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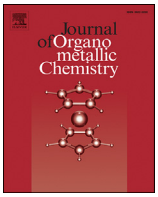

# Direct synthesis of carboranylpolystyrene and their applications for oxidation resistance of graphene oxides and catalyst support

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ABSTRACT

Radical polymerization reaction of carborane monomer *closo*-1-R-2-(4-vinylbenzyl)-1,2-$C_2B_{10}H_{10}$ (R = Me (**1**), Ph (**2**)) produced carboranyl-functionalized polystyrenes, poly(1-R-2-(4-vinylbenzyl)-1,2-*closo*-$C_2B_{10}H_{10}$) (R = Me (**3**), Ph (**4**)), in a yield of 56.3% and 85.0%, respectively. The polymers **3** and **4** were used to coat graphene oxides (GO) and the resulting products exhibited high oxidation resistance property when compared with pristine GO. Polymer **3** was also used to stabilize palladium nanoparticles (Pd-NPs) to form catalyst composite Pd-NPs/**3**. Composite Pd-NPs/**3** was found to be efficient catalyst for selective oxidation of glycerol. All new compounds were fully characterized.

## 1. Introduction

Polymers incorporating carborane units exhibit unique properties due to inherent chemical inertness, high hydrophobicity, electron deficient, thermal and radiation stability of carborane cages [1–17]. For example, silicone polymers with *closo*-carborane, $C_2B_{10}H_{12}$, incorporated in its backbone show promising oxidative stability at high temperatures [1–3]. This type of polymers could find many new applications, other than oxidation resistance reagents, in the near future including those in electrochromic device [12], neutron detector [14] and boron neutron capture therapy [18]. Various methods such as Sonogashira-Hagihara polycondensation [5,8], Stille coupling reaction [11,12] and click-grafting [19], have been used to synthesize carborane-containing polymers. Due to high oxidative and thermal stability of *closo*-carborane cage, the *closo*-carborane appended polystyrenes are expected to show improved thermal and oxidative stability when compared with pristine polystyrenes. Therefore, such polymers have good potential as catalyst supports for oxidative coupling reactions. However, in click-grafting method in which carborane cages were attached to polystyrene chain by an azide-alkyne click cycloaddition reactions, high toxic $Cu^I$-based catalyst was used [19,20]. Similar to other click reactions, the inherent drawbacks such as contamination of $Cu^I$ catalyst species even after completion of the reaction may limit their further applications such as in drug delivery. Removal of remaining metal species from polymer products is particularly challenging because they could be trapped in polymers folds. In this work, carborane-appended polystyrenes, poly(1-R-2-(4-vinylbenzyl)-1,2-*closo*-$C_2B_{10}H_{10}$) (R = Me (**3**), Ph (**4**)), were synthesized by direct radical polymerization reactions.

On the other hand, graphene oxide (GO) has been known for more than one and a half century [21], it has many intriguing properties and potential applications [22]. However, GO possesses thermal and oxidative instability and some of the carbon atoms are oxidized to carbonaceous gases at elevated temperature (~210 °C) [21]. Sandoval et al. reported that nitrogen-doped grephene oxide exhibits increased thermal stability against oxidation by air [22]. Relatively critical conditions such as high temperature (500 °C and 800 °C) and corrosive gas ($NH_3$) were used [22] in the process. Since *closo*-carborane-appended polymers have the potential resistance toward oxidation at high temperatures, polymers **3** and **4** were used to improve stability of GOs. In addition to its application in oxidation resistance, polymer **3** was also used as catalyst support. Palladium nano-particles were supported on polymer **3** to form a catalyst composite. The palladium-based catalysts play important

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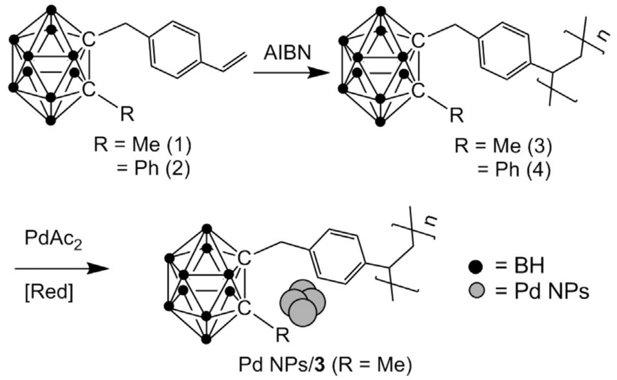
roles in many organic transformations including C–C coupling reactions that have been well-investigated and documented [23–27].

We have been using Pd catalysts in biomass conversions to value added chemicals via selective oxidation reactions [28] and demonstrated their promising catalytic activity. Dihydroxyacetone (DHA) is being the most popularly used ingredient in current sunless tanners approved by the US Food and Drug Administration (FDA) [29]. Commercially available, high-priced DHA is generally produced in an atom-inefficient fermentation process [29]. The inherent drawbacks make the existing technology not efficient from the ecological, energetic, economical, and chemical standpoint. Heterogeneous catalysts possess obvious advantages in product isolation and, therefore, received growing interest for their use [30]. It has been known for a long time that supported platinum catalysts can be used for catalytic alcohol oxidation to aldehydes or ketones in aqueous media. Nonetheless, the deactivation of these catalysts in such reactions is a serious problem [31]. The fact that carboranyl-appended polystyrene with high oxidation stability are prepared in our laboratory, we report herein the synthesis and application of catalyst composite for selective oxidation of biomass-based glycerol to 1,3-dihydroxyacetone.

## 2. Results and discussion

Carborane-appended styrene monomers **1** and **2** were prepared by substitution reactions between *in situ* generated lithium salts of [*closo*-1-R-1,2-$C_2B_{10}H_{10}$]$^-$ anion and 4-vinylbenzyl chloride in 71.2% and 81.7% yields, respectively (Scheme 1). The $^1$H, $^{13}$C, and $^{11}$B NMR spectra are similar to those found for other related structures. In $^{13}$C NMR spectra, unsaturated C=C bonds show double peaks in the region of 114.31–114.56 ppm. In $^{11}$B NMR spectra, **1** and **2** gave different resonance patterns. Compound **1** shows a 1:1:2:2:4 splitting pattern, while **2** exhibits a 2:4:4 resonance peaks. This could be due to the presence of different substituted moieties, methyl verses phenyl, on carborane cages. In the IR spectra, strong absorptions at $\nu = 2562$ cm$^{-1}$ and 2565 cm$^{-1}$ are attributed to $\nu_{BH}$ as shown in Fig. 1. Direct polymerization of carboranyl styrene monomers were carried out in toluene media. In order to avoid the risk of violent decomposition during the polymerization, benzoyl peroxide was not used, instead the safer azobisisobutyronitrile (AIBN) was chosen to be an initiator. Polymers **3** and **4**, poly(*closo*-1-R-2-(4-vinylbenzyl)-1,2-$C_2B_{10}H_{10}$) (R = Me (**3**), Ph (**4**)) were obtained with Mw of 5795 (DPI = 2.37) and 3029 (DPI = 1.79), respectively. The lower Mw of **4** could be due to steric effect of phenyl substituent on the cage carbon. The $^1$H, $^{13}$C, and $^{11}$B NMR spectra appear normal as broad peaks with the disappearance of the vinyl ($CH=CH_2$) groups when compared to those of the corresponding monomers, thus confirming the success of radical polymerizations. As found for monomers, strong absorptions around $\nu = 2560$ cm$^{-1}$ that are assigned as BH stretching mode of vibrations ($\nu_{BH}$) were also observed in the FT-IR spectra of the resulting polymers.

The GOs were coated with carboranylpolystyrene polymers by dipping into their corresponding solutions. The resulting composites were heated to 1000 °C in a stream of nitrogen gas to produce ceramic-coated GOs-based thermosets. In TGA analysis, the thermosets showed improved thermal stability at high temperatures in airflow of 100 mL/min as shown in Fig. 2. On the other hand, the pristine GOs burned completely at 221 °C in airflow (100 ml/min). Under the same conditions, thermosets 3-GOs and 4-GOs started losing weights at 536 °C and 552 °C, respectively, and thus showed significantly improved thermal and oxidative stability at >300 °C in airflow. The combustion temperature is comparable to that of previously reported nitrogen-doped GOs (520 °C and 579 °C), that were prepared under the harsh conditions of high temperatures (500–800 °C) in corrosive ammonia [22]. In comparison, the GOs were also coated with commercially available polystyrene (Mw 35000, Sigma–Aldrich) and then subjected to TGA analysis (Fig. 2). It was observed that the polystyrene-GOs composite started to lose weight at a temperature of 210 °C in air. The maximum weight loss temperature is around 292 °C. This temperature is significantly lower than that for carboranylpolystyrene-GOs composite. This results suggested that the attachment of carborane cages is crucial to improve the thermal and oxidative stability of GOs. Although the real reason is not yet clear, it was proposed that a thermally stable film was generated *in situ* from the carborane cages in the continuous heating process, and the resulting film protected GOs to improve their stability.



**Scheme 1.** Syntheses of carboranylpolystyrene and Pd NPs supported composites.

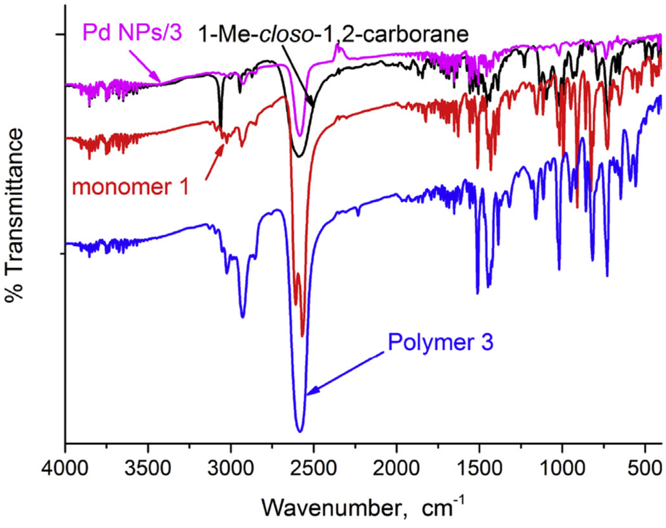


**Fig. 1.** FT-IR spectra of 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$, **1**, **3**, and Pd NPs on **3**.

Palladium (0) nanoparticles were prepared *in situ* by reducing palladium acetate with phenylboronic acid and then supported on carborane-appended polystyrene **3** following the literature procedure [32]. The synthesized catalyst composite was analyzed using ICP, XPS as well as TEM to identify the loading amount, chemical oxidation state and particle size of the supported palladium species. As shown in TEM images (Fig. 3), the produced Pd particles are small crystalline in nanometric size with an average size of around 4.7 nm and a relatively narrow size distribution (Fig. 4(A), determined from the measurement of ~100 particles). The uniform nanoparticles were well dispersed on the polymer support. The samples for XPS analysis were prepared in a glove-box as described