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Review

Poly(cyclodiborazane)s

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Abstract

This paper summarizes our recent works on the synthesis and properties of the organoboron polymers, especially poly(cyclodiborazane)s. The polymers consist of boron–nitrogen four-membered rings, and are highly stable against air and moisture. The obtained polymers exhibited interesting properties as a novel type of π-conjugated polymers with intramolecular charge transfer structure. Their stability and potential as functional materials would be important and informative both in industry and boron chemistry.

Keywords: Organoboron; Polymers; Four-membered rings; π-Conjugated polymers

1. Introduction

Recently, we have reported synthesis of a series of π-conjugated organoboron polymers via the empty p-orbital of the boron atom by means of hydroboration polymerization [1] or polycondensation [2]. These polymers exhibited unique characteristics such as intense fluorescence emission, excellent third-order non-linear optical behavior, and n-type electrochemical activity and so on. Thus, they are expected as a novel type of optical and electronic materials. They also could be mentioned as an innovative example of organoboron polymers containing boron atom in their main chain with remarkable stability.

On the other hands, hydroboration polymerization of aromatic dicyano compounds with *tert*-butylborane-trimethylamine complex gives soluble boron-containing polymers having cyclodiborazane backbones (i.e. boron–nitrogen four-membered rings) in good yields [3]. Recently, hydroboration polymerization using mesityl (2,4,6-trimethylphenyl, Mes) or tripyl (2,4,6-triisopropylphenyl, Trp) borane was found to proceed under fairly mild reaction conditions to give poly(cyclodiborazane)s with more regulated structure in relatively high molecular weights [4,5]. The resulting poly(cyclodiborazane)s were a new class of highly inorganic polymeric materials that exhibit reasonable stability toward air and moisture. These highly inorganic polymers are generally interesting as polymeric precursors to ceramics [6]. From the results of pyrolysis at 900 °C, the poly(cyclodiborazane)s can be expected as a polymeric precursor for the production of boron-containing inorganic materials. In this polymerization system, although cyano groups are utilized for polymerization, electron withdrawing property would be retained due to electron accepting property of organoboron units. Nevertheless, the extent of the electron affinity would be lower than that of the π-conjugated polymers prepared from diyne monomers and monoarylboranes. From the result of our collective experiments, this polymerization system was shown to be appropriate for polymerization of a wide variety of dicyano compounds. Although fully aromatic poly(cyclodiborazane)s should be regarded as π-conjugated organoboron polymers via the vacant p-orbital of the boron atom, no significant extension of π-conjugation length was observed when 1,4-dicyanobenzene was employed as a dicyano monomer [7]. Very recently, it was found that an incorporation of charge transferred structure in their backbone brought about a dramatic change in their electronic structure [8]. The resulting polymers showed effective π-conjugation nature and bright luminescence of visible light. This paper

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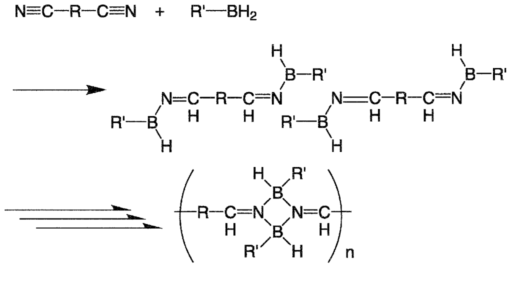
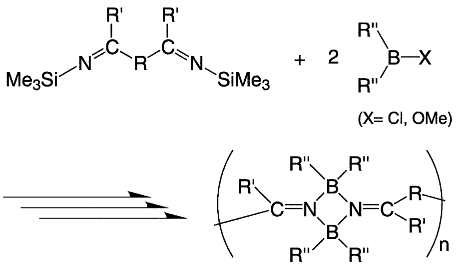
deals with a series of poly(cyclodiborazane)s prepared by hydroboration polymerization and their promising properties for the optical and electronic materials.

2. Preparation of poly(cyclodiborazane)s

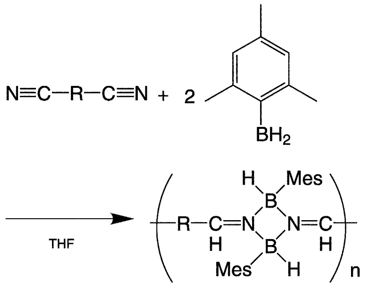
Hydroboration polymerization of dicyano compounds proceeds via dimerization of iminoborane, which is generated by monohydroboration of cyano group (Scheme 1). In early works, polyaddition by using the reaction of *tert*-butylborane-trimethylamine was examined with bifunctional dicyano compounds [3]. Although this polymerization system gave the stable and soluble polymers, it required relatively severe reaction conditions (100 °C) to remove trimethylamine ligand securing the moderate reactivity of borane monomers. As an alternative method, poly(cyclodiborazane)s were prepared by the reaction of bis(silylimine)s with chlorodialkylboranes or with methyl dialkylborinates (Scheme 2 [9]). This reaction proceeds via the condensation between *N*-silylimine and boron halide, eliminating trimethylsilyl halide followed by dimerization. However, the isolated polymer became insoluble after keeping for several hours under air, which resulted from the cross-linking reactions of unreacted trimethylsilyl groups to form trimerized hydrobenzamide derivatives.



Scheme 1.



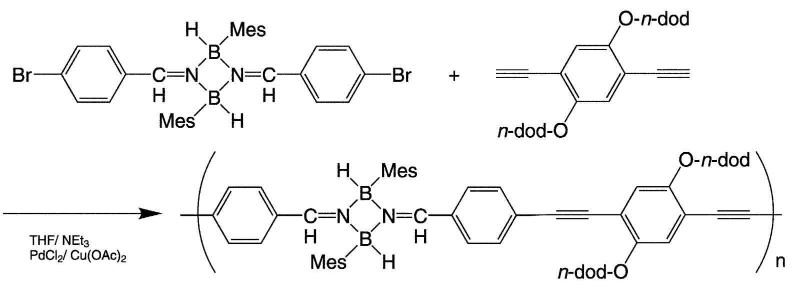
Scheme 2.



Scheme 3.

Generally, in the case of hydroboration polymerization of dicyano compounds, the formation of monomeric iminoborane or borazine structure as a structural defect is unavoidable, especially in the case where the sterically less hindered borane species were employed as described above. Thus, to improve the selectivity between monohydroboration and dihydroboration, and to obtain the higher molecular weight polymers with more regulated structure, the hydroboration polymerization was examined with sterically hindered borane monomers (Scheme 3 [7]). Hydroboration polymerization between mesitylborane and adiponitrile gave the relatively high molecular weight polymer when the reaction was carried out at 0 °C ~ r.t. The ^{11}B-NMR spectrum recorded in $CDCl_3$ showed its main peak around 1.15 ppm corresponding to four-coordinated structure. This result indicates that the further hydroboration reaction of iminoborane species during the polymerization was almost negligible. When tripylborane was employed [5], the relatively high stability of the polymer was shown by its resistance to reaction with air or water and from themogravimetric analysis behavior. However, the number-average molecular weight of the polymer was comparatively lower than the case where mesitylborane was employed, possibly due to lower reactivity or less solubility of tripylborane. Whatever, tripylborane is much easier to handle than thexylborane or mesitylborane because it does not show any sigh of decomposition even after 21 days (mesitylborane; 24 h) when kept under inert atmosphere at room temperature. Thus, the polymerization using tripylborane should be industrially more beneficial.

As another method, poly(cyclodiborazane)s were synthesized by organometallic polycondensation between cyclodiborazane-containing dibromide and 2,5-didodecyloxy-1,4-diethynylbenzene utilizing Sonogashira coupling (Scheme 4 [10]). Generally, organoboron compounds tend to retard the nickel- or palladium-catalyzed cross-coupling reaction; however, transmetalation appears to be suppressed in this system presumably owing to high steric hindrance around the boron atom or specific electronic state of boron atom. The number-average molecular weight of the resulting polymer corresponds to 8500, which is slightly higher than the polymers prepared by the previous hydroboration method. The polymerization using a cyclodiborazane monomer prepared from tripylborane was also examined in similar manner; however, the majority of the products was insoluble probably due to much poor solubility of the cyclodiborazane monomer. The ^{11}B-

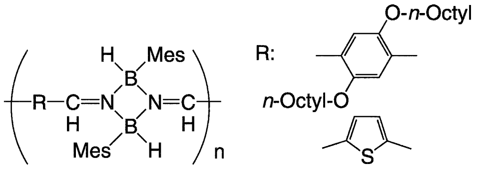


Scheme 4.

NMR spectrum showed only one peak at 0.88 ppm, indicating that typical cyclodiborazane structure is present, and that the structure was not affected by the polymerization condition where organometallic catalysts were employed. It should be also noted that no peak assignable to monomeric iminoborane (around 30 ppm) was observed in the spectrum. That is, the polymerization of the purified cyclodiborazane monomer resulted in the formation of the poly(cyclodiborazane) without structural defects such as monomeric iminoborane or borazine structure. Although this coupling polymerization with Pd/Cu catalysts gave the reasonable molecular weight polymer with high purity, hydroboration polymerization has advantages in the reaction condition and synthesis of monomers; it proceeds at room temperature without any catalysts, and is applicable to various dicyano compounds.

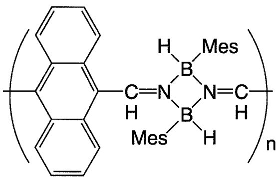
3. Functionalization of poly(cyclodiborazane)s

As mentioned above, although fully-aromatic poly(cyclodiborazane)s should be expected to show the nature of π-conjugated polymers, no significant extension of π-conjugation length was observed in the case where 1,4-dicyanobenzene was employed [7]. However, an incorporation of the electron donating structure in the polymer backbone **1** led to the dramatically bathochromic shifted absorption edges compared with their model compounds [8], which indicates the existence of some intramolecular charge transfer (ICT) interaction due to the electron accepting cyclodiborazane moiety or inter-unit conjugation along the main chain of the polymer. This also suggests that the electronic state of poly(cyclodiborazane) is very sensitive toward the electronic environment around the cyclodiborazane unit. Accordingly, poly(cyclodiborazane)s bearing ICT structure are interesting and promising as optical and electronic materials with great durability against air and moisture.



1

We examined hydroboration polymerization with a wide range of dicyano compounds. The polymer derived from dicyanoanthracene (**2** [4]) can be expected as a novel type of electron-transporting materials or polymer catalysts in photochemistry, and an intense green fluorescence emission spectrum was observed at 494 nm. The s–π conjugation utilizing disilanylene structure was also interested [11]. We synthesized poly(cyclodiborazane)s from 1,2-bis(*p*-cyanophenyl)-1,1,2,2-tetramethyldisilane and mesitylborane or tripylborane (**3**). The polymers obtained exhibited characteristics as a novel type of s–π conjugated polymers in their optical behaviors. The fluorescence emission spectra of the polymers showed an intense emission peak in the visible blue region (at 430 nm), owing to intramolecular charge transferred structure in the excited states. The potential of the peak (+0.87 V) obtained from cyclic voltammetric measurement was relatively smaller than those reported for s–π conjugated organosilicon copolymers prepared by Fang et al. [12], indicating the enhanced s–s interaction between disilanylene unit and adjacent cyclodiborazane unit. The poly(cyclodiborazane)s having various number of thiophene repeating units (**4** [13]) were synthesized. The longer thiophene repeating units of the polymers were, the more bathochromic shifted their absorption maxima were. In other words, as the number of thiophene repeating units increases, π-conjugation length extends effectively and the red shift of absorption maxima in UV–vis absorption spectra was observed. The fluorescence emission maxima of the poly(cyclodiborazane)s were successfully controlled in this way (450–530 nm). If the polymers with longer thiophene units are synthesized, the poly(cyclodiborazane)s may emit all the range of visible lights. The poly(cyclodiborazane)s containing dithiafulvene unit in the backbone (**5** [14]) were also reported. This polymer showed tan extension of conjugation between the consecutive repeat units due to the strong electron donating dithiafulvene unit. Before doping, the obtained polymer exhibited an electrical conductivity of 2×10^{-5} S cm^{-1} as measured on a cast film by conventional two-prove technique, which is relatively high conductivity probably due to its donor–acceptor pair of the dithiafulvene and the cyclodiborazane units. Moreover, the cast film of the charge transfer complex of the poly(cyclodiborazane) with 7,7,8,8-tetracyanoquinodimethane (TCNQ) had a conductivity of 2×10^{-4} S cm^{-1}, one order of magnitude greater than that for the uncomplexed polymer. Recently, the poly(cyclodiborazane)s containing transition metals such as palladium and platinum in their backbone (**6** [15]) were prepared by hydroboration polymerization with tripylborane. These polymers exhibited an extension of π-conjugation length via transition metal and boron atom. They are also expected to show third-order non-linear optical properties.



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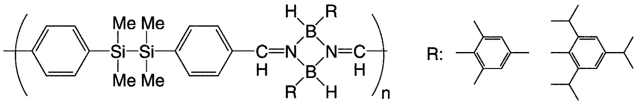
In summary, the series of poly(cyclodiborazane)s were prepared by hydroboration polymerisation.



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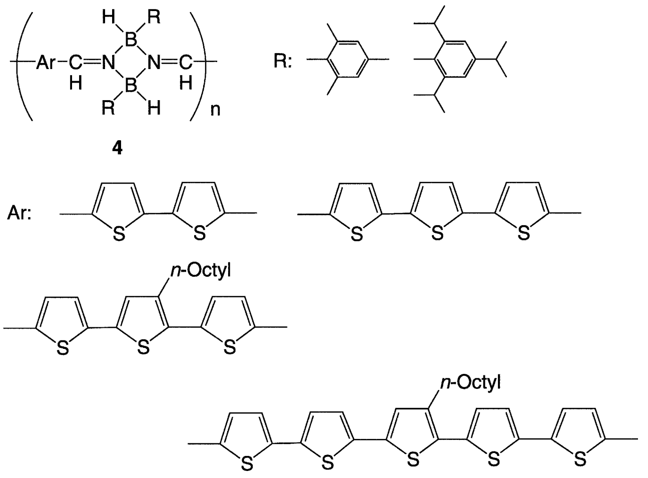
The obtained polymers showed great stability toward air and moisture, and interestingly, an effective expansion of π-conjugation was observed in the case where the ICT structures were constructed in the backbone.



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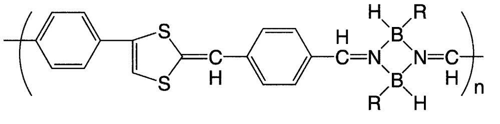
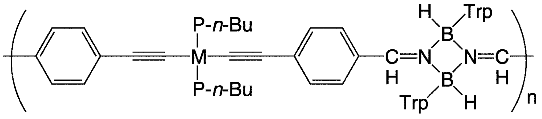
The optical and electronic properties of the polymers showed potential for application as high performance materials.



5 R: Mes, Trp

The poly(cyclodiborazane)s reported in this review would have a great importance in the boron chemistry as a novel type of boron-containing polymers with high stability.



6 M: Pd, Pt

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