figure 22b**).[110] The highly fluorescent benzophosphole oxides were readily incorporated into block copolymer micelles with excellent dispersities as low as $Đ$ = 1.02. Copolymerization with pinacolborane-functionalized monomers yielded micelles with fluoride-anion sensing properties: adding substoichiometric quantities of fluoride to solutions prepared in 30% THF in hexanes led to rapid precipitation of the micelles. Further, as part of their work on arsenic-containing conjugated materials,[111] the Naka group made use of the zirconacycle route to prepare benzoarsole heterocycles, including NBE-functionalized derivatives (**Figure 23c**).[112] The respective ROMP polymers showed aggregation-induced emission-enhancement (AIEE) properties, while oxidation of the arsoles was found to lead to dramatic emission enhancement.

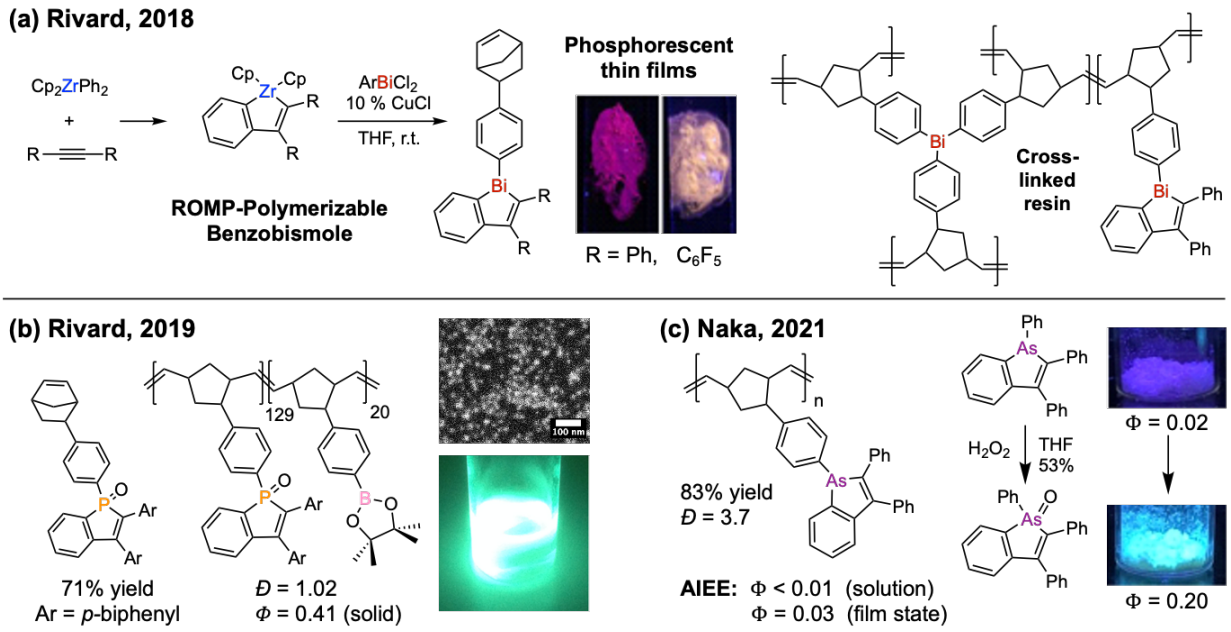


Figure 23: ROMP-polymerized phosphorescent (a) benzobismole, (b) benzophosphole oxide, and (c) benzoarsole, photographs illustrating their emissive properties, and TEM micrograph showing self-assembled micelles of a benzophosphole oxide block copolymer. Adapted with permission from Refs. [109, 110, 112]. Rivard 2018, Copyright © 2018 Wiley-VCH. Rivard 2019 Copyright © 2019 American Chemical Society. Naka 2021, Copyright © 2021 Wiley-VCH.

6. Conclusion and Outlook

As demonstrated in this brief review, ROMP has multiple characteristics that make it an advantageous method for the synthesis of functional and complex polymeric products through relatively simple and efficient syntheses with short reaction times. The use of ROMP to prepare new materials with main group elements is only just emerging, but the opportunities are limitless considering the excellent polymerization control, mild reaction conditions, and outstanding functional group tolerance. ROMP has already been very successfully applied to generate new polymers that show desirable thermomechanical, dielectric, flame-retardant, preceramic, ion-transporting, biodegradable, sensory, conductive and emissive properties, and it is easy to imagine numerous other future applications for main group ROMP polymers.

To date, many attempts have been made to improve the properties of polynorbornene and polydicyclopentadiene-based materials, but further research is needed to make direct comparisons and establish the benefits of ROMP-derived main group polymers relative to those prepared using more established polymerization methods such as free radical, ionic, or Ziegler-Natta polymerization. Further, researchers have thus far relied upon a relatively small selection of mostly lighter main group elements that include boron, aluminum, silicon, and phosphorus. On the other hand, the mild conditions of ROMP techniques are ideally suited to incorporate heavier main group elements with relatively weaker bonds into polymeric materials. Thus, expanding on the

pioneering work of the Rivard and Naka groups with heavier group 15 metallacycles, we anticipate new opportunities for utilizing heavier main group elements more broadly in the development of functional polymeric materials. Beyond expanding the scope in terms of elements, more advanced ROMP techniques such as frontal ROMP[113, 114] and ROMP-induced self-assembly[115] are yet to be implemented in main group ROMP materials. Relatively few of the plethora of ROMP initiators have been utilized in this context. Finally, and most importantly, further work is required to enable sufficiently high material performance and demonstrate the benefits of ROMP polymers in industrial applications.

CRediT Authorship contribution statement

James McQuade: Writing – original draft, Writing – review & editing, Supervision. **Mya I. Serrano:** Writing – original draft. **Frieder Jäkle:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding Acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements.

This review was prepared with support by the National Science Foundation (NSF) under Grant 1904791. J.M. gratefully acknowledges funding received through the Graduate School Newark CRRSAA/HEERF II Academic Advancement Fund. M.I.S. gratefully acknowledges receiving a research stipend from the NSF through the Garden State-LSAMP (NSF Award HRD-1909824). Supplement funding for this project was provided by the Rutgers University – Newark Chancellor's Research Office.

James McQuade graduated from the University of Limerick, Ireland, in 2015 with a B.Sc. in pharmaceutical and industrial chemistry. He then worked as a research intern studying plasmonic nanomaterials in the laboratory of Prof. Luat Vuong at Queens College, CUNY. He is currently a Ph.D. student at Rutgers University, Newark in the group of Prof. Frieder Jäkle, studying new boron compounds for polymer-supported ligands and catalysts.

Mya I. Serrano is a senior (Class of 2022) at Rutgers University in Newark, New Jersey. She will be graduating with a Bachelor of Arts in Chemistry. She has participated in research in Prof. Frieder Jäkle's lab throughout her undergraduate career, as well as participating in a research project in Prof Theodor Agapie's lab at Caltech during the summer of 2021. Mya was the president of the Chemistry Club at Rutgers Newark for the past two years, she is currently applying to graduate programs in STEM education.

Frieder Jäkle is a Distinguished Professor in the Department of Chemistry at the Newark campus of Rutgers University. He received his Diploma in 1994 and Ph.D. in 1997 from TU München, Germany, under the direction of Prof. Wagner. After a postdoctoral stint with Prof. Manners at the University of Toronto he joined Rutgers University in 2000. His research interests revolve around main group chemistry as applied to materials and catalysis, encompassing projects on organoborane Lewis acids, conjugated hybrid materials, luminescent materials for optoelectronic and sensory applications, stimuli-responsive and supramolecular polymers. He is the recipient of an NSF CAREER award (2004), an Alfred P. Sloan fellowship (2006), a *Friedrich Wilhelm Bessel Award* of the Alexander von Humboldt Foundation (2009), the ACS Akron Section Award (2012), the Boron Americas Award (2012) and the Board of Trustees Research Award at Rutgers University (2017). In 2019 he was named a *Fellow* of the American Chemical Society.

References

[1] F. Vidal, F. Jäkle, Functional Polymeric Materials Based on Main-Group Elements, Angew. Chem. Int. Edit. 58 (2019) 5846-5870.

[2] T. Baumgartner, F. Jäkle, Main group strategies towards functional hybrid materials, John Wiley & Sons, Hoboken, N.J., 2018.

[3] Y. Chujo, K. Tanaka, New Polymeric Materials Based on Element-Blocks, Bull. Chem. Soc. Jpn. 88 (2015) 633-643.

[4] A.M. Priegert, B.W. Rawe, S.C. Serin, D.P. Gates, Polymers and the p-block elements, Chem. Soc. Rev. 45 (2016) 922-953.

[5] Y.J. Chen, M.M. Abdellatif, K. Nomura, Olefin metathesis polymerization: Some recent developments in the precise polymerizations for synthesis of advanced materials (by ROMP, ADMET), Tetrahedron 74 (2018) 619-643.

[6] A. Leitgeb, J. Wappel, C. Slugovc, The ROMP toolbox upgraded, Polymer 51 (2010) 2927-2946.

[7] P. Lu, V.K. Kensy, R.L. Tritt, D.T. Seidenkranz, A.J. Boydston, Metal-Free Ring-Opening Metathesis Polymerization: From Concept to Creation, Acc. Chem. Res. 53 (2020) 2325-2335.

[8] S.T. Nguyen, L.K. Johnson, R.H. Grubbs, J.W. Ziller, Ring-Opening Metathesis Polymerization (ROMP) of Norbornene by a Group-VIII Carbene Complex in Protic Media, J. Am. Chem. Soc. 114 (1992) 3974-3975.

[9] J.C. Mol, Industrial applications of olefin metathesis, J. Mol. Catal. A: Chem. 213 (2004) 39-45.

[10] D.J. Walsh, S.H. Lau, M.G. Hyatt, D. Guironnet, Kinetic Study of Living Ring-Opening Metathesis Polymerization with Third-Generation Grubbs Catalysts, J. Am. Chem. Soc. 139 (2017) 13644-13647.

[11] I. Dragutan, V. Dragutan, P. Filip, B.C. Simionescu, A. Demonceau, ROMP Synthesis of Iron-Containing Organometallic Polymers, Molecules 21 (2016) 198.

[12] Z.L. He, L.N. Chen, L. Zhang, H.Y. Ren, M.D. Xu, Y.W. Lou, Effect of filler functional groups on the mechanical properties and relevant mechanisms of polydicyclopentadiene nanocomposites, J. Appl. Polym. Sci. 137 (2020) 49010.

[13] N.T. Tran, B.A. Patterson, D.E. Harris, E. Napadensky, J.L. Lenhart, D.B. Knorr, E.D. Bain, Influence of Interfacial Bonding on the Mechanical and Impact Properties Ring-Opening Metathesis Polymer (ROMP) Silica Composites, ACS Appl. Mater. Inter. 12 (2020) 53342-53355.

[14] X. Deng, L. Prozorovska, G.K. Jennings, Metal Chelating Polymer Thin Films by Surface-Initiated ROMP and Modification, J. Phys. Chem. C 123 (2019) 23511-23519.

[15] T.G. Pattison, A. Spanu, A.M. Friz, Q. Fu, R.D. Miller, G.G. Qiao, Growing Patterned, Cross-linked Nanoscale Polymer Films from Organic and Inorganic Surfaces Using Ring-Opening Metathesis Polymerization, ACS Appl. Mater. Inter. 12 (2019) 4041-4051.

[16] N.Y. Kim, N.L. Jeon, I.S. Choi, S. Takami, Y. Harada, K.R. Finnie, G.S. Girolami, R.G. Nuzzo, G.M. Whitesides, P.E. Laibinis, Surface-Initiated Ring-Opening Metathesis Polymerization on Si/SiO_2, Macromolecules 33 (2000) 2793-2795.

[17] Q. Chen, M. Salami-Kalajahi, Surface-Initiated Ring-Opening Metathesis Polymerization (SI-ROMP): History, General Features, and Applications in Surface Engineering with Polymer Brushes, Int. J. Polym. Sci. 2021 (2021) 1-15.

[18] H.R. Allcock, F.W. Lampe, J.E. Mark, Contemporary polymer chemistry, 3rd ed., Pearson/Prentice Hall, Upper Saddle River, N.J., 2003.

[19] R. Pietschnig, Advances and Properties of Silanol-Based Materials, in: T. Baumgartner, F. Jäkle (Eds.), Main Group Strategies towards Functional Hybrid Materials, John Wiley & Sons, Hoboken, N.J., 2018, pp. 141-162.
[20] M. Shimizu, Silole-Based Materials in Optoelectronics and Sensing, in: T. Baumgartner, F. Jäkle (Eds.), Main Group Strategies towards Functional Hybrid Materials, Wiley-VCH, Hoboken, N.J., 2018, pp. 163-195.
[21] T. Sanji, Materials Containing Homocatenated Polysilanes, in: T. Baumgartner, F. Jäkle (Eds.), Main Group Strategies towards Functional Hybrid Materials, John Wiley & Sons, Hoboken, N.J., 2018, pp. 197-208.
[22] M.A. Guseva, D.A. Alentiev, D.I. Gavrilov, E.V. Bermesheva, P.P. Chapala, E.S. Finkelshtein, M.V. Bermeshev, Stereoselective synthesis and metathesis polymerization of exo-5-(Pentamethyldisiloxanyl) norbornene, Polym. Sci. Ser. C 61 (2019) 102-106.
[23] E.V. Bermesheva, D.A. Alentiev, A.P. Moskalets, M.V. Bermeshev, New Adhesive Materials Based on Silicon-Substituted Polynorbornenes, Polym. Sci. Ser. B 61 (2019) 314-322.
[24] F.A. Andreyanov, D.A. Alent'ev, M.V. Bermeshev, Synthesis and Metathesis Polymerization of 5-(Triethylsiloxymethyl)norbornene, Polym. Sci. Ser. B 63 (2021) 109-115.
[25] B.T. Wang, K. Mireles, M. Rock, Y.Z. Li, V.K. Thakur, D. Gao, M.R. Kessler, Synthesis and Preparation of Bio-Based ROMP Thermosets from Functionalized Renewable Isosorbide Derivative, Macromol. Chem. Phys. 217 (2016) 871-879.
[26] K. Cushman, A. Keith, J. Tanaka, S.S. Sheiko, W. You, Investigating the Stress-Strain Behavior in Ring-Opening Metathesis Polymerization-Based Brush Elastomers, Macromolecules 54 (2021) 8365-8371.
[27] R.X. Xie, S. Mukherjee, A.E. Levi, V.G. Reynolds, H.B. Wang, M.L. Chabinyc, C.M. Bates, Room temperature 3D printing of super-soft and solvent-free elastomers, Sci. Adv. 6 (2020) eabc6900.
[28] V.G. Reynolds, S. Mukherjee, R.X. Xie, A.E. Levi, A. Atassi, T. Uchiyama, H.B. Wang, M.L. Chabinyc, C.M. Bates, Super-soft solvent-free bottlebrush elastomers for touch sensing, Mater. Horizons 7 (2020) 181-187.
[29] F. Chen, F. Lin, Q. Zhang, R. Cai, Y. Wu, X. Ma, Polyhedral Oligomeric Silsesquioxane Hybrid Polymers: Well-Defined Architectural Design and Potential Functional Applications, Macromol. Rapid Comm. 40 (2019) 1900101.
[30] J.F. Yin, H.Y. Xiao, P.D. Xu, J.S. Yang, Z.W. Fan, Y.B. Ke, X.K. Ouyang, G.X. Liu, T.L. Sun, L.Q. Tang, S.Z.D. Cheng, P.C. Yin, Polymer Topology Reinforced Synergistic Interactions among Nanoscale Molecular Clusters for Impact Resistance with Facile Processability and Recoverability, Angew. Chem. Int. Edit. 60 (2021) 22212-22218.
[31] E. Wiberg, N. Wiberg, A.F. Holleman, Inorganic chemistry, 1st English ed., Academic Press ; De Gruyter, San Diego, 2001.
[32] S.M.R. Billah, Dielectric Polymers, in: M. Jafar Mazumder, H. Sheardown, A. Al-Ahmed (Eds.), Functional Polymers. Polymers and Polymeric Composites: A Reference Series., Springer, Cham., 2019, pp. 241-288.
[33] J.J. Wang, J.F. Zhou, L.X. Fang, J. Sun, Q. Fang, A novel post-polymerizable polynorbornene prepared via ROMP: easy synthesis and conversion into a free-standing film with high T_g and low dielectric constant, Mater. Chem. Front. 2 (2018) 1467-1474.
[34] X.R. Chen, J. Sun, L.X. Fang, Y.Q. Tao, X.Y. Chen, J.F. Zhou, Q. Fang, Cross-Linkable Fluorinated Polynorbornene with High Thermostability and Low Dielectric Constant at High Frequency, ACS Appl. Polym. Mater. 2 (2020) 768-774.

[35] L.S. Nair, C.T. Laurencin, Biodegradable polymers as biomaterials, Progr. Polym. Sci. 32 (2007) 762-798.
[36] M.A.C. Stuart, W.T.S. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G.B. Sukhorukov, I. Szleifer, V.V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, S. Minko, Emerging applications of stimuli-responsive polymer materials, Nat. Mater. 9 (2010) 101-113.
[37] P. Shieh, W.X. Zhang, K.E.L. Husted, S.L. Kristufek, B.Y. Xiong, D.J. Lundberg, J. Lem, D. Veysset, Y.C. Sun, K.A. Nelson, D.L. Plata, J.A. Johnson, Cleavable comonomers enable degradable, recyclable thermoset plastics, Nature 583 (2020) 542-547.
[38] Y. Liang, H. Sun, W. Cao, M.P. Thompson, N.C. Gianneschi, Degradable Polyphosphoramidate via Ring-Opening Metathesis Polymerization, ACS Macro Lett. 9 (2020) 1417-1422.
[39] G. Srikanth, Membrane separation processes: Technology and business opportunities, Chem. Eng. World 34 (1999) 55-66.
[40] M. Ulbricht, Advanced functional polymer membranes, Polymer 47 (2006) 2217-2262.
[41] K.R. Gmernicki, E. Hong, C.R. Maroon, S.M. Mahurin, A.P. Sokolov, T. Saito, B.K. Long, Accessing Siloxane Functionalized Polynorbornenes via Vinyl-Addition Polymerization for CO_2 Separation Membranes, ACS Macro Lett. 5 (2016) 879-883.
[42] C.R. Maroon, J. Townsend, K.R. Gmernicki, D.J. Harrigan, B.J. Sundell, J.A. Lawrence, S.M. Mahurin, K.D. Vogiatzis, B.K. Long, Elimination of CO_2/N_2 Langmuir Sorption and Promotion of "N_2-Phobicity" within High-T_g Glassy Membranes, Macromolecules 52 (2019) 1589-1600.
[43] C.R. Maroon, J. Townsend, M.A. Higgins, D.J. Harrigan, B.J. Sundell, J.A. Lawrence, J.T. O'Brien, D. O'Neal, K.D. Vogiatzis, B.K. Long, Addition-type alkoxysilyl-substituted polynorbornenes for post-combustion carbon dioxide separations, J. Membrane Sci. 595 (2020) 117532.
[44] V.A. Zhigarev, A.A. Morontsev, R.Y. Nikiforov, M.L. Gringolts, N.A. Belov, N.G. Komalenkova, V.G. Lakhtin, E.S. Finkelshtein, Synthesis and Gas-Separation Properties of New Silacyclopentane-Containing Polynorbornenes, Polym. Sci. Ser. C 61 (2019) 107-119.
[45] V.A. Zhigarev, M.L. Gringolts, M.P. Filatova, E.S. Finkelshtein, Synthesis and Metathesis Polymerization of New Monomer 7-Trimethylsilyltricyclo[4.2.2.$0^{2,5}$]deca-3,9-diene, Polym. Sci. Ser. B 63 (2021) 470-479.
[46] J.W. Li, R. Fernandez-Alvarez, Z. Tosner, P. Kozlik, M. Stepanek, A. Zhigunov, M. Urbanova, J. Brus, M. Uchman, P. Matejicek, Polynorbornene-Based Polyelectrolytes with Covalently Attached Metallacarboranes: Synthesis, Characterization, and Lithium-Ion Mobility, Macromolecules 54 (2021) 6867-6877.
[47] M. Treichel, C.T. Womble, R. Selhorst, J. Gaitor, T.M.S.K. Pathiranage, T. Kowalewski, K.J.T. Noonan, Exploring the Effects of Bulky Cations Tethered to Semicrystalline Polymers: The Case of Tetraaminophosphoniums with Ring-Opened Polynorbornenes, Macromolecules 53 (2020) 8509-8518.
[48] J. Green, Mechanisms for Flame Retardancy and Smoke suppression -A Review, J. Fire Sci. 14 (1996) 426-442.
[49] P. Brown, A. Cordner, Lessons Learned From Flame Retardant Use And Regulation Could Enhance Future Control Of Potentially Hazardous Chemicals, Health Affairs 30 (2011) 906-914.
[50] R. Nazir, S. Gaan, Recent developments in P(O/S)–N containing flame retardants, J. Appl. Polym. Sci. 137 (2019) 47910.
[51] A. Battig, J.C. Markwart, F.R. Wurm, B. Schartel, Hyperbranched phosphorus flame retardants: multifunctional additives for epoxy resins, Polym. Chem. - UK 10 (2019) 4346-4358.

[52] E. lşıksel, G. Kahraman, N. Ceren Süer, D.Y. Wang, T. Eren, Synthesis and characterization of phosphonate and aromatic-based polynorbornene polymers derived from the ring opening metathesis polymerization method and investigation of their thermal properties, J. Appl. Polym. Sci. 136 (2018) 47085.
[53] G. Turgut, E. Isiksel, G. Kahraman, T. Eren, G. Özkoç, Synthesis of phosphorus- and phenyl-based ROMP polymers and investigation of their effects on the thermomechanical and flammability properties of a polypropylene-IFR system, J. Appl. Polym. Sci. 135 (2018) 45998.
[54] J. Grubb, F. Carosio, M. Vasireddy, S. Moncho, E.N. Brothers, C.E. Hobbs, Ring opening metathesis polymerization (ROMP) and thio-bromo "click" chemistry approach toward the preparation of flame-retardant polymers, J. Polym. Sci. A, Polym. Chem. 56 (2018) 645-652.
[55] Introduction to Ceramics (Chapter 1), in The Ceramic Society of Japan (Ed), Advanced Ceramic Technologies & Products, Springer, Tokyo, 2012.
[56] J.A. Lewis, Colloidal Processing of Ceramics, J. Am. Cer. Soc. 83 (2004) 2341-2359.
[57] S. Yajima, K. Okamura, J. Hayashi, M. Omori, Synthesis of Continuous SiC Fibers with High Tensile Strength, J. Am. Cer. Soc. 59 (1976) 324-327.
[58] S. Yajima, J. Hayashi, M. Omori, K. Okamura, Development of a silicon carbide fibre with high tensile strength, Nature 261 (1976) 683-685.
[59] J. Bill, F. Aldinger, Precursor-derived Covalent Ceramics, Adv. Mater. 7 (1995) 775-787.
[60] F. Thévenot, Boron carbide—A comprehensive review, J. Eur. Ceram. Soc. 6 (1990) 205-225.
[61] R.T. Paine, C.K. Narula, Synthetic routes to boron nitride, Chem. Rev. 90 (2002) 73-91.
[62] X. Wei, P.J. Carroll, L.G. Sneddon, New Routes to Organodecaborane Polymers via Ruthenium-Catalyzed Ring-Opening Metathesis Polymerization, Organometallics 23 (2003) 163-165.
[63] D.T. Welna, J.D. Bender, X. Wei, L.G. Sneddon, H.R. Allcock, Preparation of Boron-Carbide/Carbon Nanofibers from a Poly(norbornenyldecaborane) Single-Source Precursor via Electrostatic Spinning, Adv. Mater. 17 (2005) 859-862.
[64] X. Wei, P.J. Carroll, L.G. Sneddon, Ruthenium-Catalyzed Ring-Opening Polymerization Syntheses of Poly(organodecaboranes): New Single-Source Boron-Carbide Precursors, Chem. Mater. 18 (2006) 1113-1123.
[65] P.R.L. Malenfant, J. Wan, S.T. Taylor, M. Manoharan, Self-assembly of an organic–inorganic block copolymer for nano-ordered ceramics, Nat. Nanotechnol. 2 (2007) 43-46.
[66] X.J. Zhang, J. Li, K. Cao, Y. Yi, J.X. Yang, B. Li, Synthesis and characterization of B-C polymer hollow microspheres from a new organodecaborane preceramic polymer, RSC Adv. 5 (2015) 86214-86218.
[67] J. Li, K. Cao, J. Li, M.F. Liu, S. Zhang, J.X. Yang, Z.W. Zhang, B. Li, Synthesis and Ceramic Conversion of a New Organodecaborane Preceramic Polymer with High-Ceramic-Yield, Molecules 23 (2018) 2461.
[68] J.L. Wang, Y.Z. Gou, Q.C. Zhang, K. Jian, Z. Chen, H. Wang, Linear organodecaborane block copolymer as a single-source precursor for porous boron carbide ceramics, J. Eur. Ceram. Soc. 37 (2017) 1937-1943.
[69] G.I. Dzhardimalieva, I. E. Uflyand, Metal Complexes with Polymer Chelating Ligands. In: , Chemistry of Polymeric Metal Chelates. Springer Series in Materials Science, vol 257, Springer, Cham2018, pp. 199-366.

[70] C.G. Hardy, J. Zhang, Y. Yan, L. Ren, C. Tang, Metallopolymers with transition metals in the side-chain by living and controlled polymerization techniques, Prog. Polym. Sci. 39 (2014) 1742-1796.
[71] A. de Bettencourt-Dias, J.S.K. Rossini, Ligand Design for Luminescent Lanthanide-Containing Metallopolymers, Inorg. Chem. 55 (2016) 9954-9963.
[72] G. Fu, H. Feng, W. Feng, X. Lü, W.-K. Wong, PNBE-supported metallopolymer-type hybrid materials through grafting of Ln_3-benzimidazole-arrayed (Ln=Nd, Yb or Er) complex monomers with efficient NIR luminescence, Inorg. Chem. Commun. 76 (2017) 30-32.
[73] H. Gu, R. Ciganda, P. Castel, S. Moya, R. Hernandez, J. Ruiz, D. Astruc, Tetrablock Metallopolymer Electrochromes, Angew. Chem. Int. Edit. 57 (2018) 2204-2208.
[74] G.M. Pawar, J.B. Sheridan, F. Jäkle, Pyridylborates as a New Type of Robust Scorpionate Ligand: From Metal Complexes to Polymeric Materials, Eur. J. Inorg. Chem. (2016) 2227-2235.
[75] G.M. Pawar, R.A. Lalancette, E.M. Bonder, J.B. Sheridan, F. Jäkle, ROMP-Derived Pyridylborate Block Copolymers: Self-Assembly, pH-Responsive Properties, and Metal-Containing Nanostructures, Macromolecules 48 (2015) 6508-6515.
[76] M. Oestreich, J. Hermeke, J. Mohr, A unified survey of Si-H and H-H bond activation catalysed by electron-deficient boranes, Chem. Soc. Rev. 44 (2015) 2202-2220.
[77] D.W. Stephan, Frustrated Lewis Pairs, J. Am. Chem. Soc. 137 (2015) 10018-10032.
[78] D.W. Stephan, The broadening reach of frustrated Lewis pair chemistry, Science 354 (2016) aaf7229.
[79] J.R. Lawson, R.L. Melen, Tris(pentafluorophenyl)borane and Beyond: Modern Advances in Borylation Chemistry, Inorg. Chem. 56 (2017) 8627-8643.
[80] Y. Qin, G.L. Cheng, A. Sundararaman, F. Jäkle, Well-defined boron-containing polymeric Lewis acids, J. Am. Chem. Soc. 124 (2002) 12672-12673.
[81] F. Vidal, J. McQuade, R. Lalancette, F. Jäkle, ROMP-Boranes as Moisture-Tolerant and Recyclable Lewis Acid Organocatalysts, J. Am. Chem. Soc. 142 (2020) 14427-14431.
[82] H.Q. Fang, M. Oestreich, Reductive Deamination with Hydrosilanes Catalyzed by $B(C_6F_5)_3$, Angew. Chem. Int. Edit. 59 (2020) 11394-11398.
[83] V. Fasano, J.E. Radcliffe, M.J. Ingleson, $B(C_6F_5)_3$-Catalyzed Reductive Amination using Hydrosilanes, ACS Catal. 6 (2016) 1793-1798.
[84] N. Eghbarieh, N. Hanania, A. Zamir, M. Nassir, T. Stein, A. Masarwa, Stereoselective Diels-Alder Reactions of gem-Diborylalkenes: Toward the Synthesis of gem-Diboron-Based Polymers, J. Am. Chem. Soc. 143 (2021) 6211-6220.
[85] S.M. Parke, M.P. Boone, E. Rivard, Marriage of heavy main group elements with π-conjugated materials for optoelectronic applications, Chem. Commun. 52 (2016) 9485-9505.
[86] Q. Li, J. Hu, J.H. Lv, X.D. Wang, S.Y. Shao, L.X. Wang, X.B. Jing, F.S. Wang, Through-Space Charge-Transfer Polynorbornenes with Fixed and Controllable Spatial Alignment of Donor and Acceptor for High-Efficiency Blue Thermally Activated Delayed Fluorescence, Angew. Chem. Int. Edit. 59 (2020) 20174-20182.
[87] N. Xie, K. Feng, J.Q. Shao, B. Chen, C.H. Tung, L.Z. Wu, Luminescence-Tunable Polynorbornenes for Simultaneous Multicolor Imaging in Subcellular Organelles, Biomacromolecules 19 (2018) 2750-2758.
[88] M.P. Thompson, L.M. Randolph, C.R. James, A.N. Davalos, M.E. Hahn, N.C. Gianneschi, Labelling polymers and micellar nanoparticles via initiation, propagation and termination with ROMP, Polym. Chem. - UK 5 (2014) 1954-1964.

[89] M. Hollauf, G. Trimmel, A.C. Knall, Dye-functionalized polymers via ring opening metathesis polymerization: principal routes and applications, Monatsh. Chem. 146 (2015) 1063-1080.
[90] E.K. Riga, D. Boschert, M. Vohringer, V.T. Widyaya, M. Kurowska, W. Hartleb, K. Lienkamp, Fluorescent ROMP Monomers and Copolymers for Biomedical Applications, Macromol. Chem. Phys. 218 (2017) 1700273.
[91] D. Frath, J. Massue, G. Ulrich, R. Ziessel, Luminescent Materials: Locking π-Conjugated and Heterocyclic Ligands with Boron(III), Angew. Chem. Int. Edit. 53 (2014) 2290-2310.
[92] Y. Li, Y.G. Bai, N. Zheng, Y. Liu, G.A. Vincil, B.J. Pedretti, J.J. Cheng, S.C. Zimmerman, Crosslinked dendronized polyols as a general approach to brighter and more stable fluorophores, Chem. Commun. 52 (2016) 3781-3784.
[93] D.A. Hinton, J.D. Ng, J. Sun, S. Lee, S.K. Saikin, J. Logsdon, D.S. White, A.N. Marquard, A.C. Cavell, V.K. Krasecki, K.A. Knapper, K.M. Lupo, M.R. Wasielewski, A. Aspuru-Guzik, J.S. Biteen, P. Gopalan, R.H. Goldsmith, Mapping Forbidden Emission to Structure in Self-Assembled Organic Nanoparticles, J. Am. Chem. Soc. 140 (2018) 15827-15841.
[94] Y. Li, K. Huth, E.S. Garcia, B.J. Pedretti, Y.G. Bai, G.A. Vincil, R. Haag, S.C. Zimmerman, Linear dendronized polyols as a multifunctional platform for a versatile and efficient fluorophore design, Polym. Chem. - UK 9 (2018) 2040-2047.
[95] G. Ulrich, R. Ziessel, A. Harriman, The Chemistry of Fluorescent Bodipy Dyes: Versatility Unsurpassed, Angew. Chem. Int. Edit. 47 (2008) 1184-1201.
[96] S. Novoa, J.A. Paquette, S.M. Barbon, R.R. Maar, J.B. Gilroy, Side-chain boron difluoride formazanate polymers via ring-opening metathesis polymerization, J. Mater. Chem. C 4 (2016) 3987-3994.
[97] S. Novoa, J.B. Gilroy, (Co)polymers containing boron difluoride 3-cyanoformazanate complexes: emission enhancement via random copolymerization, Polym. Chem. - UK 8 (2017) 5388-5395.
[98] D. Cappello, A.E.R. Watson, J.B. Gilroy, A Boron Difluoride Hydrazone (BODIHY) Polymer Exhibits Aggregation-Induced Emission, Macromol. Rapid Comm. 42 (2021) 2000553.
[99] N.R. Paisley, S.V. Halldorson, M.V. Tran, R. Gupta, S. Kamal, W.R. Algar, Z.M. Hudson, Near-Infrared-Emitting Boron-Difluoride-Curcuminoid-Based Polymers Exhibiting Thermally Activated Delayed Fluorescence as Biological Imaging Probes, Angew. Chem. Int. Edit. 60 (2021) 18630-18638.
[100] Y. Qin, C. Pagba, P. Piotrowiak, F. Jäkle, Luminescent organoboron quinolate polymers, J. Am. Chem. Soc. 126 (2004) 7015-7018.
[101] Y. Qin, I. Kiburu, S. Shah, F. Jäkle, Synthesis and characterization of organoboron quinolate polymers with tunable luminescence properties, Macromolecules 39 (2006) 9041-9048.
[102] F. Cheng, F. Jäkle, RAFT polymerization of luminescent boron quinolate monomers, Chem. Commun. 46 (2010) 3717-3719.
[103] F. Cheng, E.M. Bonder, A. Doshi, F. Jäkle, Organoboron star polymers via arm-first RAFT polymerization: synthesis, luminescent behavior, and aqueous self-assembly, Polym. Chem. - UK 3 (2012) 596-600.
[104] F. Cheng, E.M. Bonder, S. Salem, F. Jäkle, Pyridine-Functionalized Luminescent Organoboron Quinolate Block Copolymers as Versatile Building Blocks for Assembled Nanostructures, Macromolecules 46 (2013) 2905-2915.
[105] F. Cheng, E.M. Bonder, F. Jäkle, Luminescent Boron Quinolate Block Copolymers via RAFT Polymerization, Macromolecules 45 (2012) 3078-3085.

[106] A. Meyers, M. Weck, Solution and solid-state characterization of Alq_3-functionalized polymers, Chem. Mater. 16 (2004) 1183-1188.
[107] A.V. Rozhkov, G.V. Basova, A.O. Korshunov, L.N. Bochkarev, T.A. Glukhova, V.A. Il'ichev, Synthesis and luminescent properties of functionalized polynorbornenes with boron-containing fragments in side chains, Russ. Chem. Bull. 64 (2015) 1949-1954.
[108] B.T. Luppi, A.V. Muralidharan, N. Ostermann, I.T. Cheong, M.J. Ferguson, I. Siewert, E. Rivard, Redox-Active Heteroatom-Functionalized Polyacetylenes, Angew. Chem. Int. Edit. 61 (2022) e202114586.
[109] S.M. Parke, E. Hupf, G.K. Matharu, I. de Aguiar, L. Xu, H. Yu, M.P. Boone, G.L.C. de Souza, R. McDonald, M.J. Ferguson, G. He, A. Brown, E. Rivard, Aerobic Solid State Red Phosphorescence from Benzobismole Monomers and Patternable Self-Assembled Block Copolymers, Angew. Chem. Int. Edit. 57 (2018) 14841-14846.
[110] S.M. Parke, S. Tanaka, H.Y. Yu, E. Hupf, M.J. Ferguson, Y.Q. Zhou, K. Naka, E. Rivard, Highly Fluorescent Benzophosphole Oxide Block-Copolymer Micelles, Macromolecules 52 (2019) 7477-7488.
[111] H. Imoto, K. Naka, Recent progress on arsenic-containing functional polymers, Polymer 241 (2022) 124464.
[112] K. Ishijima, S. Tanaka, H. Imoto, K. Naka, 2,3-Diarylbenzo[b]arsole: Structural Modification and Polymerization for Tuning of Photophysical Properties, Chem. Eur. J. 27 (2021) 4676-4682.
[113] B.A. Suslick, K.J. Stawiasz, J.E. Paul, N.R. Sottos, J.S. Moore, Survey of Catalysts for Frontal Ring-Opening Metathesis Polymerization, Macromolecules 54 (2021) 5117-5123.
[114] A. Ruiu, D. Sanna, V. Alzari, D. Nuvoli, A. Mariani, Advances in the frontal ring opening metathesis polymerization of dicyclopentadiene, J. Polym. Sci. A. Polym. Chem. 52 (2014) 2776-2780.
[115] S. Varlas, J.C. Foster, R.K. O'Reilly, Ring-opening metathesis polymerization-induced self-assembly (ROMPISA), Chem. Commun. 55 (2019) 9066-9071.