

Carborane-Containing Polymers: Synthesis, Properties, and Applications

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Cite This: *ACS Polym. Au* 2024, 4, 7–33

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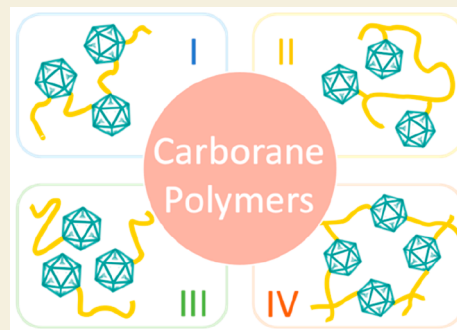
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ABSTRACT: Carboranes are an important class of electron-delocalized icosahedral carbon–boron clusters with unique physical and chemical properties, which can offer various functions to polymers including enhanced heat-resistance, tuned electronic properties and hydrophobicity, special ability of dihydrogen bond formation, and thermal neutron capture. Carborane-containing polymers have been synthesized mainly by means of step-growth polymerizations of disubstituted carborane monomers, with chain-growth polymerizations of monosubstituted carborane monomers including ATRP, RAFT, and ROMP only utilized recently. Carborane-containing polymers may find application as harsh-environment resistant materials, ceramic precursors, fluorescent materials with tuned emissive properties, novel optoelectronic devices, potential BNCT agents, and drug carriers with low cytotoxicity. This review highlights carborane-containing polymer synthesis strategies and potential applications, showcasing the versatile properties and possibilities that this unique family of boron compounds can provide to the polymeric systems.

KEYWORDS: carboranes, chain-growth polymerization, polycondensation, step-growth polymerization, RAFT polymerization, ATRP, click chemistry, polymer networks



1. INTRODUCTION

Natural and synthetic polymers have played a crucial role in the development of society, providing numerous types of functional and advanced materials.¹ Over the years, polymer scientists have integrated new functionalities into polymer chains to enhance their physicochemical characteristics. Incorporating an icosahedral carborane ($C_2B_{10}H_{12}$) cluster is one important example of this research endeavor due to the unique physical and chemical properties of this heteroborane, including high hydrophobicity and lipophilicity, outstanding heat-oxidation and metabolic stability, unique aromatic structure, the high neutron capture propensity of the naturally occurring ^{10}B isotope, and steric effects.²

First prepared in the 1950s, carboranes are an important class of 3D σ -electron delocalized carbon–boron clusters.³ Polyhedral boranes and the related heteroboranes such as the carboranes are mainly categorized into *closo*, *nido*, *arachno*, and *hypho* structures, whereby the *closo* structures are complete deltahedra and *nido*, *arachno*, and *hypho* cage structures have 1, 2, and 3 vertices missing, respectively. Ranging from the conventional, small 4-vertex CB_3 derivatives⁴ to the 16-vertex $C_2B_{14}H_{14}$ cage first synthesized by Zheng et al.,⁵ the physicochemical properties of carboranes with different sizes and shapes can vary quite considerably. The most common carborane is known as a dicarba-*closo*-dodecaborane and is commonly referred to as “carborane” or “*closo*-carborane”, which

is composed of 2 carbon and 10 boron atoms arranged at each vertex of an icosahedron.⁶ Depending on which positions the carbon atoms occupy, *closo*-carboranes consist of 3 isomers, namely *closo*-1,2- (*ortho*-), 1,7- (*meta*-), and 1,12- (*para*-) carboranes (Figure 1). The molecular volumes of the carborane clusters lie between 140 \AA^3 and 150 \AA^3 (*closo*-1,2-carborane: $\sim 148 \text{ \AA}^3$, *closo*-1,7-carborane: $\sim 143 \text{ \AA}^3$, and *closo*-1,12-

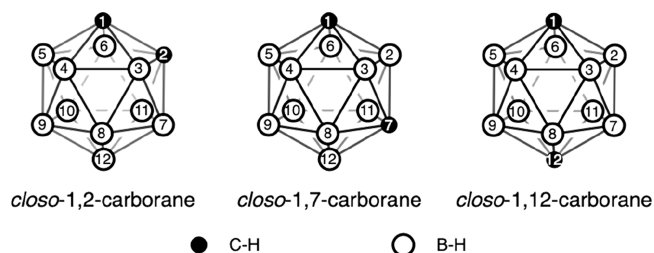


Figure 1. *Closo*-carborane isomers.

Received: September 21, 2023

Revised: November 23, 2023

Accepted: November 27, 2023

Published: December 15, 2023



carborane: $\sim 141 \text{ \AA}^3$), slightly larger than a rotating phenyl ring (102 \AA^3) and adamantane cage (136 \AA^3).⁷

Closo-carboranes exhibit unique electronic framework structures. The low electronegativities of B and H lead to low-polarity B–H bonding, which gives rise to the high hydrophobicity of *closo*-carboranes and enables the formation of unusual “dihydrogen” bonding (B–H \cdots H–X) with suitable proton donors (X = N, O and C).^{8,9} The clusters can also exhibit boron neutron capture properties ($^{10}\text{B} + ^1_0\text{n} \rightarrow ^7\text{Li} + \alpha + 2.4 \text{ MeV}$).¹⁰ *Closo*-carboranes are kinetically stable under a wide range of harsh conditions, showing high resistance and robustness against protic acids, oxidants, and heat.¹¹ However, it is possible to deprotonate the slightly acidic CH groups ($\text{p}K_{\text{a}} \sim 22$)¹² using strong bases such as $^n\text{BuLi}$, and the resulting carbanion can be reacted with a large number of suitable electrophiles.⁶ Alternatively, a single BH unit can be removed from *closo*-carboranes to afford the corresponding hydrophilic *nido*-[$\text{C}_2\text{B}_9\text{H}_{12}$] $^-$ anion via an efficient, regioselective and high-yielding deboronation reaction involving nucleophiles including hydroxide, fluoride, tertiary amines, and other nitrogenous bases.^{7,13} Over the years, carborane molecules have been intensively studied as, e.g., fluorophores,^{14,15} drug carriers,² enzyme inhibitors,^{16,17} antibiotics,¹⁸ and potential agents for boron neutron capture therapy (BNCT),^{17,19} an experimental binary cancer treatment that exploits the thermal neutron capture reaction of ^{10}B to kill tumor cells by means of an intracellular fission process.

The first series of carborane-containing polymer studies were published by Green et al. between 1964 to 1967,^{20–24} shortly after the disclosure of the preparation of icosahedral *closo*-carboranes in late 1963,³ in which the syntheses of carborane polyesters, polyformals, polyacrylates, and polysiloxanes were described and discussed in detail. In these early studies, high thermal resistance was the main focus of carborane polymers, and heat-resistant carborane-containing polysilanes, polysiloxanes, and aromatic polyacetylenes were intensively studied and developed. While thermo-oxidation resistant materials still remain a key research field of carborane polymers today, it was in the past two decades that carborane polymers expanded into the fields of dendrimers,^{25,26} coordination polymers,^{27–30} luminescent materials,^{31–33} host–guest chemistry,³⁴ and medicinal chemistry.^{2,35} Controlled polymerization methods have been used in the synthesis of carborane polymers, including atom transfer radical polymerization (ATRP),³⁶ ring-opening metathesis polymerization (ROMP),³⁷ and reversible addition–fragmentation chain-transfer (RAFT) polymerization.³⁵ Examples of carborane polymers include: ceramic precursors and thermo-oxidative resistant coatings, where carboranes provide greatly enhanced thermo-oxidative stability to the resulting polymer networks by the formation of a boron oxide, boron carbide, or boron silicate layer at the surface of the networks under high temperature;^{38,39} fluorescent polymers, where carboranes were added to adjust their emission properties by interfering with conjugation,^{33,40} and amphiphilic self-assemblies, where carboranes serve as hydrophobic components in drug delivery² and imaging,¹⁰ and boron-rich fragments for BNCT.^{10,35,41–43} By incorporating carboranes into polymer chains, the advantages of both carborane clusters and polymeric systems can be combined, and therefore key properties including hydrophobicity/lipophilicity, thermal and oxidative stability, optoelectronic properties, and aromaticity can be tuned as well.

Carborane-containing polymers can be largely divided into 4 groups (Figure 2), depending on the relative position of the

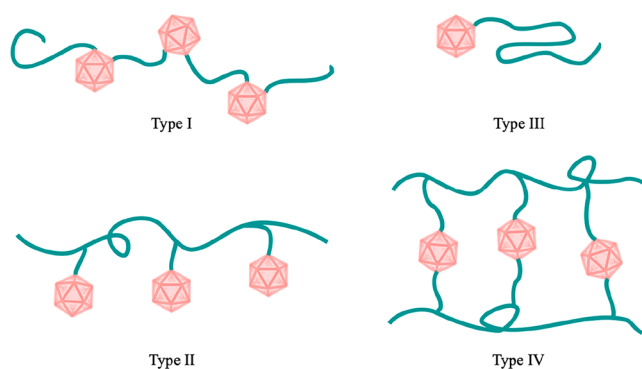


Figure 2. Four types of carborane-containing polymers discussed in this review.

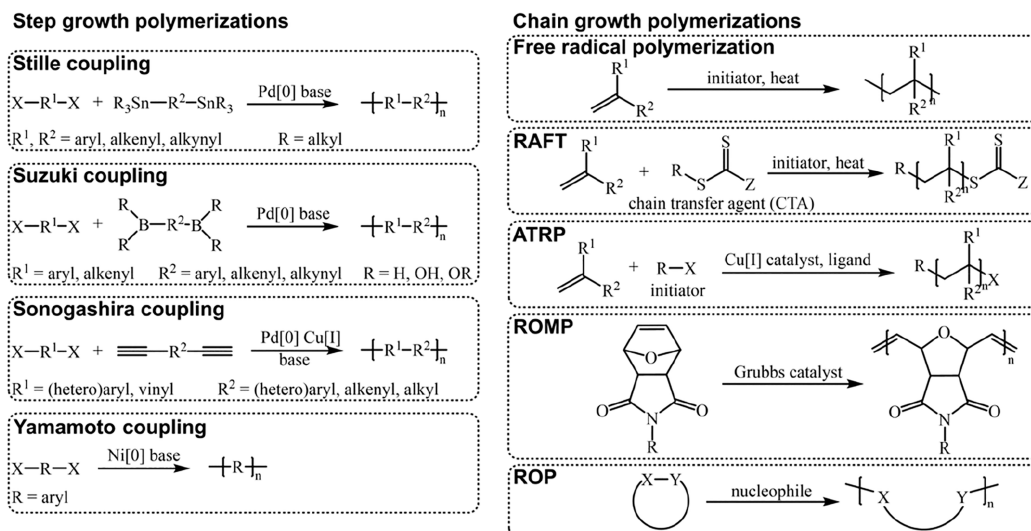
boron clusters, viz: (a) polymers which contain carboranes in the main chain (Type I), (b) polymers with carboranes appended to the main chain (Type II), (c) polymers with carboranes that are only incorporated as end groups (Type III), and (d) polymers with carboranes covalently cross-linked between the polymer chains (Type IV). Different polymerization methods and postpolymerization modifications have been explored accordingly.

In this review, the main focus will be on the synthesis of each class of carborane-containing polymers, including their properties and applications. To the best of our knowledge, only *closo*-carboranes have been exploited in carborane-containing polymer studies, with only a few examples of *nido*-carborane polymers generated upon regioselective deboronation of the *closo*-carborane cage(s). Carboranes that have been incorporated into large dendritic structures (e.g., dendrimers) or metal–organic frameworks are beyond the scope of this review.

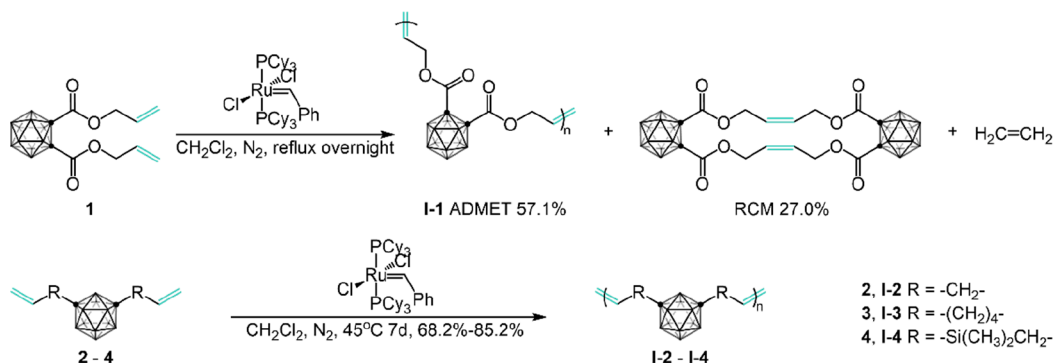
2. SYNTHETIC STRATEGIES FOR CARBORANE-CONTAINING POLYMERS

The synthetic strategies of carborane-containing polymers include direct polymerization and postpolymerization methods, the application of which depends on the type of carborane-containing polymers. Step-growth polymerization methods including Stille coupling, Yamamoto coupling, Sonogashira coupling, Suzuki coupling, amide coupling, hydrolytic condensation, and Steglich esterification, to name a few, are the most widely applied methods for the synthesis of Type I carborane polymers; chain-growth polymerization methods including RAFT polymerization, ATRP, free-radical polymerization and ring-opening polymerization (ROP) are more favorable in the synthesis of Type II polymers (Scheme 1). Postpolymerization methods including “click” chemistry reactions, hydrosilylation, decaborane ($\text{B}_{10}\text{H}_{14}$)-alkynyl reactions and small molecule modifications of catalysts, initiators, and chain transfer agents, can be used in the preparation of all types of carborane-containing polymers, but these are the main methods for obtaining Type III and Type IV polymers. Selected Diels–Alder reactions and cyclotrimerization reactions have been utilized as well for the preparation of these polymer systems.

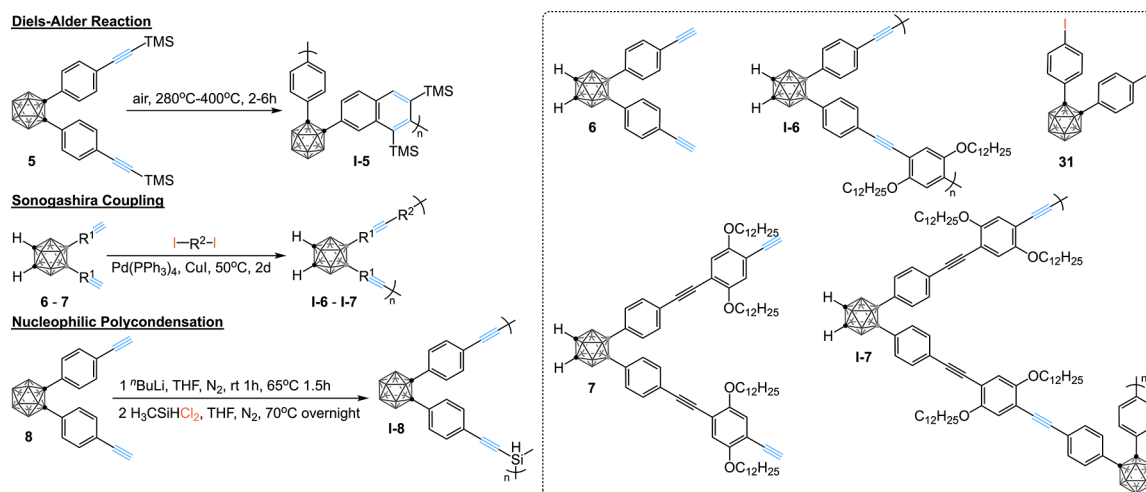
Scheme 1. Some of the Key Polymerization Reactions Discussed in This Review



Scheme 2. Divinyl Carborane Monomers and Their Resulting Polymers Prepared by Means of ADMET and RCM



Scheme 3. Dialkynyl Carborane Monomers and Their Resulting Type I Polymers

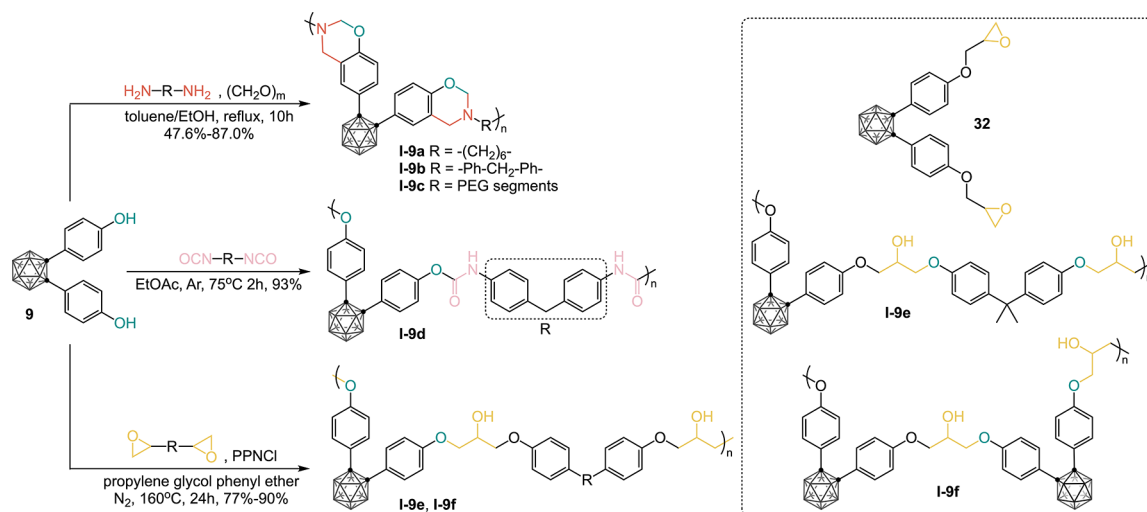


2.1. Polymerization Methods

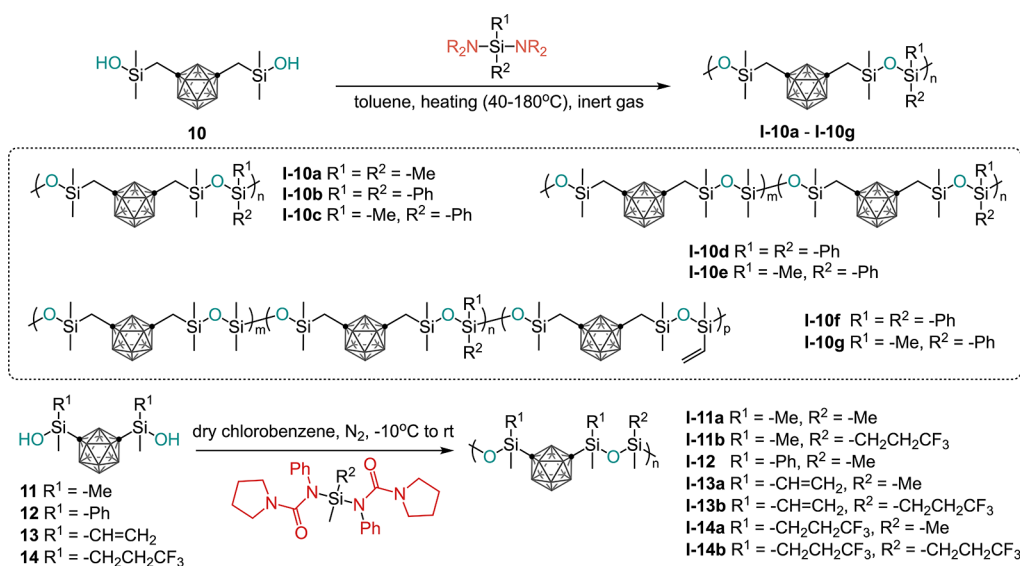
2.1.1. Type I Polymers (i.e., Carboranes located within the polymer main chain). More than one-half of known carborane polymers fall into this category. To incorporate the carborane cage structure into the polymer backbone by means of typical polymerization reactions, various disubstituted carborane monomers were developed, most commonly divinyl- (1–4),

dialkynyl- (5–8), dihydroxyl- (9–17), diamino-carboranes (18–24) and carborane dihalides (25–31) and, less frequently, diepoxy- (32), dichloroacyl- (33, 34), dicarboxyl- (35, 36), distannyl- (37–39), diazido- (40), diacetyl-carboranes (41), and carborane itself (42). Condensation polymerization reactions were found to be the most favorable methods for the preparation of Type I polymer systems.

Scheme 4. Di(hydroxyphenyl)-carborane Monomer and Its Resulting Type I Polymers



Scheme 5. Di(hydroxysilyl)-carborane Monomers and Their Resulting Type I Polymers



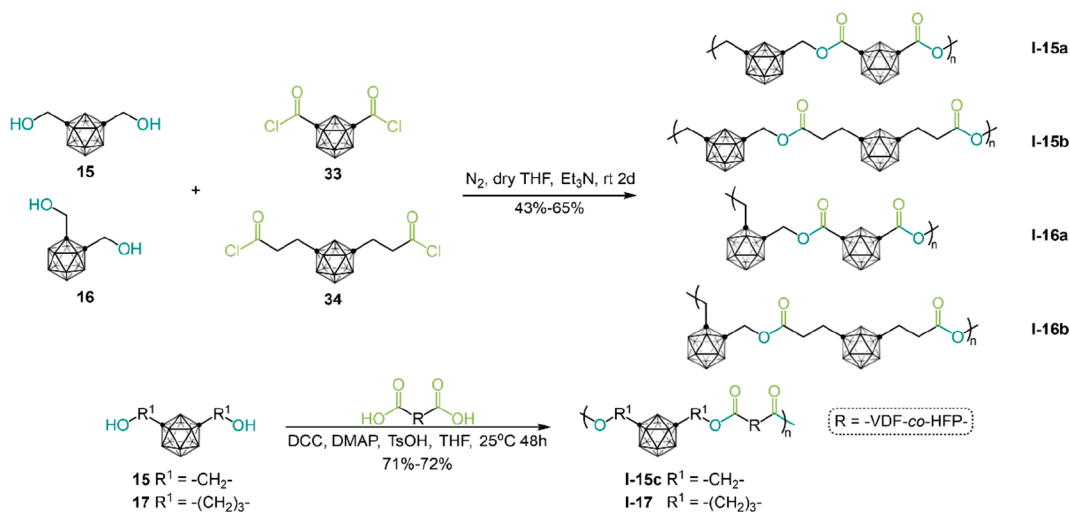
Divinyl carboranes (1–4) have been polymerized to obtain vinyl-linked carborane polymers (I-1–I-14) by means of acyclic diene metathesis (ADMET) in the presence of Grubbs II catalysts (Scheme 2). While higher concentrations and the nonadjacent C atom substituents in *closo*-1,7-carborane led to intermolecular reactions forming linear polymers and cyclic dimers, the adjacent positions of the two alkenyl groups in *closo*-1,2-carborane and lower concentrations favored an intramolecular ring-closing metathesis (RCM) reaction to afford closed-ring molecules in high yields.⁴⁴

Dialkynyl carboranes (5–8) were found useful in preparing carborane-containing polyarylenes and poly(arylacetylene)s (Scheme 3). Carborane-containing polyarylenes were obtained by means of a Diels–Alder reaction at high temperatures, whereby a phenyl linker was formed between two monomers by intermolecular cyclization of the alkynyl groups (5, I-5);⁴⁵ whereas carborane poly(arylacetylene)s were prepared by means of Sonogashira coupling^{31,46} and nucleophilic polycondensations.⁴⁷ Sonogashira coupling was successfully carried out between a terminal alkyne and an aryl halide in the presence of a Pd catalyst and a base, with or without a Cu(I) cocatalyst

(Scheme 1).⁴⁸ Tominaga et al. prepared two carborane-containing poly(arylacetylene)s I-6³¹ and I-7⁴⁶ by means of Sonogashira coupling between dialkynyl carborane monomers 6, 7 and aryl halides, using Pd(PPh₃)₄ and CuI as the catalysts in the presence of triethylamine in THF. Notably, these polymers were composed of the unusual B-disubstituted (rather than C-substituted) carborane monomers, especially polymer I-7 composed of monomer 7 and carborane diiodide monomer 31 represents the only example of a polymer with alternating 1,2- and 9,12-disubstituted carboranes. Nucleophilic polycondensation (via a dilithio intermediate) can occur between a dialkynyl carborane monomer and a dihalide upon lithiation of the ethynyl group using *n*-butyllithium (8, I-8).⁴⁷

Carborane diols (9–17) were utilized to produce polybenzoxazines, polyurethanes, polyhydroxyethers, polysiloxanes, and polyesters by polymerizing with diamines,^{49–52} diisocyanates,⁵³ diepoxys,⁵⁴ di(acyl halide)s,⁵⁵ and dicarboxylic acids.⁵⁶ Di(hydroxyphenyl)-carborane monomer 9 was found to be useful in preparing several polymer systems (Scheme 4). Carborane-containing poly(benzoxazine)s I-9a to I-9c were synthesized by means of a Mannich reaction, in which 9 reacted

Scheme 6. Di(hydroxyalkyl)-carborane Monomers and Their Resulting Type I Polymers



with formaldehyde and a variety of diamines in toluene/ethanol upon heating;⁴⁹ polyurethane **I-9d** was obtained by reacting **9** with a diisocyanate in ethyl acetate under an inert atmosphere;⁵³ poly(carborane-hydroxyether)s **I-9e** and **I-9f** were obtained by means of an epoxy ring-opening reaction of **9** with diepoxy compounds in 1-phenoxy-2-propanol in the presence of bis(triphenylphosphine)iminium chloride (PPNCl).⁵⁴ The same polymers can also be obtained from a diepoxy carborane **32** using the same condition with corresponding diols.⁵⁴ The polycondensations mentioned above all gave acceptable yields of the desired products.

Di(hydroxysilyl) carboranes (**10–14**) were coupled with diamino-silanes^{50–52} or bisureidosilanes⁵⁷ under inert atmosphere to afford poly(carborane-siloxane) systems **I-10–I-14** (Scheme 5). While the reactions with diamines required different levels of heating (40–180 °C), those with bisureidosilanes can proceed at lower temperatures.

Di(hydroxyalkyl) carborane monomers (**15–17**) were used to prepare carborane-containing polyesters (**I-15–I-17**) by means of esterification reactions, either with carborane di(acyl chloride)s (**33**, **34**) in the presence of triethylamine,⁵⁵ or with organic dicarboxylic acids in the presence of DCC and DMAP (Scheme 6).⁵⁶

Carborane diarylamines (**18–23**) were largely reported in the preparation of polyimides (**I-18–I-23**) by means of a traditional two-step polycondensation reaction. *Closo*-1,7-carborane diarylamines were coupled with different tetracarboxylic dianhydrides followed by imidization of the resulting poly(amic acid)s (PAA).^{39,58–60} The imidization reaction was achieved by either thermal treatment under vacuum^{39,60} or by chemical treatment using acetic anhydride and pyridine.^{58,59} A carborane disilylamine (**24**) was reported in the preparation of a carborane polysiloxane (**I-24**) by coupling with a disilanol.⁵² (Scheme 7)

Carborane dihalides **25–30** were found to form diverse polymers by means of different polycondensation mechanisms. The dibromofluorenyl carborane monomer **25** were largely used by Carter's group in the preparation of carborane polyfluorenes and poly(fluorene-thiophene)s by means of Yamamoto, Suzuki, and Stille polycondensations (Scheme 8).^{15,33,61,62} The Yamamoto self-polymerization of carborane monomer **25** was first reported in 2009 and poly(carborane fluorene) **I-25a** was prepared.⁶¹ The reaction used a nickel catalyst that was stabilized by cyclooctadiene and 2,2'-bipyridine ligands, and

proceeded upon heating or microwaving. Carborane-fluorene random copolymer **I-25b** was prepared by using the same method.¹⁵ Suzuki polycondensation of **25** with a fluorene diboric acid bis(1,3-propanediol) ester produced copolymer **I-25c**;³³ Stille polycondensation with a distannyl thiophene generated **I-25d**.⁶² Both reactions were catalyzed by the use of a palladium catalyst.

Aromatic dichlorocarboranes **26**, **27**, and **28** were self-polymerized by means of Yamamoto polycondensation, whereby a Ni(II) compound and a reducing agent (Zn) were used, generating poly(carborane-phenylene)s **I-26**, **I-27**,^{63–65} and a carborane-containing aromatic polyether **I-28**.⁶⁶ While carborane disilyl chlorides **29** and **30** provided another synthetic route to obtain carborane-containing poly(arylacetylene silane/siloxane) which involved the coupling reaction between halides and Grignard reagents. The aromatic dialkynyl Grignard reagents were reacted to introduce alkynyl groups into the resulting polymers (**I-29**, **I-30**), giving alkynyl-bearing carborane-containing polymers that could be further cross-linked under high temperature.^{38,67} (Scheme 9)

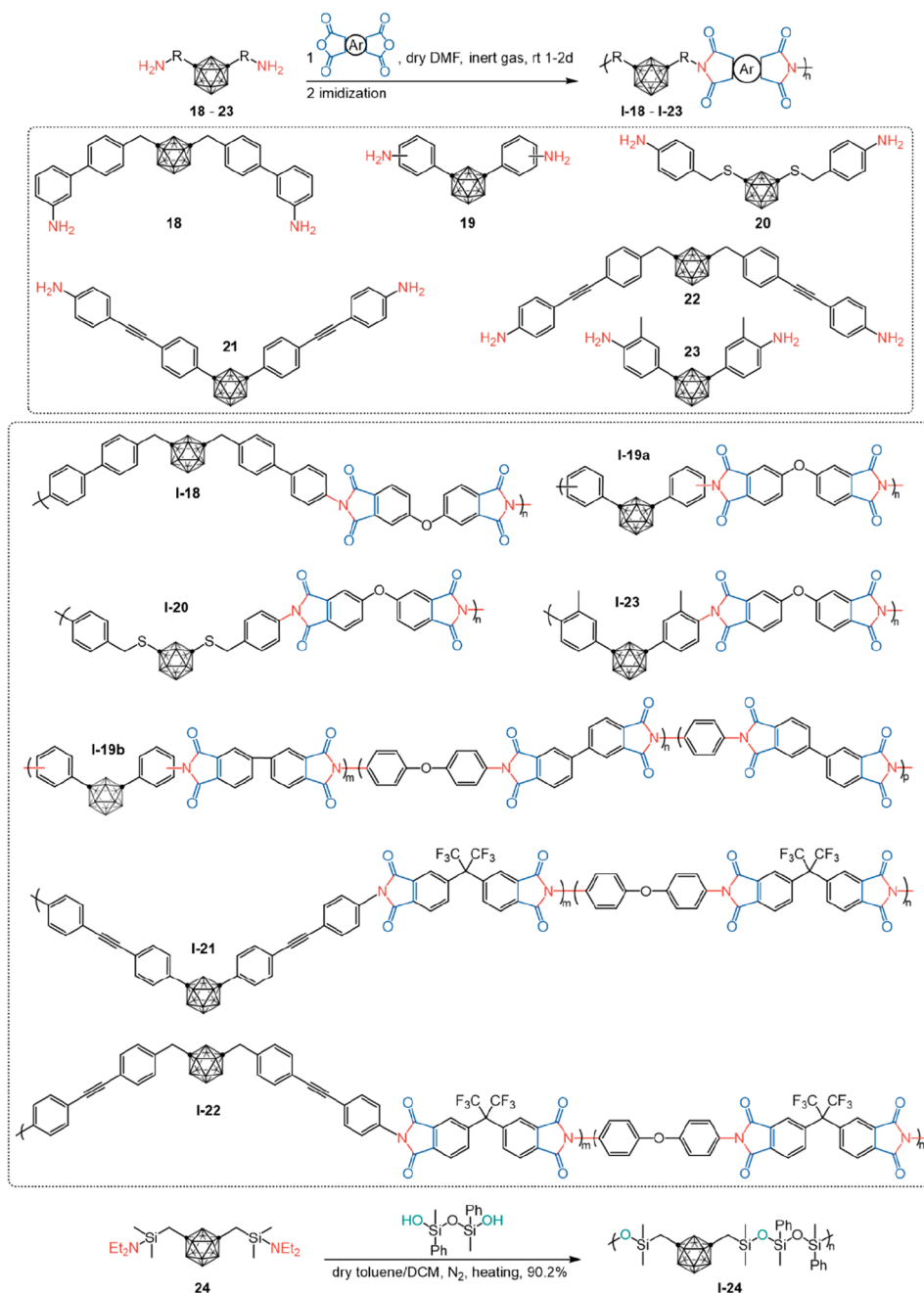
Some less common carborane monomers including dicarboxyl- (**35**, **36**),⁵³ distannyl- (**37–39**),⁶⁸ diazido- (**40**),⁶⁹ diacetyl-carboranes (**41**)⁷⁰ have also been reported.

Carborane dicarboxylic acids (**35**, **36**) were used in the preparation of carborane-containing aromatic polyesters and polyamines. Diphenylcarboxyl carborane **35** was coupled with a few aromatic diols by means of an esterification reaction in the presence of benzenesulfonyl chloride (BsCl) in pyridine, producing polyesters **I-35a–I-35c** in relatively high yields⁵³ polyamides **I-36a** and **I-36b** were obtained by means of amide coupling of dicarboxylcarborane **36** with diamines.⁷¹ (Scheme 10)

Carborane distannanes **37–39** were used in preparing carborane-containing poly(naphthalenediimide)s (**I-37–I-39**) by means of Stille coupling with dibromonaphthalenediimide;⁶⁸ diazidomethyl *closo*-1,7-carborane **40** was used in an azide-alkyne click-coupling cycloaddition reaction with a diacetylene bisbenzoxazine to form a carborane-containing poly-(benzoxazine) **I-40**;⁶⁹ and diacetyl carborane **41** was found to be useful in producing a polyazomethine **I-41** by coupling with a diamine in toluene at 80 °C.⁷⁰ (Scheme 11)

Other than the disubstituted carborane monomers mentioned above, the *closo*-carborane cage itself could be used as a

Scheme 7. Carborane Diamine Monomers and Their Resulting Type I Polymers



monomer. A vinyl-appended poly(carborane-silane) (**I-42**) was prepared from *closo*-1,7-carborane (**42**) by means of nucleophilic polycondensation (via a dilithio intermediate). The carborane **42** was lithiated using *n*-butyllithium and refluxed with a vinyl dichlorosilane to give the final product (Scheme 12), which was reported to be a convenient way to produce carborane polymers containing vinyl pendant groups.⁷²

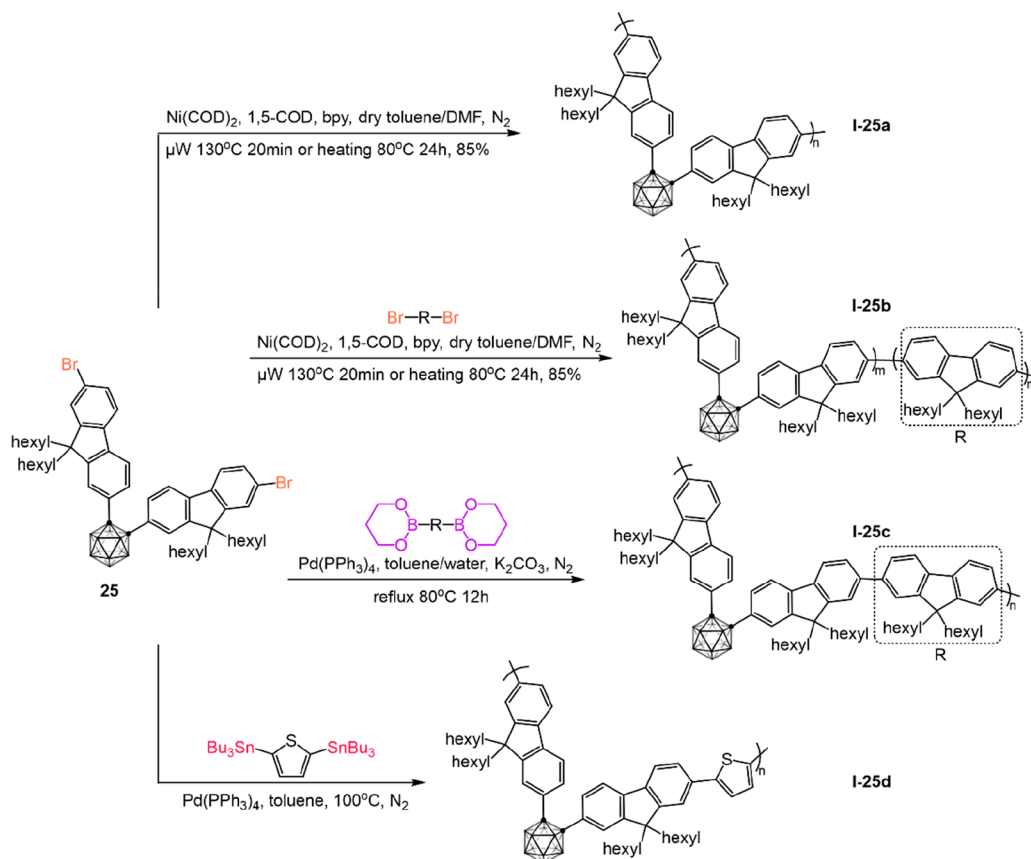
The above studies exemplify several viable synthetic routes that can be applied to a variety of disubstituted carborane monomers to obtain desired carborane-containing polymers.

2.1.2. Type II Polymers (i.e., Carboranes used as pendant groups). While Type I polymers are mainly homopolymers and random copolymers, half of the reported Type II polymers are block copolymers. In the preparation of Type II polymers, carborane monomers were substituted at the

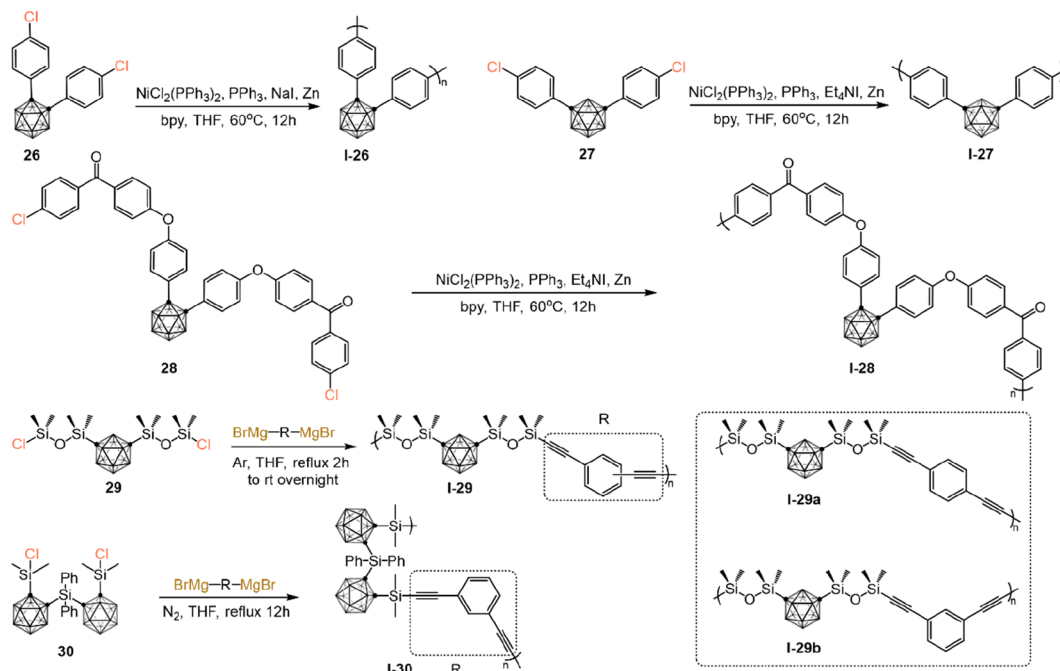
carborane C-vertex and contained only one polymerizable functional group. Step-growth polymerizations and chain-growth polymerizations were both used in the synthesis of Type II polymers, however block copolymers were all prepared by means of chain-growth polymerization. Some well-controlled chain-growth polymerization methods that provide the resulting polymers with controlled chain length and narrow dispersity (*D*) were found to be more favorable in the biological and medicinal fields.

2.1.2.1. Step-Growth Polymerizations. Step-growth polymerization methods were reported in a few studies in the field of materials science, which included Sonogashira polycondensation,³² Stille polycondensation,^{73–75} and hydrolytic polycondensation reactions.⁷⁶

Scheme 8. Dibromo-carborane Monomers and Their Resulting Type I Polymers



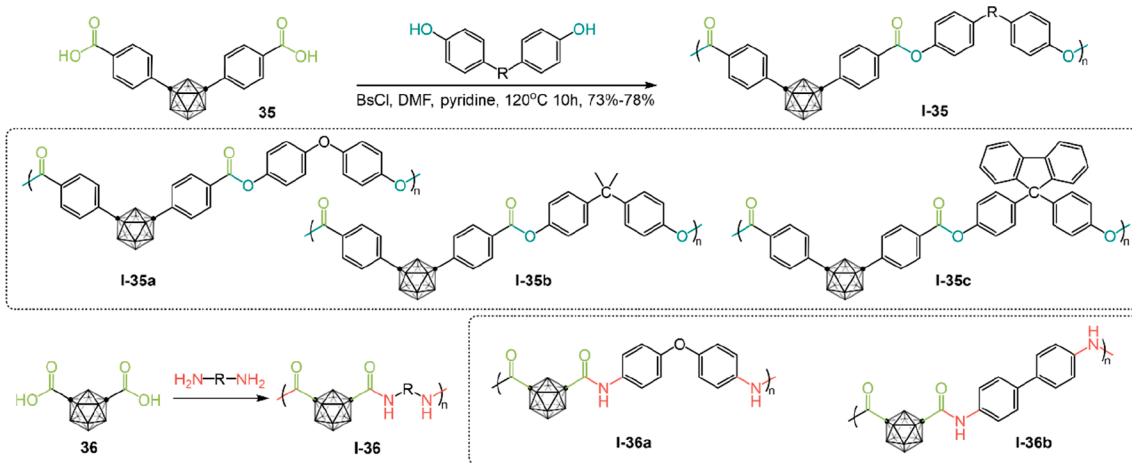
Scheme 9. Dichloro-carborane Monomers and Their Resulting Type I Polymers



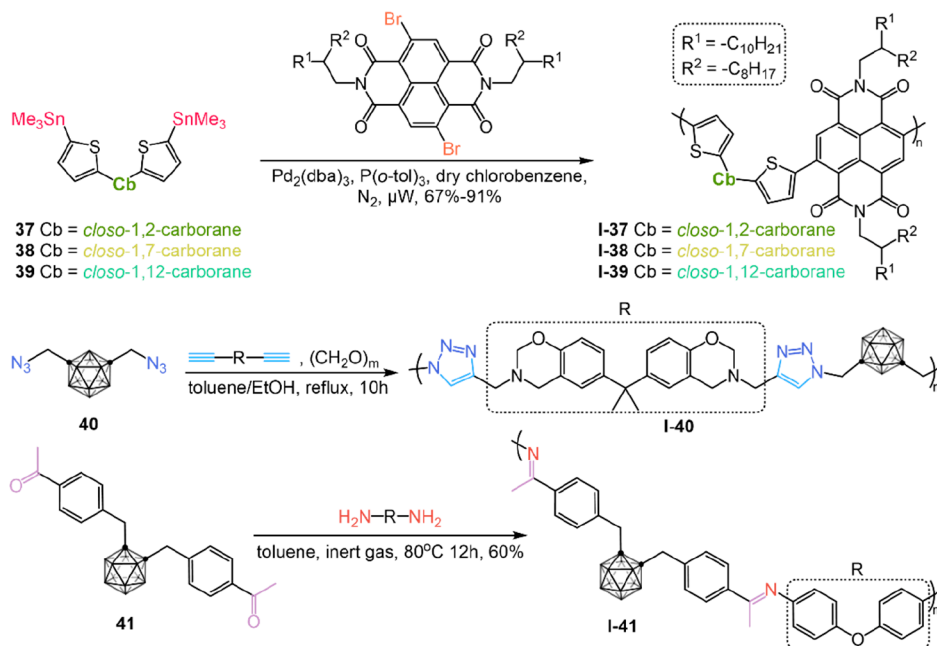
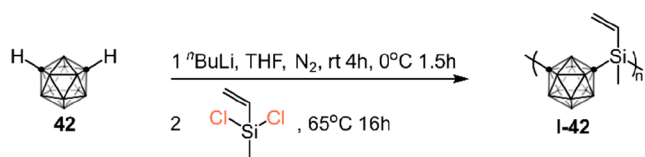
In 2010, Kokado et al. reported benzocarborane-containing π -conjugated polymers (II-1a, II-1b), which were obtained by means of a Sonogashira polycondensation reaction between a di(iodophenyl)benzocarborane monomer (43) and diethynyl aromatic monomers (Scheme 13).³² Although benzocarborane

was located in the main chain, polymers containing benzocarborane are categorized into Type II polymers in this review as the benzocarborane units behaved more like diene linkers and that carborane cages did not take part in the π -conjugation within the polymer backbone,^{32,75} making them

Scheme 10. Dicarboxyl-carborane Monomers and Their Resulting Type I Polymers



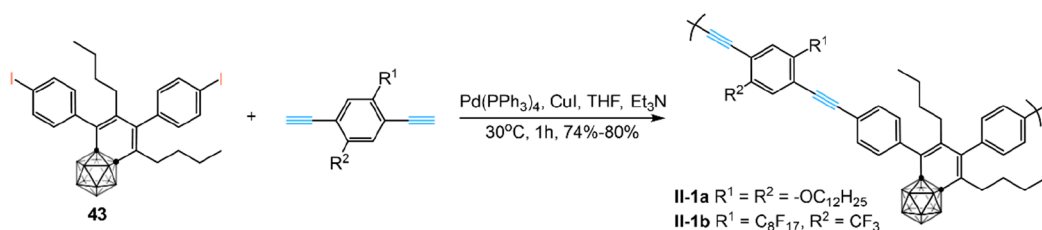
Scheme 11. Distannyl-, Diazido-, and Diacetyl-Carborane Monomers and Their Resulting Type I Polymers

Scheme 12. Nucleophilic Polycondensation (via Dilithio Intermediate) of *closo*-1,7-Carborane

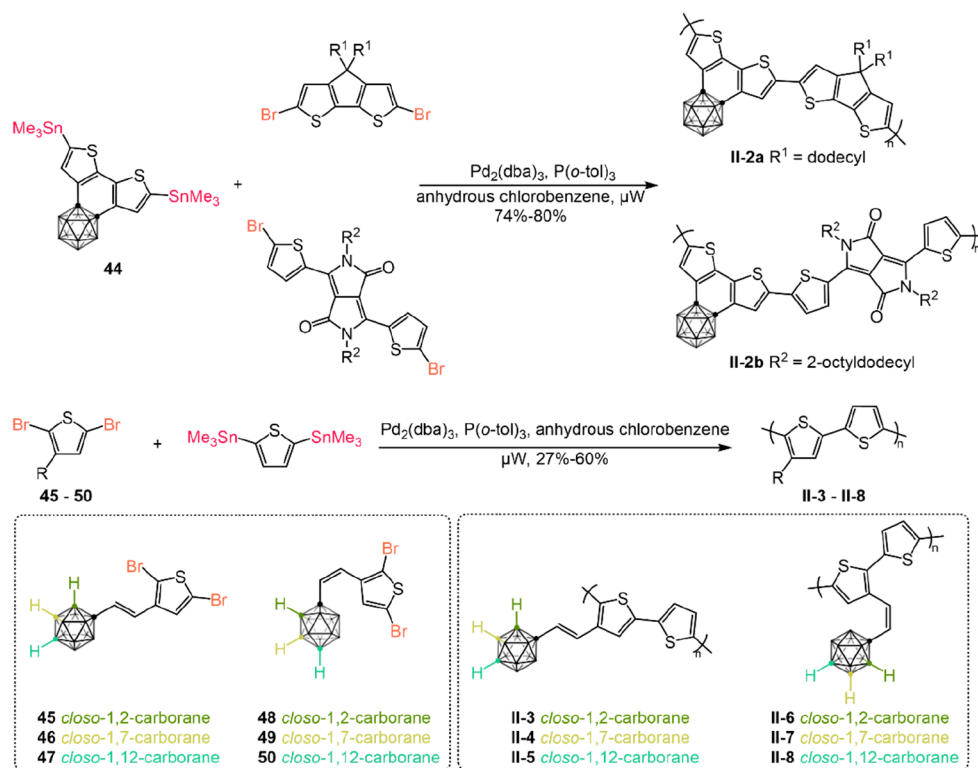
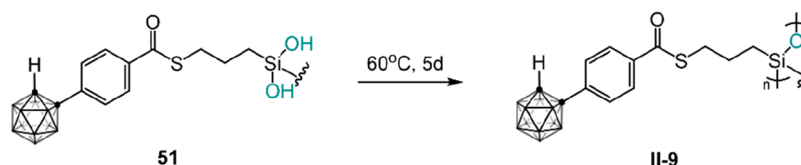
more like electron-withdrawing pendants rather than main-chain linkers.

Furthermore, Marshall et al. successively developed several conjugated polythiophene-based benzocarborane polymers (II-2a, II-2b) from a distannyl benzocarborane monomer 44 and carborane polythiophenes (II-3–II-8) from distannyl thiophene-appended carborane monomers 45–50 (Scheme 14). These polymers were prepared in low to moderate yields (27%–

Scheme 13. Sonogashira Polycondensation of a Diiodo-benzocarborane



Scheme 14. Polythiophene-based Carborane Polymers Obtained via Stille Polycondensation

Scheme 15. Nucleophilic Polycondensation (Dilithio Intermediate) of *closo*-1,7-Carborane

80%) by means of Stille polycondensation under microwave conditions using Pd(dba)₃ as the catalyst.^{73–75}

A carborane polysiloxane (II-9) obtained by means of hydrolytic polycondensation reactions between carboranyl hydroxysilanes was also reported. The carborane polymer was obtained from a two-step hydrolytic condensation reaction: the carborane trihydroxysilane monomer (**51**) was first coupled with the hydroxyl groups of the cellulose, the resulting carboranyl hydroxysilane then underwent a further hydrolytic self-polycondensation reaction to form a carborane polysiloxane.⁷⁶ (Scheme 15)

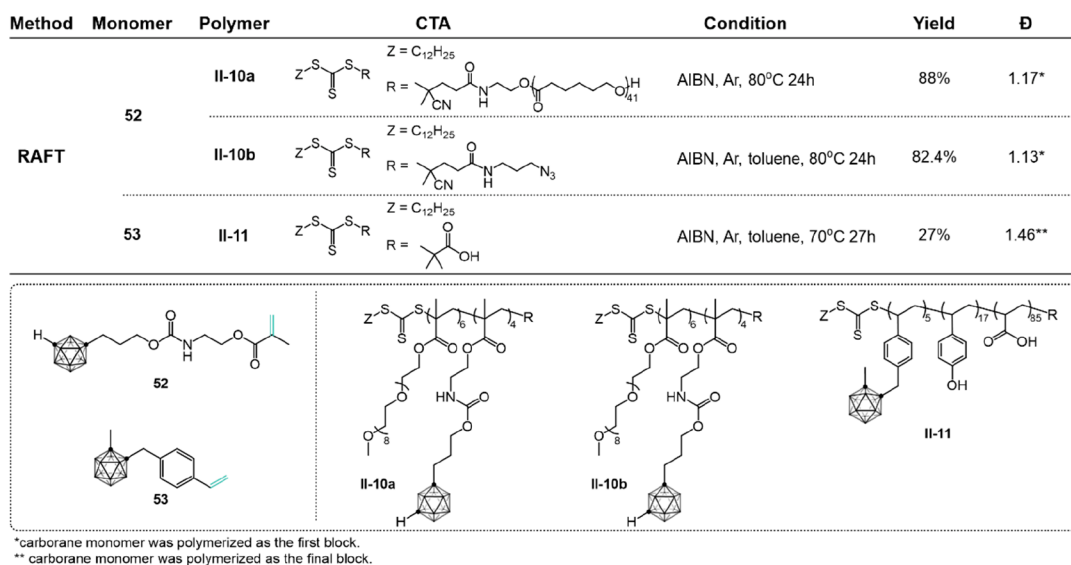
2.1.2.2. Chain-Growth Polymerization Reactions. As mentioned earlier, Type II polymers obtained by means of chain-growth polymerization methods are mainly block copolymers. Since the synthesis of the blocks in a polymer can be accomplished via different methods, herein we focus on the synthesis of the carborane-appended block. The chain-growth polymerization methods that have been adopted include RAFT polymerization, ATRP, ROP, which provide uniformity to the polymer molecular weight distribution, giving researchers better control over the structure of the desired polymers and enabling a detailed study of their properties.

Reversible Addition–Fragmentation Chain-Transfer (RAFT) Polymerization. RAFT polymerization is a type of reversible deactivation radical polymerization (RDRP). Over the past two decades, it has become one of the most adaptable polymer-

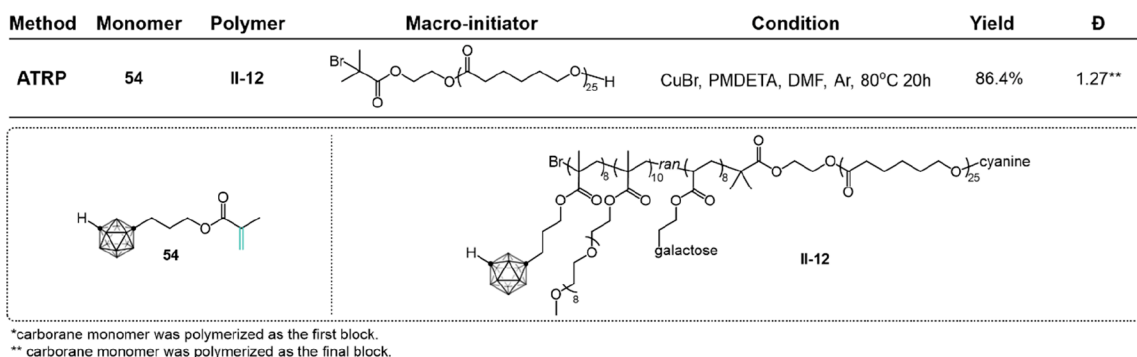
ization methods, and has been discussed in detail elsewhere.^{77,78}

Thermal RAFT reactions typically require vinyl monomers, a thermal initiator as the radical source, a dithioester or trithiocarbonate chain transfer agent (CTA) for chain growth mediation. Ruan *et al.* prepared two amphiphilic *closo*-1,7-carborane-appended block copolymer pOEGMA-*pmCBA* **II-10a**³⁵ and **II-10b**⁷⁹ from monomer **52** by means of RAFT polymerization. The reactions were continued at 80 °C in toluene for 1 day in each step, with azobis(isobutyronitrile) (AIBN) as the initiator. The carborane-containing blocks were obtained in high yields (88.0% for **II-10a** and 82.4% for **II-10b**) and low dispersity (*D* = 1.17 for **II-10a** and 1.13 for **II-10b**). Even after the chain extension of the pOEGMA blocks, the dispersity remained lower than 1.25, demonstrating a suitable RAFT route for Type II carborane polymer synthesis. Postpolymerization end group modifications were carried out by means of esterification and click reactions to attach a functional targeting and/or a fluorescent end group. Similarly, Fernandez-Alvarez *et al.* developed a carborane-containing terpolymer (**II-11**) in 3 steps by successively polymerizing *tert*-butyl acrylate, 4-acetoxystyrene, and a *closo*-1,2-carborane-containing styrene monomer **53** as the first, second, and third block. The reactions were carried out at 70 °C, initiated by AIBN and mediated by a trithiocarbonate CTA. However, the carborane block was prepared in a modest yield of 27%, which was explained by the tension of the polymer backbone resulted

Scheme 16. RAFT Polymerization of Vinyl Carborane Monomers Used to Obtain Type II Polymers



Scheme 17. ATRP of a Vinyl Carborane Monomer Used to Obtain a Type II Polymer



from the steric hindrance of the carborane cluster in each unit, and a relatively high \bar{D} of 1.46.⁸⁰ (Scheme 16)

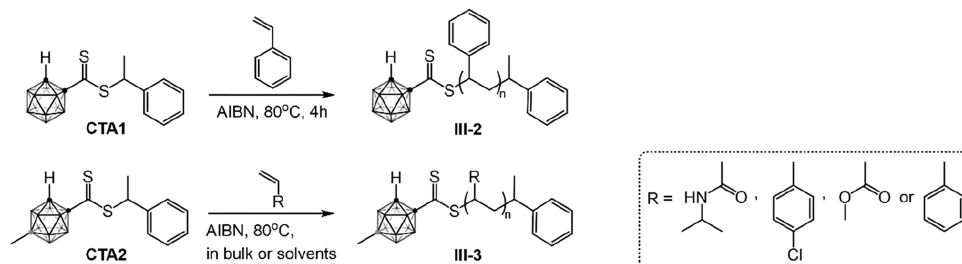
Atom-Transfer Radical Polymerization (ATRP). ATRP is another RDRP method that preserves controlled “living” characteristics in the resulting polymers. A typical ATRP reaction requires vinyl monomers, an alkyl halide initiator, a redox active transition metal catalyst (e.g., Cu(I)) and sometimes a ligand for the metal catalyst.⁷⁸ In 2018, Ruan et al. reported a *closo*-1,7-carborane-containing multiblock copolymer (II-12) obtained by means of ATRP.¹⁰ The reaction was carried out in the presence of a CuBr catalyst and a *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) ligand at 80 °C. A random copolymer macroinitiator was first synthesized by polymerizing oligo(ethylene glycol) methacrylate (OEGMA) and acryloyl-D-galactose pentaacetate, followed by the addition of *closo*-1,7-carboranylpropyl methacrylate (54) (Scheme 17). The resulting copolymer was obtained in 86% yield with a low \bar{D} of 1.27, and a fluorescent cyanine group was then covalently attached as the end group.¹⁰

Ring-Opening Polymerization (ROP). ROP is a kind of polymerization applied to cyclic monomers to prepare linear polymers with well-defined structures. On the basis of different mechanisms, it can be divided into several types such as radical ROP, anionic ROP, cationic ROP and ring-opening metathesis polymerization (ROMP).⁸¹ Carborane-containing ring monomers 55 and 56 are both *closo*-1,2-carborane-appended. Inspired by the work of Sneddon’s group published in the early 2000s on

the application of ruthenium alkene metathesis catalysts in obtaining alkenyl carboranes,⁸² Coughlin’s group developed several carborane-appended polyoxonorborenes (II-13) from monomer 55 catalyzed by Grubbs I and Grubbs III catalysts.^{37,83} Although II-13a and II-13b gave satisfactory yields and low \bar{D} within a very short reaction time,⁸³ in the synthesis of II-13c, the reaction gradually lost control as the molar percentage of the cyclooctene monomer grew.³⁷ Their work then encouraged the use of ROMP and other ROP methods in preparing carborane polymers and resulted in more carborane polyoxonorborenes and carborane polycarbonates. For example, Kahraman et al. developed the first phosphorus-containing carborane polyoxonorborenes (II-13d, II-13e) by means of ROMP of monomer 55 using Grubbs III catalyst,⁸⁴ and Xiong et al. developed a carborane polycarbonate (II-14) by means of anionic ROP of monomer 56 catalyzed by triazabicyclodecene (TBD).⁴¹ All the resulting polymers exhibited good levels of conversion and low polydispersities, as was desired. (Scheme 18)

Other synthetic methods included: an ethylene- α -olefin polymerization between ethylene gas and octenyl methyl-*closo*-1,2-carborane (57) using a Group 4 organometallic complex $\text{Me}_2\text{Si}(\eta^5\text{C}_5\text{Me}_4)(\eta^1\text{-}N\text{-}t\text{Bu})\text{TiCl}_2/\text{methylaluminoxane}$ (CGC/MAO) catalyst system to afford II-15,⁸⁵ and free radical polymerizations of methyl- or phenyl-substituted *closo*-1,2-carboranylstyrenes (53 and 58) initiated by AIBN that gave carborane-appended polystyrenes II-16a and II-16b.⁸⁶ (Scheme 19)

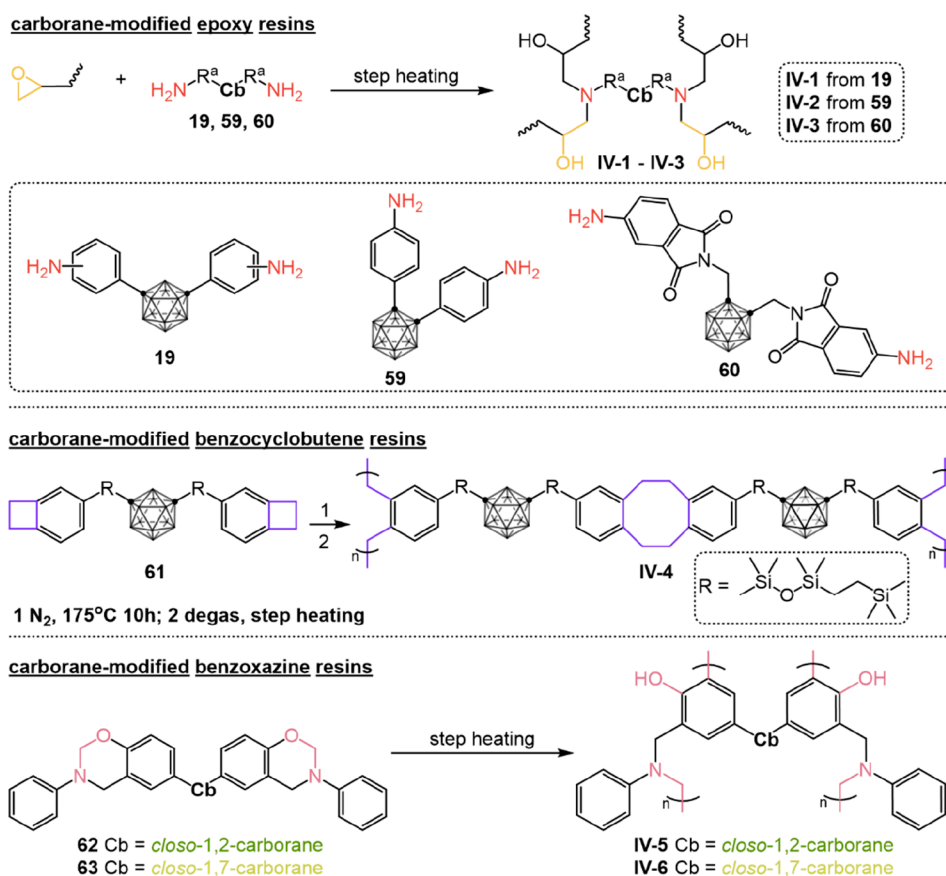
Scheme 21. Type III Polymers Obtained from Carborane CTAs



Scheme 22. Type III Polymers Obtained from Carborane ATRP Initiators



Scheme 23. Syntheses of Type IV Carborane-Modified Resins

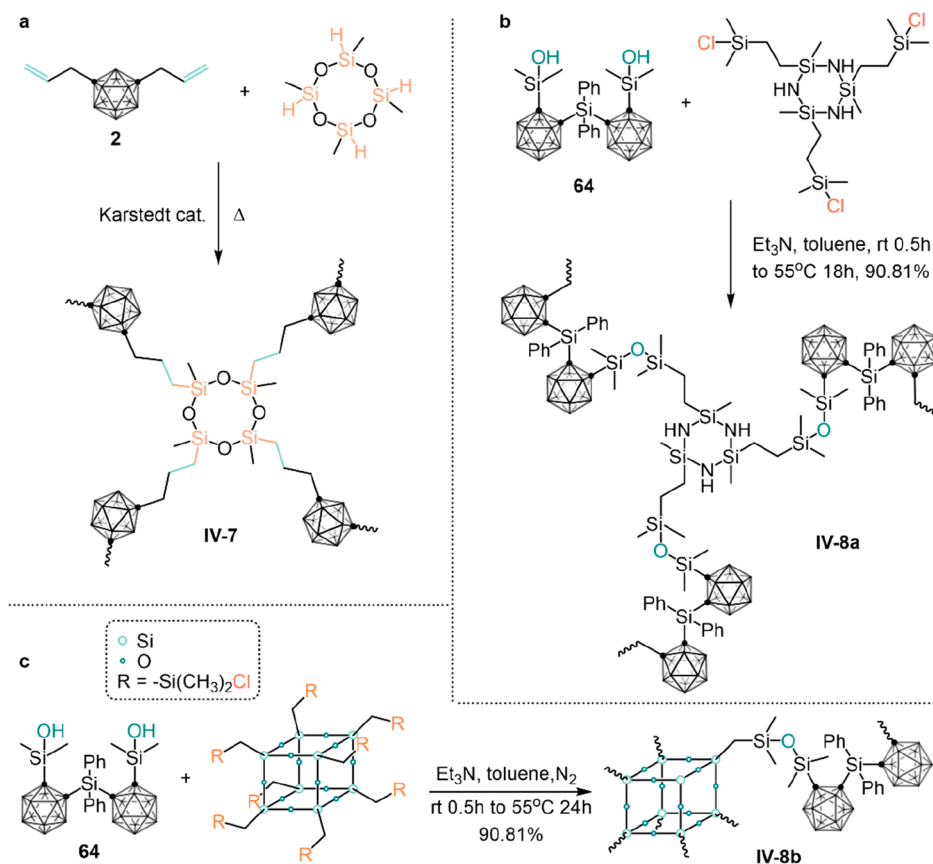


It should be noted that in chain-growth polymerization reactions, the bulkiness and low polarity of pendant carborane groups caused some difficulties in the polymerization reaction, leading to reaction inefficiency, low yields and low molecular weights, as described in some publications.^{35,80,86} Also, from the yields and SEC results, it appears that *closo*-1,2-carborane-containing vinyl monomers behaved poorly in reactions compared to *closo*-1,7-carborane-appended monomers, however it is difficult to know if there are indeed synthetic differences involving the two isomeric carborane cages due to the limited number of publications in this area. Furthermore, in living-like polymerizations (RAFT, ATRP, and ROMP), *closo*-1,12-carborane monomers and unprotected monosubstituted *closo*-

1,2-carborane monomers were not reported in these publications. The former was likely due to its low availability and high cost, while the latter was possibly due to the potential deboronation reaction of the mono-C-substituted carborane cage under these reaction conditions, although no explanation was given in any of the studies mentioned above.

2.1.3. Type III Polymers (i.e., Carboranes used as end groups). Type III polymers with carborane end groups were mainly obtained by means of postpolymerization methods. However, by using catalysts or initiators with carborane clusters, the cages can indeed be attached at the end(s) of a polymer during the polymerization process. For example, di-(hydroxymethyl) *closo*-1,7-carborane **15** was found to enhance

Scheme 24. Syntheses of Type IV Carborane-Modified Si-based Polymeric Networks



the polymerization rate of a phthalonitrile resin by means of $\text{B}_{\text{cage}}-\text{H}/-\text{C}\equiv\text{N}$ and $\text{O}-\text{H}/-\text{C}\equiv\text{N}$ addition reactions, resulting in a polymer network with a few carborane cages attached at the ends (Scheme 20).⁸⁷

In other cases, *closo*-1,2-carborane was incorporated into initiators for living polymerizations to afford polymers with a carborane cage at one end of the chain. The only carborane RAFT agent known to date was reported by Messina et al. in 2019. These researchers generated two dithioester CTAs with either *closo*-1,2-carborane (CTA1) or methylated *closo*-1,2-carborane (CTA2) as the Z group. CTA2 was tested by RAFT polymerizations of 4-chlorostyrene, *N*-isopropylacrylamide (NIPAAm), methyl acrylate (MA), and styrene in bulk and in solution (Scheme 21). Although high molecular weight shoulders in SEC showed up for pNIPAAm in toluene and poly(4-chlorostyrene) in bulk, and polymerizations in bulk lost control in uniformity in the process, all RAFT polymerizations carried out in solutions resulted in polymers with narrow molecular weight distributions (\bar{D} ranging from 1.08 to 1.20).

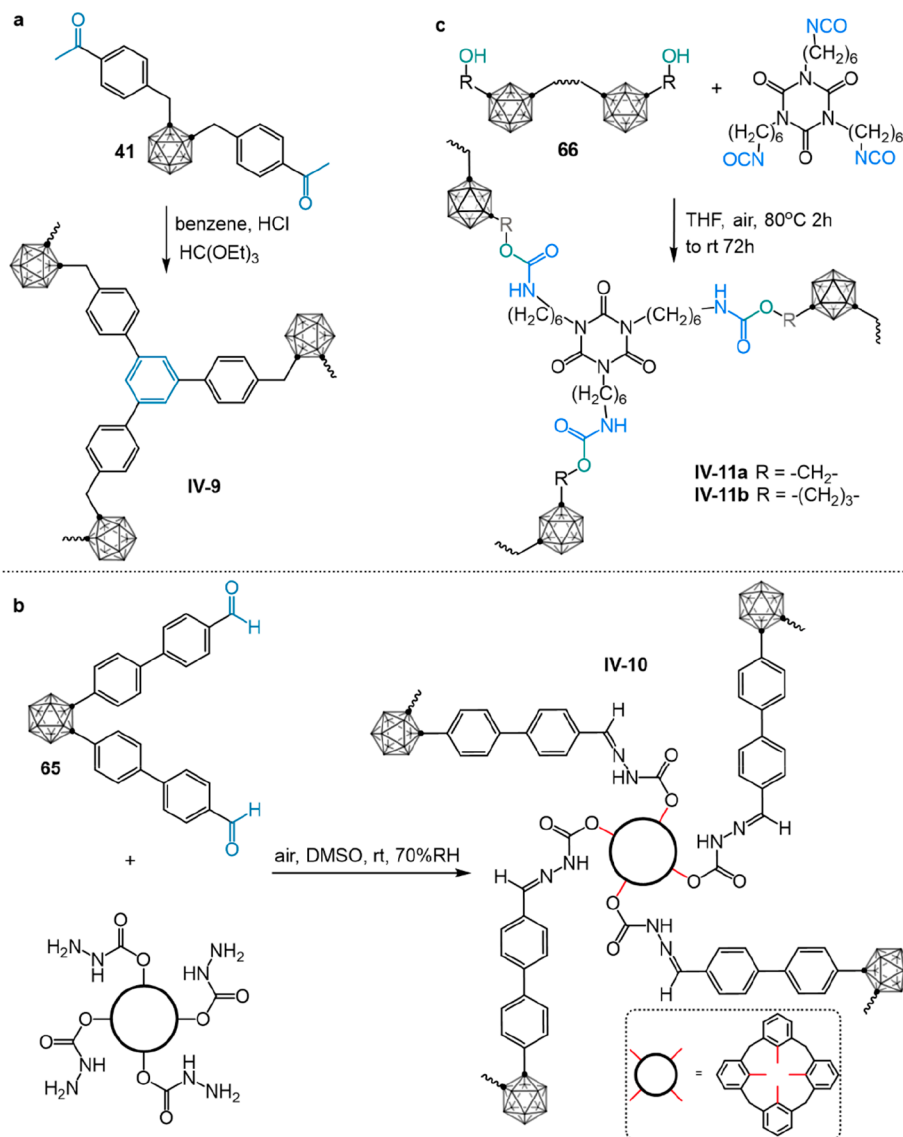
Carborane ATRP initiators have also been reported (Scheme 22). Qu et al. synthesized the first carborane ATRP initiator 1-bromomethyl-*closo*-1,2-carborane (II) and tested its efficiency in an ATRP polymerization reaction of methyl methacrylate (MMA), giving polymers with dispersities as low as 1.17 in a 94% conversion yield when 2-butanone was used. However, polymerizations in toluene and anisole were relatively poorly controlled, which gave a dispersity higher than 1.35.⁸⁸ Sha et al. developed monosubstituted (I2) and disubstituted (I3, I4) carborane ATRP initiators with which they synthesized poly(methyl acrylate)s, but focused on the potential of carboranes to be “mechanophores” rather than the efficiency

of the carborane initiators themselves.⁸⁹ Polymers generated from I3 and I4 had carboranes located in the middle of the chain and thus will be introduced in the Type IV polymers section below.

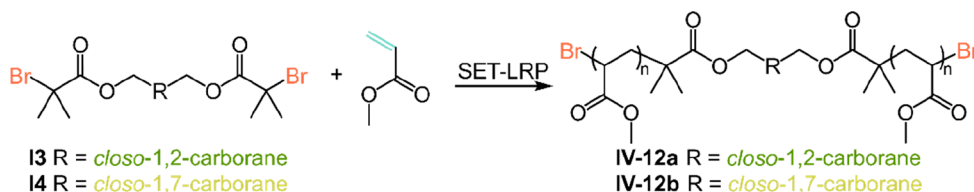
2.1.4. Type IV Polymers (i.e., Carboranes in polymer networks). Type IV carborane polymers are typically covalently cross-linked polymeric networks synthesized mainly by means of polycondensation methods. One large group of Type IV polymers include different types of carborane-modified resins cross-linked by disubstituted carborane linkers, such as epoxy resins, benzocyclobutene resins, and benzoxazine resins. Several carborane-modified epoxy resins (IV-1–IV-3) were prepared by multistage thermal curing of the degassed mixture of commercial epoxy resins and aromatic carborane diamines (19, 59, 60).^{90–93} A carborane-containing benzocyclobutene resin (IV-4) was formed by cross-linking a dibenzocyclobutene functionalized *closo*-1,7-carborane siloxane (61). The four-membered ring end group underwent different mechanisms during the heating process to form either the polymer backbone by means of self-coupling or eight-membered linker rings by means of a Diels–Alder reaction, resulting in a cross-linked network.⁹⁴ A few benzoxazine resins (IV-5, IV-6) have been synthesized by means of ring-opening reactions of *closo*-1,2-(62) or *closo*-1,7-carborane bisphenol benzoxazines (63) at 200–220 °C.⁹⁵ (Scheme 23)

Another group of Type IV polymers include carborane-incorporated silicon polymer networks, usually obtained by coupling difunctional carboranes with multifunctional silicon compounds including cyclosiloxanes, cyclosilazanes, and POSS. For example, a novel cyclosiloxane-carborane polymer network IV-7 was prepared by curing a cyclotetrasiloxane monomer with

Scheme 25. Other Type IV Carborane-Containing Polymer Networks and Their Synthesis Methods



Scheme 26. A Non-network Type IV Polymer Obtained from Carborane ATRP Initiators I3 and I4



divinyl *closo*-1,7-carborane **2** at 80 and 150 °C by means of a hydrosilylation reaction in the presence of Karstedt's catalyst (Scheme 24a);⁹⁶ Li's group obtained a poly(carboranesilazane)⁹⁷ **IV-8a** and a carborane POSS prepolymer⁹⁸ **IV-8b** using a dihydroxy carborane monomer **64**. The former was synthesized by means of coupling with a trichlorosilazane linker (Scheme 24b), and the latter generated with an octachloro-POSS compound (Scheme 24c).²²

Other types of Type IV polymer networks include: carborane-linked phenylene polymer networks formed by (1) cyclotrimerization of a diacyl carborane **41** in the presence of a triethyl orthoformate cross-linking agent and HCl (Scheme

25a),⁷⁰ or (2) amine-coupling of a diformyl carborane **65** with a tetra-arm amine cross-linker (Scheme 25b).⁴⁰ A few carborane-linked polyurethane networks **IV-11a** and **IV-11b** have been prepared from a hydroxyl-ended carborane-containing Type I polymer and a hexamethylene isocyanate (Scheme 25c).^{53,56,99}

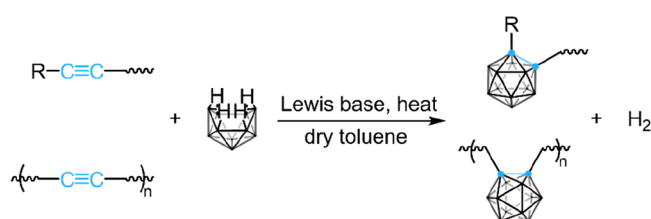
The only non-network Type IV carborane polymer reported to date was prepared by means of a single-electron transfer-living radical polymerization (SET-LRP) reaction initiated by carborane-containing initiators **I3** and **I4**⁸⁹ (Scheme 26). A SET-LRP reaction uses the same components as an ATRP reaction, while the alkyl halide initiator is activated by a highly reactive Cu(0) species instead of a Cu(I) catalyst.¹⁰⁰

2.2. Postpolymerization Modification Methods

Postpolymerization methods for carborane-containing polymer synthesis include cage-generating and cage-attaching methods. The carborane cage-generating method involves the alkynyl-decarborane reaction commonly used to generate a *closo*-carborane cage in situ, which was largely used in the preparation of Type I–III polymers. Cage-attaching methods are various coupling reactions to append carborane cages onto the polymer chains, giving Type II–IV polymers.

2.2.1. Cage-Generating Methods. *Closo*-1,2-carborane cage can be generated directly by reacting alkynyl-bearing polymers with *nido*-B₁₀H₁₄ in the presence of a Lewis base (e.g., acetonitrile) in an inert solvent (e.g., toluene) upon heating (Scheme 27).^{2,43,101–106} This is the most common postpoly-

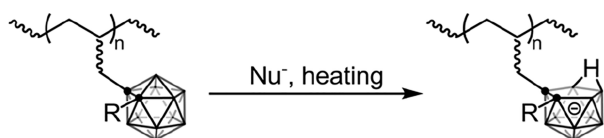
Scheme 27. B₁₀H₁₄-Alkynyl *closo*-1,2-Carborane Cage-Generating Reaction



merization modification route to carborane-containing polymers which provides an alternative route to carborane polymers, avoiding the multistep and low-yielding preparation of some carborane-containing monomers. However, this method can only lead to *closo*-1,2-carborane polymers, and when generating Type I polymers (parent polymers are internal alkynes) the reaction can be low yielding and require heating for more than 24 h, particularly in the case of internal alkynes.^{101,102,105,107} Additionally, the use of highly toxic and potentially explosive *nido*-decaborane makes this method less preferred compared to the low toxicity and stable *closo*-carborane routes described earlier.

Polymers bearing *nido*-[C₂B₉H₁₂][−] cage have been reported in Type II polymer studies, which were generated by means of regioselective deboronation of *closo*-1,2-carborane-containing polymers in the presence of a fluoride ion or a strong base upon heating (Scheme 28). CsF was reacted with polymer II-11 in an

Scheme 28. *Nido*-carborane-Appended Polymers Generated from *closo*-1,2-Carborane Polymers by Means of a Regioselective Deboronation Reaction



aqueous solution to obtain the anionically charged *nido*-carborane-appended polymer,⁸⁰ while polymer II-15 was deboronated using KOH in ethanol.⁸⁵

2.2.2. Cage-Attaching Methods. “Click” reactions. An azide/yne “click” reaction has been exploited using carborane ethynes and azido-appended polymers to afford Type II polymers.^{42,108} Depending on the solubility of the reactant polymer, the reactions can be carried out either in a dry organic solvent (anhydrous THF) in the presence of Et₃N and a CuI

catalyst, or in an organic aqueous mixture (THF/water) with CuSO₄ catalyst and excess sodium ions (Scheme 29a). The carborane-appended polystyrene was obtained in good yield (66%) and a PDI of 1.52 after a 2-step modification of the original poly(chloromethylstyrene), which was obtained by free radical polymerization with a PDI of 1.26. However, conversions of other Type II polymers prepared by means of the “click” reaction were not mentioned. Another thiol/ene “click” reaction between thiolcarboranes and vinyl-ended polymers were applied in the preparation of Type III polymers through Michael addition¹⁰⁹ or under UV irradiation.¹¹⁰ Both methods gave nearly quantitative conversion and low polydispersities of around 1.1. However, the Michael addition of dithiol-*closo*-1,2-carborane required a primary amine as the catalyst and a reaction time of 2 days to proceed with reasonable conversion, while UV irradiation required excessive thiolcarborane and harsher conditions to avoid the formation of side products (Scheme 29b).

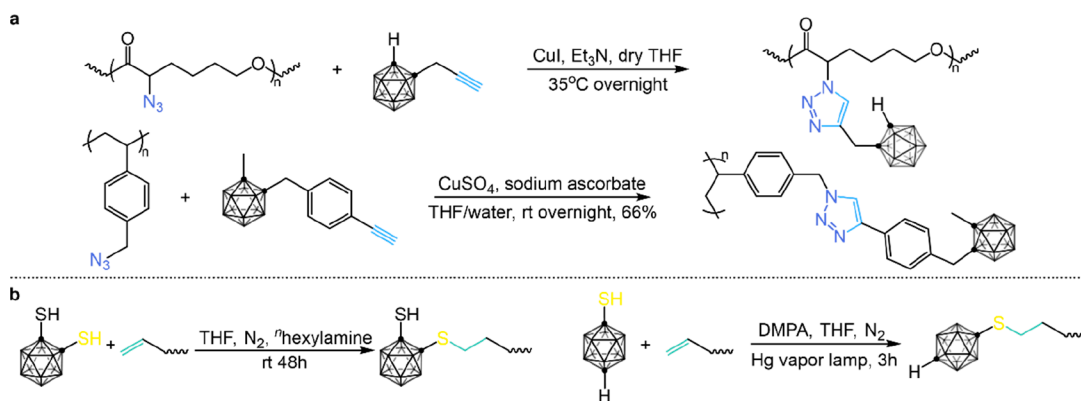
2.2.2.1. Hydrosilylation Reaction. Hydrosilylation reactions between carborane vinyls and terminal Si–H groups were used to incorporate a carborane cage as an end group. The reactions were reported to give high yields (97%) in the presence of Karstedt’s catalyst after 1 h at room temperature (Scheme 30). However, using an excess of Karstedt’s catalyst, a double-bond internal migration reaction was observed, which resulted in a low conversion because internal alkenyl groups do not react with organic silicon monohydrides.¹¹¹

2.2.2.2. Esterification Reaction. A classic esterification reaction was carried out between a *closo*-1,2-carborane carboxylic acid and free hydroxy groups in dextran to obtain a Type II carborane-modified dextran. The reaction was proceeded with DCC and DMAP in DMSO in a good yield of 72% (Scheme 31).³⁴

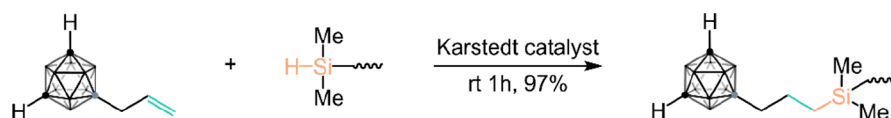
2.2.2.3. Noncovalent Host–Guest Interaction. Carboranes are known to form noncovalent host–guest (supramolecular) interactions with β -cyclodextrin under aqueous conditions, and linear polymers and noncovalently cross-linked networks have been obtained by mixing carborane polymers with β -cyclodextrin-modified polymers in water. Xiong et al. reported the first carborane-containing amphiphilic host–guest molecule composed of a β -cyclodextrin-linked polyethylene glycol and a carborane capped alkyl ester, which formed stable self-assemblies with carborane-octane at the core in aqueous solution.¹⁰⁶ Later in 2020, this group developed another 3D cross-linked host–guest interaction-based polymer network from carborane-pendent dextran and β -cyclodextrin-appended poly(acrylic acid). The noncovalently cross-linked 3D structure was obtained within a short period (ca. 1 min) by simply mixing together the host and guest polymer solutions (Scheme 32).³⁴

Notably, for the synthesis of Type IV polymers, other than polycondensation reactions between difunctional carboranes and other multifunctional monomers, postpolymerization thermal curing of Type I polymers produced a large number of Type IV polymer networks. These alkynyl and aromatic group containing Type I polymers were able to be cross-linked at higher temperatures through further polymerization of vinyl or alkynyl groups,^{72,107} cycloaddition reactions involving alkynyl groups, and aromatic rings^{38,47,67,105} and atom rearrangement.⁵²

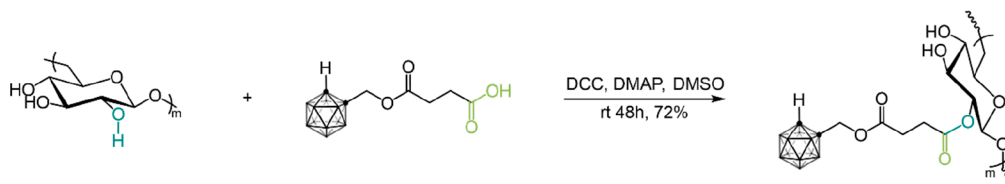
Scheme 29. “Click” Reactions Used to Attach Carborane Cages to Polymers



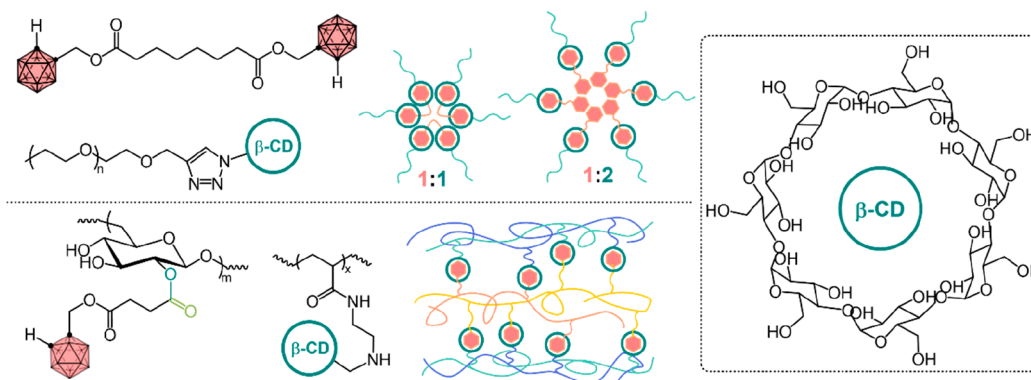
Scheme 30. Hydrosilylation Reaction Used to Attach Carborane Cages to Polymers



Scheme 31. Esterification Reaction Used to Attach Carborane Cages to Polymers



Scheme 32. Host–Guest Interaction Used to Generate Carborane-Containing Polymer Networks



3. APPLICATIONS AND PROPERTIES OF CARBORANE-CONTAINING POLYMERS

3.1. Thermo-oxidation Stability Properties

Carboranes were well-known for their outstanding thermal and oxidation stabilities. They are typically incorporated into different polymer systems to improve their thermo-oxidation properties. Such polymer systems include polyimides, polybenzoxazines, polysilanes, polysiloxanes, polyphenylenes, polyesters, and polyurethanes, to name a few. To date, most of carborane-containing polymer studies have been focusing on the thermo-oxidation stability. The thermal properties of polymers are indicated by the following parameters: glass transition temperature T_g , melting point T_m , initial decomposition temperature T_i , the temperature at which 1%/5%/10% weight loss is observed during heating $T_{d1}/T_{d5}/T_{d10}$ (where T_{d1} or T_{d5}

were sometimes used as alternatives for T_i), residual mass and residual yield, which are often characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). The thermal performance of carborane-containing polymers is summarized in Table 1.

3.1.1. Glass Transition Temperature. Carboranes generally showed reversed effects on the T_g of polymers, as monitored by DSC. On the one hand, the bulky clusters impeded chain mobility,³⁹ which led to a higher T_g ; whereas in contrast, the bulkiness of the clusters reduced interchain charge transfer and loosened chain packing,⁵⁸ causing a lower T_g . For example, **I-19b** with a 50% carborane unit molar ratio exhibited a 67 °C increase in T_g compared to its carborane-free (where $m = 0$) analogue,³⁹ **I-25a** and **I-25d** showed T_g more than 25 °C higher than their parent polymers,⁶² and cured **I-40** had a T_g

Table 1. Summary of the Thermo-oxidation Resistance of Carborane-Containing Polymers^{a,b,c,d,e,f,g,h,i,j}

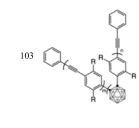
Entry	Polymer	Ref.	Structure	Processing	Details	M _w (GPC)	T _g (°C)	T _{as} (°C)		Char Yield (%)											
								N ₂	Air	T (°C)	N ₂	Air									
1	polyphenylene	65	I-26	polymer		30700	>450	707	>1000	1000	93.2	97.9									
2													ceramics	/	/	/	/	1000	/	100.8-101.6	
3		70	IV-9	cured		/	/	/	200-300	1000	/	80-90									
4		45,46	I-6	polymer		11000	57	/	~300	700	/	71									
5													I-7	polymer		21100	62	300-350	~300	700	51
6		45	I-5	thermoset		/	/	669.5	>1000	1000	92	98.8									
7		63	I-27	polymer		13800	/	500-550	>900	900	90.25	120.61									
8	poly(phenylene acetylene)	103		polymer	0.05 ^a	10700	/	/	283.6	1050	/	1.11									
9													polymer	0.08 ^a	12400	/	/	282.1	1050	/	6.3
10													polymer	0.14 ^a	4200	/	/	258.1	1050	/	13.92
11													polymer	Non-carborane	12000	/	/	316.9	1050	/	0
12	polybenzoxazin ^e	49	I-9a	polymer		8500	/	420	553	900	80.10	86.10									
13													I-9b	polymer	9500	/	543	708	900	90.3	83.3
14													I-9c	polymer	7700-15000	/	/	/	900	13.8-19.1	13.4-23.9
15													69	I-40	thermoset	26000	>300	398	404	800	75
16	polyarylate	53	I-35a	polymer		7500	/	376	/	700	81	/									
17													I-35b	polymer	2400	/	269 ^b	/	700	68 ^b	/
18													I-35c	polymer	1600	/	231 ^b	/	700	34 ^b	/
19													polymer	ether analogue of I-35b	12000	/	308	/	700	33	/
20	poly(thiophene naphthalene)	68	I-37	polymer		9000	/	445	/	700	56	/									
21													I-38	polymer	29000	/	449	/	700	49	/
22													I-39	polymer	53000	/	450	/	700	45	/
23													polymer	Non-carborane	/	/	~440	/	700	32	/
24	polysilane	72	I-42	polymer		/	/	600 ^c	>1000	1000	82 ^c	133									
25													cured	/	/	600 ^c	>1000	1000	89 ^c	145	
26	polysiloxane	50	I-10	polymer		47000-165000	-13 ~ -50	380-425 ^{c,d}	350-380 ^{c,d}	/	/	/									
27													polymer	80800	-18.4	509	439	800	80-85	83.94	
28		52	I-10c	cured		/	/	570	536	800	85-90	87.21									
29													polymer	55500	-16.2	625	727	800	~90	93.51	
30		I-24	cured	/	/	704	775	800	90-95	94.52											
31		I-11a	57	polymer		11200	/	460	250	900	23.7	71.4									
32	I-11b												polymer	9200	/	381	/	900	12.5	/	
33	I-12												polymer	12900	/	476	/	900	81.6	/	
34	I-13a												polymer	8800	/	555	/	900	87.6	/	
35	I-13b												polymer	16000	/	507	/	900	61.4	/	
36	I-14a												polymer	9500	/	402	371	900	12.6	44.7	

Table 1. continued

Entry	Polymer	Ref.	Structure	Processing	Details	M _w (GPC)	T _g (°C)	T _{as} (°C)		Char Yield (%)					
								N ₂	Air	T (°C)	N ₂	Air			
37			I-14b	polymer		12000	/	326	/	900	/	42.6			
38	Polyoctahedral silsesquioxanes	98	IV-8b	polymer		9631	<25	170.5 ^d	/	900	74.3	/			
39				ceramic		/	/	799.9	587.9	1000	93.9	75.6			
40	polysilazane	97	IV-8a	polymer		/	<25	~300	/	1000	65.6	/			
41	polycyclosiloxane	96	IV-7	cured	1:1	/	/	~500 ^e	>1000	1000	~50 ^e	95-96			
42				cured	4:3	/	/	~500 ^e	~600	1000	~50 ^e	92-93			
43				cured	2:1	/	/	~520 ^e	~600	1000	~70 ^e	91-92			
44	poly(silane-arylacetylene)	38	I-30	polymer		2202.6	<25	165 ^d	/	1000	77.6	/			
45				ceramic		/	/	650	664	1000	84.5	88			
46				cured		47	I-8		11200	>350	709.3	>1000	1000	93.2	110.3
47		67	I-29a	polymer		10944	/	400 ^e	/	1000	85 ^e	93			
48			I-29b	polymer		7862	/	349 ^e	/	1000	85 ^e	93			
49		113	I-29b	polymer		4200	<25	226	/	1000	75	/			
50				cured I ^e		/	/	550	602	1000	84	89			
51				cured II ^e		/	/	555	641	1000	84	91.5			
52	poly(siloxane-arylacetylene)	102	Scheme 33a	P1	thermoset	/	/	647	619	800	92.8	91.2			
53				P2	thermoset	/	/	605	605	800	90.8	91			
54				P3	thermoset	/	/	594	587	800	91.1	89			
55				Scheme 33b	thermoset	101	/	/	1974	/	552	>800	800	91.5	95.8
56					thermoset	Non-carborane	/	/	636	562	800	90	37.8		
57							thermoset	Non-carborane	755	<25	446	420	1000	72.6	22.7
58				thermoset	0.9 ^f	/	<25	421	475	1000	77	84.3			
59		105	Scheme 33c	thermoset	1.5 ^f	/	/	395	526	1000	81.3	88.2			
60				thermoset	2.0 ^f	/	/	362	584	1000	81.3	88.2			
61				thermoset	2.7 ^f	/	/	331	922	1000	82.6	92.4			
62		58	I-21	polymer	n=0	75000	206	536	572	600	70	/			
63				polymer	n=m	33000	220	539	545	600	/	/			
64				polymer	n=2m	34000	224	537	570	600	/	/			
65				polymer	n=0	23000	227	539	549	600	~72	/			
66				polymer	n=m	24000	226	541	549	600	/	/			
67				polymer	n=2m	60000	221	529	533	600	/	/			
68				polyimides	39,60	I-19b	polymer	0% ^g	/	304	582	561	750	68.6	5.4
69							polymer	5% ^g	/	320	601	602	750	71.2	64.8
70	polymer	10% ^g	/				329	598	604	750	74.4	69			
71	polymer	20% ^g	/				340	597	606	750	79.4	76.2			
72	polymer	30% ^g	/				352	596	611	750	82.6	81.2			
73	polymer	40% ^g	/				366	595	615	750	85.9	86.5			
74	polymer	50% ^g	/	371	596	632	750	87.9	90						
75		59	I-18	polymer		18000	223	604	1099	1200	85-90	~70			
76			I-19a	polymer		19000	242	786	1083	1200	85-90	~80			

Table 1. continued

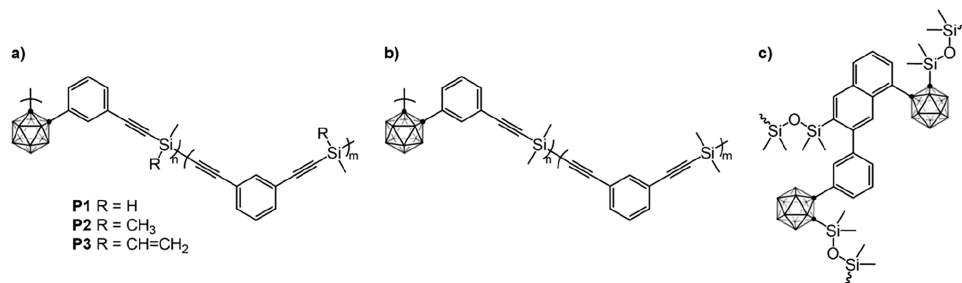
Entry	Polymer	Ref.	Structure	Processing	Details	M _w (GPC)	T _g (°C)	T _{as} (°C)		Char Yield (%)				
								N ₂	Air	T (°C)	N ₂	Air		
77			I-20	polymer		10000	249	382	388	1200	~65	35-40		
78			I-23	polymer		24000	247	615	1128	1200	85-90	~80		
79			I-15a	polymer		7334	/	289	281	700	69	91		
80			I-15b	polymer		7907	/	269	259	700	59	75		
81		55	I-16a	polymer		5443	/	264	260	700	60	76		
82	polyester		I-16b	polymer		5867	/	253	253	700	47	64		
83				polymer	Non-carborane	/	/	251	249	700	5	0.3		
84				I-15c	polymer		12500	/	/	285	800	/	32.1	
85		56	I-17	polymer		13100	/	/	229	800	/	22.2		
86				polymer	Non-carborane	14400	/	/	161	800	/	6		
87						11900	/	406	308	850	42.8	57.1		
88	poly(hydroxy ether)	54	I-9e	polymer		8900	/	365	317	850	49.9	64.2		
89			I-9f	polymer		13000	/	439	353	850	64.2	74		
90	poly(aryl ether ketone)	66	I-28	polymer		89000	209.6	533	750	1000	87.30	85.3		
91	polyazomethine	56,70	I-41	polymer		/	/	/	100-200	1000	/	70-80		
92			IV-11a	polymer		/	/	/	335	800	/	66.6		
93	polyurethane	56	IV-11b	polymer		/	/	/	238	800	/	58		
94					polymer	Non-carborane	/	/	/	141	800	/	34.3	
95				polymer	n=0	63900	153	370	/	700	31.6	/		
96				polymer	m:n=75:25	887500	99	310	/	700	14.6	/		
97	polyoxonorborane	37	II-13c	polymer	m:n=50:50	587100	78	300	/	700	13.2	/		
98				polymer	m:n=25:75	103000	32	241	/	700	9	/		
99				polymer	Non-carborane	98000	131	396	/	700	9.8	/		
100				hydrogenated	n=0	46100	145	/	700	15.5	/			
101			hydrogenated	m:n=75:25	686900	88	410	/	700	11	/			
102			hydrogenated	m:n=50:50	450800	/	407	/	700	10.2	/			
103			hydrogenated	m:n=25:75	135400	32	393	/	700	6.7	/			
104			hydrogenated	Non-carborane	100000	103	411	/	700	3.2	/			
105						polymer	m=0	/	/	/	/	600	32.2	40
106						polymer	n=0	/	/	/	/	600	52.2	/
107		84	II-13d	polymer	m:n=1:4	56756 ^h	/	~120	~200	600	41.2	62.4		
108				polymer	m:n=4:1	55102 ^h	/	~250	~140	600	59.3	48.4		
109				polymer	m:n=1:1	54081 ^h	/	~150	~170	600	51.1	56.8		
110			II-13e	polymer		/	/	~100 ^d	~90	600	60.4	60.6		
111				cured	Non-carborane	/	/	487-538	462-542	1000	67.4-75.8	0.0-6.4		
112				cured	5mg ⁱ	/	/	492-535	460-547	1000	73.5-74.8	14.0-28.5		
113	Biphenyl phthalonitrile resin	87	III-1	cured	10mg ⁱ	/	/	570-580	565-575	1000	79.3-80.3	31.1-40.6		
114				cured	15mg ⁱ	/	/	590-609	591-597	1000	82.1-84.2	47.6-48.4		
115				cured	20mg ⁱ	/	/	592-594	595	1000	83.2-83.3	28.6-32.2		
116				cured	30mg ⁱ	/	/	613-615	598	1000	84.9-86.5	38.2-38.9		

Table 1. continued

Entry	Polymer	Ref.	Structure	Processing	Details	M_w (GPC)	T_g (°C)	T_{as} (°C)		Char Yield (%)			
								N ₂	Air	T (°C)	N ₂	Air	
117	epoxy resin	90	IV-3	resin	Non-carborane	/	/	~325	250-350	800	~18	0	
118				resin	20% ^j	/	/	250-300	250-350	800	~57	~55	
119				resin	30% ^j	/	/	~240	250-350	800	~58	~62	
120				resin	40% ^j	/	/	250-300	250-350	800	~61	~65	
121		resin	IV-2	butynyl analogue	/	/	~400	~400	700	~65	~65		
122		resin	91	IV-1	resin	4,4'-DDS linker	/	/	~350	~340	700	~5	~5
123	Benzocyclobutene resin	92	IV-1	resin		/	/	385 ^e	378	800	43.7 ^e	50.5	
124				resin	4,4'-DDS linker	/	/	385 ^e	374	800	15.1 ^e	3.3	
125		resin	IV-4		/	49.3	433 ^e	444	1000	26 ^e	59		
126		resin	IV-5		/	/	347	412	900	76.8	51.1		
127		benzoxazine resin	95	IV-6	resin		/	/	354	359	900	72.6	77.1
128		resin			bisphenol A linker	/	/	319	261	900	33.1	0.5	

^aNumber of carborane cages per unit determined by GPC. ^bLow MW polymers. ^cTested under Ar. ^d T_{d1} . ^eCure I: 2h at 230 °C, 2h at 250 °C, and 2 h at 270 °C. Cure II: Ramp to 300 °C at 2 °C/min, hold at 300 °C for 2 h, ramp to 350 °C at 2 °C/min, hold at 350 °C for 2 h, ramp to 371 °C at 2 °C/min, hold at 371 °C for 2 h, and cool to room temperature at a 2 °C/min. ^fNumber of carborane cages per chain determined by NMR spectroscopy. ^gCarborane monomer mole ratio. ^h M_n determined by NMR. ⁱAmount of carborane catalyst added. ^jCarborane diamine monomer ratio.

Scheme 33. Structures of Some Thermo-oxidation Resistant Carborane Polymers



value more than 55 °C higher than its phenyl analogue. However, for polymer I-21, an increase in carborane content was found to cause a decrease in T_g .⁵⁸ Some carborane-containing polymers also exhibit melting and crystallization peaks in the DSC. Polymers in Scheme 33c showed melting peaks at 69–76 °C (2.0 carborane cages per chain) and 85–93 °C (2.7 carborane cages per chain);¹⁰⁵ polymer I-29a was shown to have melting points at 121 and 150 °C,⁶⁷ and the melting point for I-26 was estimated to be above 500 °C based on that of the dimer.⁶⁵ Polymer I-7 represents the only example of a carborane polymer to show a crystallization peak (170–195 °C).⁴⁶

3.1.2. Thermal Stability. In most cases, carboranes can provide great improvements on the thermal stability of the resulting polymers and their cured ceramics, resins, and thermosets. Most of the carborane polymers exhibiting excellent thermal and oxidation stabilities possessed aryl, acetylene, or silyl groups in the polymer main chain that could undergo cyclotrimerization reactions, Diels–Alder reactions, or hydrosilylations during curing and heating treatment to form highly cross-linked networks. For aromatic polymer networks, the σ -aromatic carborane cages in the main chain functioned as a shield for the adjacent aromatic moieties, which further improved their thermal stability, e.g., poly(carborane-benzoxazine) systems I-9a and I-9b showed high T_{d5} under a N₂

atmosphere (420 and 543 °C, respectively) compared to the carborane-free ($m = 0$) polybenzoxazines;⁴⁹ cured *closo*-1,2-carborane incorporated poly(siloxane-arylacetylene) thermosets (Scheme 33a) had high residue yields at 1000 °C in N₂, which increased from 77.0% to 82.6% when the carborane cage content increased from 10% to 40%.¹⁰⁵

In some cases, the presence of carborane cages in the main chain has led to negative effects on the thermal stability of the polymer. For example, Wang et al. found a T_{d5} decrease of 84 °C under a N₂ atmosphere in carborane-containing aromatic poly(acetylsilane) (CB-PSEPE, Scheme 33b) compared to the carborane-free ($n = 0$) PSEPE although a slight increase in the residual yield (1.5%) under N₂ at 800 °C was observed. This was thought to be the result of carborane cluster decomposition at around 600 °C, supported by the disappearance of $\nu(B-H)$ band at 2568 cm⁻¹ in the FT-IR spectrum.¹⁰¹ Jiang et al. reported a decrease in T_{d5} of poly(siloxane-arylacetylene) thermosets (Entries 57–61, Table 1) with higher carborane loads, which was explained by the relative weakness of Si–C_{cage} bond, and steric hindrance and electron-withdrawing effects, although the residual yields at 1000 °C increased with higher carborane content.¹⁰⁵ The same problem caused by the weak Si–C_{cage} bond was also reported in a carborane polysiloxane

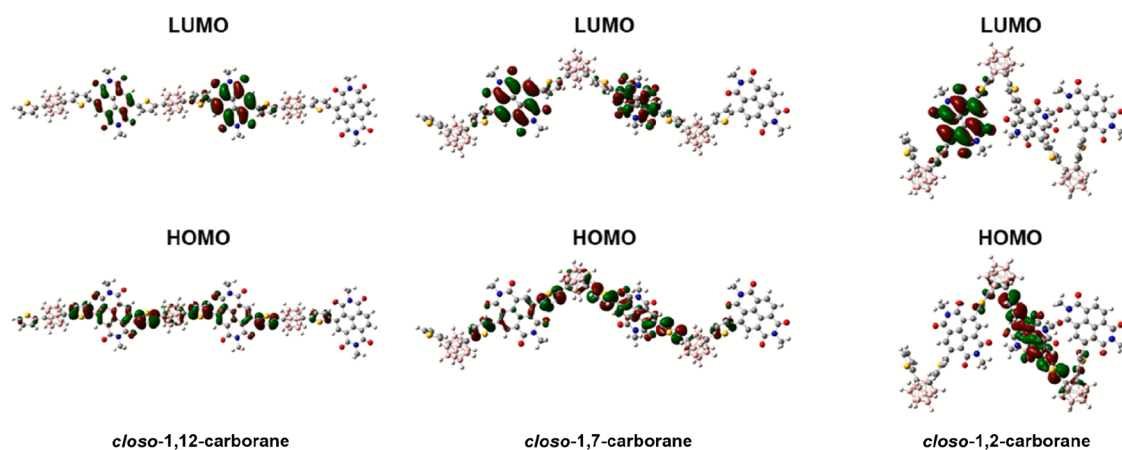


Figure 3. DFT calculations of trimer structures and HOMO/LUMO distributions of I-37–I-39. Reprinted with permission from Filip Aniéš et al.⁶⁸ Copyright © 2022 Elsevier.

system, which was prevented by introducing a methylene group between C_{cage} atom and the Si atom.⁵⁰

3.1.3. Oxidation Resistance. In an oxygen environment, the carborane polymers experience thermal degradation, oxidation, and even structural rearrangements at high temperatures. The degradation process forms volatile gases such as CO_2 and H_2O and causes a decrease in the sample mass; while the oxidation and structure rearrangement form self-healable boron oxide,⁴⁹ boron carbide⁵⁵ or borosilicate³⁸ layers on the polymer surface at higher temperatures, which leads to an increase in the sample mass and retards further weight loss by preventing gas penetration. The changes in the initial decomposition temperature and char yield are the results of the competition between the decomposition and the oxidation and structure rearrangement processes. Generally, carborane polymers showed a higher T_i and char yield compared to their phenyl analogues or noncarborane polymer species in air, or their behaviors in inert atmosphere; while in some polymer systems where oxygen reactive groups are present and the degradation process is dominant, a decrease in T_{d5} was commonly observed,⁵⁴ however, the char yield drops were rare due to the formation of the compact protective layers.^{49,66} Other oxidation environments have not been reported to date.

Some unprocessed carborane polymers exhibit strong resistance to heat and oxidation, with carborane polyimides as excellent examples. Compared to its carborane-free ($n = 0$) polyimide species, polyimide I-19b with only 5 mol % carborane content experienced a surge of 40 °C in T_{d5} in air. As the carborane content increased from 0 to 50%, the T_{d5} was found to increase from 561 to 632 °C; at the same time, the residual yield improved drastically from 5.4% to 90%.^{39,60} Xing et al. reported carborane polyimides I-18, I-19a, and I-23 with extremely high T_{d5} in air of ca. 1100 °C, whereas common phenyl polyimides normally have a T_{d5} below 600 °C.⁵⁹ Carborane polyesters I-15–I-16 also showed a great improvement on their residual yields in air, which were 91%, 75%, 76%, and 64%, respectively, compared to that of the carborane-free polyester (CFP), which was only 0.3%, although the exact structure of the CFP was not mentioned.⁵⁵ These enhancements were attributed to the introduction of carborane moieties in the main chains, which enabled the formation of B_2O_3 and boron carbide to delay the thermal degradation process.

Thermoset and ceramics cured from carborane-containing polymers showed stronger heat/oxidation resistance under air

compared to the unprocessed carborane polymers. In order to understand the mechanism of their thermo-oxidation stability, Du's group published a series of studies on the thermal behavior, structure, and crystallization of high-performance ceramics (CB-1000, CB-1200, CB-1300, CB-1450) cured from carborane poly(acetylene-phenylene-silylene) (CB-PSA, Scheme 33b) under high temperatures of 1000 °C, 1200 °C, 1300 °C, and 1450 °C, which could serve as a reference point for oxidation study of other carborane-containing aromatic polysilylenes. The highly oxidation-resistant CB-PSA showed a residual yield higher than 75% when heated up to 1450 °C, as confirmed by means of TGA.¹⁰¹ As the temperature increased from 600 °C, the polymer successively experienced three distinctive stages: C and H loss (<600 °C), further C, H, B and Si loss (600 °C to 800 °C), and a relatively steady state where all element contents remained relatively stable between 800 and 1450 °C. Accordingly, structural changes from amorphous Si–B–C material (600 °C onset), β -SiC nanocrystals and partly graphitized C (1100 °C onset) to B_4C nanocrystals (1300 °C onset) were observed,¹⁰⁴ which is in accordance with other studies.¹¹² The formation of an integral borosilicate layer was considered the key to the oxidation resistant behavior of these ceramics, which prevented the penetration of oxygen from the environment and carbon dioxide from inside the ceramics. This was supported by the fact that ceramic CB-1450, which showed only 7% weight loss after being heated at 1200 °C for 10 h in dry O_2 , formed the largest β -SiC and B_4C crystallites.¹¹³ Additionally, it was reported that the existence of boron was found to hinder the nucleation of β -SiC but benefit the crystallization of carbon to graphite and its growth.¹⁰⁴

Although the incorporation of carboranes normally provides a positive effect on the heat-oxidation resistance of the polymers, the polymer structure was also important for the overall behavior of the polymers. Factors such as molecular weight, the strength of the linking groups, the electronic properties of pendant groups, the length of the linkers between carborane cages, and the type of carborane isomers could affect the extent of the heat-oxidation resistance. For example, the electron-withdrawing vinyl pendant group was found to be more beneficial to increasing the initial degradation temperature and the residual yield of carborane polysiloxanes compared to electron-donating phenyl, methyl and trifluoropropyl pendant groups (I-11–I-14);⁵⁷ the weak $-\text{S}-\text{CH}_2-$ linker in carborane polyimide I-20 makes it less competent in heat/oxidation resistance;⁵⁹ the

shorter linkers between carborane moieties and the inclusion of the *closo*-1,7-carborane were found to provide a stronger enhancement on the residual yields in both N₂ and air of the carborane polyesters mentioned above.⁵⁵

For potential applications, the great enhancement in thermo-oxidation stability, together with the hydrophobic and boron-rich nature of carborane molecules, make carborane polymers useful as harsh environment resistant-coating materials and neutron shielding materials for space and nuclear facilities. Sun et al. reported the study of a carborane-POSS prepolymer (**IV-8b**) and coating properties of the resulted ceramic on carbon fibers. The ceramic coating was found to provide excellent antioxidation protection to the optimally coated fibers, which showed a satisfactory residual mass of nearly 65% after being oxidized at 700 °C for 2 h.⁹⁸

3.2. Optoelectronics

C-disubstituted *closo*-1,2-carborane in the main polymer chain is known to disrupt the π -conjugation within the polymer backbone in part due to the inductive electron-withdrawing effect at the C sites. This has been confirmed by several HOMO/LUMO visualizations and calculations, showing the molecular orbitals were only localized on the conjugated moieties between carborane cages (Figure 3).⁶⁸ Notably, *closo*-1,2-carborane incorporated polymers had the lowest HOMO and LUMO energy levels.³¹

The emissions of these polymers occurred via different mechanisms, such as aggregation induced emission (AIE) from intramolecular charge transfer (ICT) state³³ and local excited state (LES) emission.¹⁵ The shorter conjugation due to the incorporation of carborane cages was often indicated by hypsochromic shift in the UV-vis absorption spectra, while the emission caused by aggregation and ICT were usually represented by bathochromic shifts in photoluminescence spectra compared to their carborane-free analogues; the latter could be further confirmed by increasing red shifts and decreasing quantum yields in more polar solvents.^{28,33} Many researchers reported the introduction of bulky carborane clusters caused an AIE in solid polymer films, most of which emitted long-wavelength fluorescence. Carter's group reported the first fabrication of polymer light-emitting diodes (PLEDs) and thin film transistors (TFTs) from *closo*-1,2-carborane-containing emissive conjugated polymers (**I-25a**, **I-25d**) in 2012;⁶² in 2019, they also described carborane polyfluorenes (**I-25b**, **I-25c**) with solvatochromic properties in solution due to the combined effect of both LES emission from the fluorene moieties and the ICT state formed by electron transfer from fluorene to carborane moieties upon UV excitation.³³ They also obtained a series of photoluminescent polymer solutions in toluene or chloroform, which were found to exhibit a wide range of colors upon excitation by tuning the ratio of carborane units and fluorene units.¹⁵

Notably, B-disubstituted carboranes behaved differently in the polymer chain (*cf.* C-substituted analogues) due to the inductive electron-donating effect of the functionalized B sites. Tominaga et al. found that conjugated polymers with only B-disubstituted carboranes in the main chain (**I-6**) showed higher HOMO/LUMO energies and aggregation caused quenching (ACQ) behavior without changing the excited state of the conjugated units.³¹ Additionally, a combination of both C- and B-disubstituted carboranes situated in the main chain in an alternating manner (**I-7**) allowed the resulting polymer to retain the emissive properties of the C-disubstituted *closo*-1,2-

carborane polymers as well as the thermal behaviors of the B-disubstituted carborane polymers.⁴⁶

Furthermore, different C-substituted carborane isomers (*closo*-1,2-, 1,7- or 1,12-carborane) and stereochemistry (*cis* or *trans*) can also influence the optoelectronic properties of polymers. *Closo*-1,2-carborane polymers often showed the lowest HOMO/LUMO energies and the strongest electron-withdrawing effects compared to the other two carborane isomers. Anié et al. compared the effects of *closo*-1,2-, 1,7-, and 1,12-carboranes incorporated into a conjugated naphthalenediimide polymer main chain (**I-37–I-39**) on its optical and semiconductive properties. Compared to the *closo*-1,12-carborane incorporated polymer (**I-39**), the *closo*-1,2-carborane incorporated polymer (**I-37**) showed a stronger hypsochromic shift in the emission spectra and a bathochromic shift in the absorption spectra over the *closo*-1,7-carborane incorporated polymer (**I-38**). However, the most promising N-type semiconductive properties and photovoltaic behavior were found in *closo*-1,7-carborane polymers.⁶⁸ Marshall et al. prepared and characterized a set of *cis/trans* *closo*-1,2-, 1,7-, and 1,12-carborane appended polythiophenes (**II-3–II-8**) with different ionization potentials and backbone twisting, and observed similar optical properties. As shown in Figure 4, the UV-vis

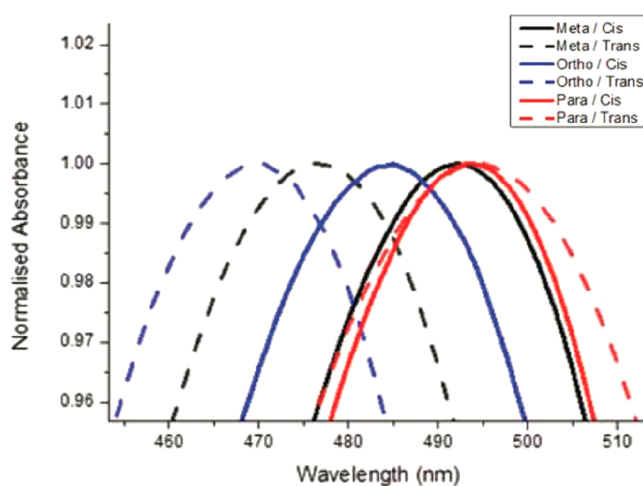


Figure 4. UV-vis absorption spectra of the *closo*-carborane polymers **II-3–II-8** in dilute chlorobenzene solution. Reprinted with permission under a Creative Commons Attribution 3.0 Unported License from Jonathan Marshall et al.⁷⁴ Copyright © 2014 Royal Society of Chemistry.

absorption of polymers experienced a red shift in the order of *closo*-1,2-, 1,7- and 1,12-carborane appended polymer. Additionally, *trans* polymers showed hypsochromic shifts compared to *cis* polymers for *closo*-1,2- and *closo*-1,7-carborane polymers, while for *closo*-1,12-carborane polymers, the *trans* polymer showed a broader absorption peak without obvious shift. Furthermore, with the same stereochemistry, *closo*-1,2-carborane polymer possessed the highest open-circuit voltage but the lowest fill factor and photocurrent compared to *closo*-1,7- and *closo*-1,12-carborane polymers; within the same isomer, *trans* polymers showed lower open-circuit voltage but higher fill factor and photocurrent than the corresponding *cis* polymers. Despite the *trans* *closo*-1,12-carborane polymer not being able to be manufactured into an organic photovoltaic (OPV) device, the related *cis* *closo*-1,12-carborane polymer was found to exhibit the highest power conversion efficiency of 2.03% among all reported

carborane-containing polymers at the time of publication (Table 2).⁷⁴

Table 2. Summary of OPV Characteristics of Carborane Polymers II-2–II-7

polymer	V_{OC} (V)	J_{SC} (mA cm^{-2})	fill factor	PCE ^a (%)
<i>closo</i> -1,2-Cb/ <i>cis</i>	0.92	2.28	0.30	0.63 (0.59, 5)
<i>closo</i> -1,2-Cb/ <i>trans</i>	0.82	2.92	0.37	0.88 (0.86, 3)
<i>closo</i> -1,7-Cb/ <i>cis</i>	0.85	3.11	0.32	0.86 (0.80, 3)
<i>closo</i> -1,7-Cb/ <i>trans</i>	0.56	4.34	0.42	1.01 (0.95, 4)
<i>closo</i> -1,12-Cb/ <i>cis</i>	0.85	5.44	0.44	2.03 (1.90, 4)
<i>closo</i> -1,12-Cb/ <i>trans</i>				

^aHighest performance (Average performance, sample size).

The unique electronic properties of carboranes give researchers the opportunity to finely tune the electronic, photovoltaic, semiconductive, and emissive properties of the conjugated polymers, thus allowing the potential development of novel luminescent materials, semiconductors, optoelectronic devices, and sensors in the future.

3.3. Medicinal Chemistry

Carboranes have been widely studied in medicinal chemistry over the years as small molecules for bioimaging, as chemical probes and as medicinal agents due to their low toxicity, lipophilicity, metabolic stability, structural robustness, and “dihydrogen” bond forming ability.⁷ However, these cages can be poorly soluble in an aqueous environment in addition to rapid clearance in vivo because of their high hydrophobicity,³⁵ yet nanoparticles are known to have extended circulation time in the blood and longer retention time in tumor cells as well as improved stability and good solubility.¹⁰ Thus, nanoscaled self-assemblies formed from carborane-containing amphiphilic copolymers with carboranes at the core have been prepared in aqueous solution. In this way, carboranes were explored as potential BNCT agents and/or drug delivery systems carrying other drug molecules by means of intermolecular dihydrogen bonding. Additionally, dyes such as cyanine and rhodamine B could be attached as end groups to provide imaging-guiding. For example, Ruan et al. published several papers on imaging-guided BNCT of *closo*-1,7-carborane-containing cyanine-attached amphiphilic copolymers (II-10a, II-10b, and II-12), where *closo*-1,7-carborane served as a boron carrier and other blocks provided tumor targeting and self-assembling abilities.^{10,35,79} Xiong et al. successively developed PEGylated *closo*-1,2-

carborane-containing copolymers for antitumor therapies, using either a multitherapy combining chemotherapy with doxorubicin (DOX) and BNCT by encapsulating DOX in carborane-containing nanoparticles,² or simply using BNCT.⁴¹ Notably, the carborane nanoparticles loaded with doxorubicin exhibited low cytotoxicity, prolonged circulation time, higher B accumulation in tumor sites, stability in the presence of light, and high therapeutic efficacy.² In order to address the problem of boron leakage caused by the use of an excess amount of *nido*-decaborane during postpolymerization modification and to tune of nanoparticle size and boron load, ring-opening polymerization of carborane monomers was carried out, and self-assembled nanoparticles from II-11 were obtained in 3 different sizes and the B content was improved to as high as 16 wt % (Figure 5).⁴¹ These authors have also reported the first linear amphiphilic supramolecules composed of a PEGylated β -cyclodextrin and carborane-terminated octyl chain that showed the potential to deliver light sensitive TPP with limited water solubility for photodynamic therapy. The 1:1 (β -cyclodextrin: carborane) amphiphilic supramolecule formed spherical nanoparticles sized ca. 120 nm, more stable than the 2:1 (β -cyclodextrin: carborane) amphiphilic supramolecules, which also formed spherical nanoparticles but grew in size from ca. 90 nm to ca. 180 nm over time.¹⁰⁶ Chen et al. prepared a PEG₂₀₀₀ and rhodamine B modified *closo*-1,2-carborane polymer as a potential BNCT agent with bioimaging and controlled drug release properties.¹⁰⁹ The endocytic pathway and cytotoxicity of *closo*-1,2-carborane-PEG₂₀₀₀ were investigated, showing cholesterol dependent endocytosis and exhibiting almost no cytotoxicity, as supported by no change in cell membrane including fluidity, recovery, microviscosity and integrity, cell apoptosis, cell cycle, or morphology before and after endocytosis.¹¹⁴

Other than their use as antitumor agents, more recently carborane polymers have also been designed and investigated for theranostics and tissue engineering. Carborane-polymers were attached to gold nanoparticles as coatings and stabilizers to facilitate their theranostics;⁴² Xiong et al. developed the first self-healable carborane-cyclodextrin supramolecular hydrogel (Scheme 32) exploiting the noncovalent host–guest interaction between carborane clusters and β -cyclodextrin. The resulting gel showed porous 3D cross-linked structures, efficient self-healing ability and good biocompatibility, for potential tissue engineering applications.³⁴

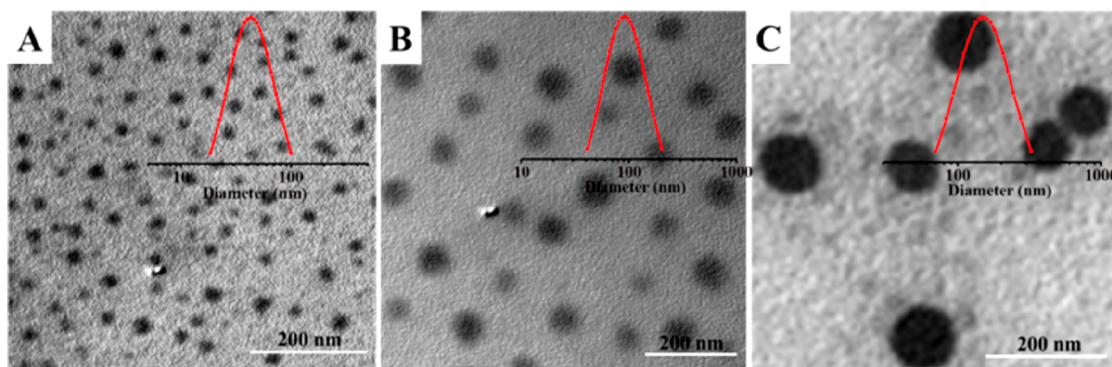


Figure 5. TEM image of carborane self-assemblies of II-12 in water. (A) mPEG₄₄-*b*-PMPCB₆, (B) mPEG₁₁₃-*b*-PMPCB₃, and (C) mPEG₁₁₃-*b*-PMPCB₁₀. Reprinted with permission from Hejian Xiong et al.⁴¹ Copyright © 2016 American Chemical Society.

3.4. Other Applications

Other than the properties and applications mentioned above, carborane polymers have also been studied as catalyst supports,⁸⁶ nanoparticle coatings for stabilization improvement,¹⁰⁸ graphene oxide coatings for microwave absorption enhancement,⁶⁴ hydrophobic coatings for nanopapers,⁷⁶ responsive materials to nucleophiles,^{80,85} shape-memory materials,⁹⁴ and as chain-scission sites during ultrasonication of mechanomaterials.⁸⁹ In terms of analysis, some carborane-containing polymers were found to have unique spectroscopic handles in their characterization. For example, Type III polymers mediated by CTA2 have an upfield ¹H NMR signal at ca. 0.2 ppm due to the methyl_{Cb} group, and a Raman $\nu(\text{B-H})$ vibration at 2549 cm⁻¹ which occurs within a silent region of biological tissues.¹¹⁵

4. CONCLUSIONS

Closo-carboranes possess nonclassical 3D aromatic structures, unique photophysical and physicochemical properties, including high hydrophobicity (or hydrophilicity in the case of *nido*-carboranes), chemical and thermal stability, biocompatibility, and the ability to form unusual dihydrogen bonds. Their use has been increasingly studied in the field of polymer science over the last two decades. Various polymerization methods involving closo-carboranes such as polycondensations, RDRP, free radical polymerization, and ROP, and organic synthetic methods including pre- and postpolymerization modifications have been carried out for the preparation of polymers with closo-carboranes incorporated into the main polymer chain, as pendant, end, or linker groups. Studies on carborane-containing polymers have revealed the important role of carborane clusters in tuning polymer properties and providing new characteristics to the systems such as heat and oxidation stability, amphiphilicity, and fluorescence. The proposed applications span across several fields, including heat/oxidation resistant coatings, ceramic precursors, neutron shielding materials, optoelectronic devices, luminescent materials, sensors, anti-tumor therapies, drug delivery, and bioimaging. Explorations of novel synthetic methods and structure control of carborane polymers are far from complete, however, and systematic investigations on the effects of various carborane derivatives on the physical properties of different polymer systems and the underlying mechanisms are still required. A thorough understanding of the many types of carborane polymers will certainly pave the way for the development of novel advanced materials with unique physicochemical properties, and there is little doubt that many more exciting potential applications of these materials will be discovered in the future.

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Notes

The authors declare no competing financial interest.

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