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Defining Self-Assembling Linear Oligo(dioxaborole)s

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A route to self-assembling linear oligo(dioxaborole)s and detailed characterization using Fourier transform infrared and ^{1}H NMR spectroscopies compared to small molecule analogues is described. The oligomer formed through the reaction between benzene-1,4-diboronic acid and 1,2,4,5-tetrahydroxybenzene is linked via covalent yet reversible cyclic boronate esters. Comparison of the spectral data for this oligomer compared to bis(dioxaborole) (diester) and anhydride containing model compounds forms a basis on which to derive information about bonding outcomes for larger polymeric systems from small molecule analogues. From this analysis, it is clear that caution must be exercised when evaluating the spectroscopic signatures related to certain boronate containing species because they are not always obvious and are highly dependent on molecular structure and environmental factors such as solvent. X-ray diffraction data along with ^{11}B NMR and molecular modeling confirmed the planarity of the bis(dioxaborole)s and provided adequate information to propose a supramolecular π-stacking orientation for the oligomeric compounds. Careful interpretation of information obtained about small molecule boronate esters in the structural analysis of macromolecular structures creates a foundation for developing and analyzing self-assembling polymers and covalent organic frameworks on the basis of this assembly motif.

Introduction

As boronate ester formation becomes more popular as a self-assembly strategy, the need for approaches to better characterize and classify these materials becomes particularly important. There is a great deal of information in the literature related to the characterization of small molecules containing boronic acids, boronate esters, and anhydrides. Still, many of these reports offer conflicting results, and there is virtually no comparisons drawn between compound types. Moreover, there are few details to be found on how this information can be applied to understand bonding in larger oligomers and polymers. Many of these analyses rely on expected spectral changes upon conversion, from acid to anhydride for example, using ^{1}H or ^{11}B NMR[1] or infrared[2] spectroscopies. However, the spectral alterations related to certain boronate containing species are not always obvious and are highly dependent on molecular structure and environmental factors such as solvent. Furthermore, there is virtually no comparison between the solution phase and solid-state characterization of these materials. Herein a study is presented comparing the spectral characterization of a pair of small molecule bis(dioxaborole)s and a simple boronate anhydride, in coordinating and non-coordinating solvents, to help interpret data from oligomeric and polymeric analogues. Solid state analyses of these model compounds is also used to better define bonding and structural ordering in these macromolecular materials.

Over the past 30 years, boronic acids have been used primarily as synthetic intermediates (e.g., in Suzuki coupling reactions)[3] and as recognition units for the complexation of sugars and other bioactive molecules: functioning, for example, in inhibition,[4] transport,[5] sensing,[6] and chromato-

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graphic[7] applications. The boronic acids described in this manuscript are used to create highly organized macromolecular assemblies. Molecular self-assembly is a powerful tool for the synthesis of polymeric and nanoscopic materials. There has been much interest in self-assembled supramolecules based on noncovalent interactions such as hydrogen bonding[8] and metal−ligand interactions.[9] One benefit derived from using boronate ester formation for the generation of polymeric materials is the *covalent yet reversible bonding interaction* between aromatic boronic acids and 1,2- and 1,3-diols forming 5- and 6-membered cyclic boronate esters (Figure 1).[10] Boronate ester formation, with its covalent yet reversible nature, maintains all of the desired attributes of self-assembling materials including ease of synthesis and dynamic self-repair capabilities (accessing a thermodynamic minimum) while at the same time offering stable, covalently linked materials by a route often times more facile than conventional polymer synthesis (typically through a simple dehydration process).

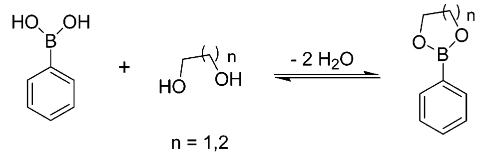

Figure 1. Interaction between PBA and a 1,2- or 1,3-diol to form a covalent boronate ester linkage.

While materials based on boron exist,[11] most are not assembled through boronate ester formation. For example, Wuest et al. have demonstrated porous networked systems based on boronic acids that use hydrogen bonding as a central assembly motif.[12] Alternatively, boronic acids have been used a side-chain appendages on more traditional polymers such as poly(styrene)[13] and poly(aniline),[14] yet these materials do not use the boron as an integral linkage theme. The majority of the materials that are based on boronate ester formation often result from diboronic acids interacting with sugars and typically result in gels.[15]

Our laboratory and others have been involved in the synthesis and characterization of linear polymeric, macrocyclic, and extended network structures using various phenylboronic acids and diols as building blocks. The 6-membered aliphatic esters, referred to as dioxaborolanes, have formed the basis for the generation of highly soluble, linear, self-repairing polymers[16] as well as discreet macrocyclic structures.[11,17] Given the enhanced rigidity afforded by using aromatic 1,2-diols, these 5-membered boronate esters, called dioxaboroles, have found great utility in the synthesis of self-organizing crystalline solids[18] and highly crystalline, porous

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networks (covalent organic frameworks, COFs)[19] as well as leading to the development of a novel class of conjugated polymer.[20] Analysis of linear oligo(dioxaborole) products by ^{1}H and ^{11}B NMR, Fourier transform infrared (FTIR), and X-ray diffraction techniques, as compared to small molecule bis(dioxaborole) and anhydride model compounds, has proven most useful in correlating structure between small and larger assemblies. Specific examples are discussed below including a cautionary note on how solvent can dramatically perturb the expected spectroscopic signature for various boronate based species.

Experimental Section

Materials. 1,2,4,5-Tetrahydroxybenzene (THB; **6**) was obtained according to a literature procedure.[21] All reagents used were purchased from Acros and used without further purification, with the exception of benzene-1,4-diboronic acid which was purchased from Sigma-Aldrich and used as received. All solvents used were obtained from solvent purification systems from Innovative Technologies.

Instrumentation. Solution phase ^{1}H and ^{11}B NMR spectra were collected on a Varian Mercury/VX 300 MHz spectrometer. Solid-state ^{11}B NMR spectra were collected on a Varian Inova 500 MHz spectrometer with a Doty 4 mm XC-MAS probe. FTIR spectra of starting materials, model compounds, and oligo(dioxaborole) were obtained as KBr powder mixtures using a ATI Mattson Infinity Series FTIR spectrometer. The spectra were obtained in diffuse reflectance mode at 300 scans. The FTIR spectrum of bis(dioxaborole) **6** was obtained on a Thermo Nicolet Nexus 470 FTIR using KBr salt plates in transmission mode. Powder X-ray diffraction (PXRD) data was collected on a Rigaku DMax 2200 using Cu Kα radiation. The sample was mounted in a deep well glass slide. Data was collected from 2 to 70° 2θ with steps of 0.02° with a count time of 12 s per step. There were no observable diffraction lines beyond 50° 2θ, so these data were not used in the data analysis.

Preparation of Bis(dioxaborole) 2. To a mixture of benzene-1,4-diboronic acid (0.1011 g, 0.61 mmol) and catechol (0.1402 g, 1.27 mmol) were added 40 mL of toluene and 4 mL of methanol. The solution was heated at reflux for 90 min with a Dean–Stark trap filled half full with 3 Å sieves. During this time a white solid began to precipitate from solution. The solution was evaporated to dryness and excess catechol removed by sublimation using a Kugel-Rohr at 80 °C under reduced pressure (1 mmHg). The resulting product was white needle-like crystals (0.1856 g, 97% yield), mp > 300 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.21 (s, 4H), 7.35 (dd, 4H), 7.16 (dd, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 112.7, 123.0, 134.5, 148.5. ^{11}B NMR (160 MHz, $CDCl_3$, δ, $BF_3{\cdot}Et_2O$ = 0 ppm, external reference): 32 ppm. Solid MAS ^{11}B NMR (160.49 MHz, $BF_3{\cdot}Et_2O$ at 0 ppm as the external reference and boric acid as the second reference at 19.3 ppm): δ 29 ppm. FTIR: 3079, 3041, 1520, 1470, 1360, 1328, 1227, 1084, 748, 663, 639. MS calcd for $C_{18}H_{12}B_2O_4$: m/z = 314.0928. Found: m/z = 314.0933.

Preparation of Bis(dioxaborole) 3. Compound **3** was prepared as described above for **2**: phenylboronic acid (PBA; 0.1280 g, 1.04 mmol) and THB (0.1061 g, 0.550 mmol) in 40 mL of toluene plus 4 mL of methanol. As the solution cooled slowly to room temperature, a white crystalline solid formed. The product was isolated by vacuum filtration, washed with acetonitrile, and dried under vacuum for 12 h. The resulting product was white crystalline needles (0.1542 g, 93% yield), mp > 300 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): 8.06 (d, 4H), 7.57 (t, 2H), 7.48 (t, 4H), 7.31(s, 2H). ^{13}C NMR (75 MHz, CD_2Cl_{23}, δ): 98.2, 128.3, 132.4, 134.8 134.9. ^{11}B NMR (160.49 MHz, $CDCl_3$, δ; $BF_3{\cdot}Et_2O$ = 0 ppm, external reference): 30 ppm. Solid MAS ^{11}B NMR (160.49 MHz, $BF_3{\cdot}Et_2O$ at 0 ppm as the external reference and boric acid as the second reference at 19.3 ppm): δ 31 ppm. FTIR: 3113, 3060, 1596, 1463, 1392, 1373, 1321, 1245, 1139, 1068, 1053, 970, 850, 775, 759, 680, 649. MS calcd for $C_{18}H_{12}B_2O_4$: m/z = 313.0960. Found: m/z = 313.0956.

Preparation of Anhydride 4. Compound **4** was prepared as described above for **2**: PBA (0.0665 g, 0.5 mmol) in 40 mL of toluene plus 4 mL of methanol. Upon cooling slowly to room temperature a white crystalline solid formed. The solvent was evaporated under reduced pressure to yield a white solid that was dried under vacuum for 12 h to afford 98% isolated yield (0.054 g), mp >300 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): 8.26 (d, 4H), 7.61 (t, 2H), 7.54 (t, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 128.3, 133.1, 136.0. ^{11}B NMR (160.49 MHz, $CDCl_3$, δ; $BF_3{\cdot}Et_2O$ = 0 ppm, external reference): 29 ppm. Solid MAS ^{11}B NMR (160.49 MHz, $BF_3{\cdot}Et_2O$ at 0 ppm as the external reference and boric acid as the second reference at 19.3 ppm): δ 31 ppm. FTIR: 3055, 3027, 1603, 1442, 1371, 1182, 1090, 1026, 761, 701, 580. MS calcd for $C_{18}H_{15}B_3O_3$: m/z =312.1308. Found: m/z = 312.1310.

Preparation of Oligo(dioxaborole) 1. Compound **1** was prepared and worked up as described above for **3**: benzene-1,4-diboronic acid (0.2017 g, 1.2 mmol) and THB (0.3478 g, 1.8 mmol) in 40 mL of toluene and 4 mL of methanol. The original solution was clear and colorless. The resulting product was an off white powder (0.2425 g, 69% yield). ^{1}H NMR (300 MHz, DMSO-d_6): 8.1 (br s, terminal OH), 7.70 (s, 4H), 6.19 (s, 2H). Solid MAS ^{11}B NMR (160.49 MHz, $BF_3{\cdot}Et_2O$ at 0 ppm as the external reference and boric acid as the second reference at 19.3 ppm): δ 30 ppm. FTIR: 3474, 3110, 3055, 1609, 1521, 1472, 1392, 1361, 1140, 861, 653.

Results and Discussion

The synthesis and characterization of oligo(dioxaborole)s based on THB (**6**)[21] and benzene-1,4-diboronic acid (**5**) demonstrate how spectral patterns found in small molecule analogues can be used to understand bonding and structural features in polymeric and network materials. In this process one can examine whether the expected boronate esters are indeed forming in a macromolecular assembly process using data from ^{1}H and ^{11}B NMR and FTIR. *Caution must be exercised because solvent can greatly influence these analyses.* Additionally, solid state analysis employing PXRD coupled with molecular modeling provides information about backbone geometries as well as intermolecular packing orientations for these novel compounds.

Synthesis of Model Bis(dioxaborole)s, Anhydride, and Oligo(dioxaborole)s. A series of bis(dioxaborole)s have been previously reported.[18] For this study, an improved synthetic method was employed to obtain bis(dioxaborole)s **2** and **3** and anhydride **4** in excellent yields (Figure 2). The principle modification from existing methods used toluene with 10% methanol to improve solubility of the starting materials and facilitate the error checking mechanism associated with the reversibility and self-repair of the boronate formation. A

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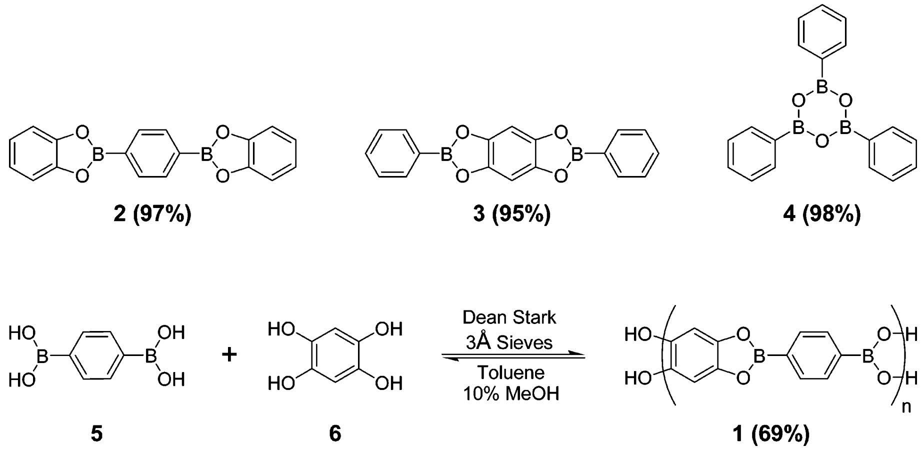

Figure 2. Structures of model bis(dioxaborole)s **2** and **3** and anhydride **4** as well as the synthesis of oligo(dioxaborole) **1**.

Dean−Stark apparatus filled with 3 Å molecular sieves was used for the azeotropic removal of water while allowing the methanol to circulate back to the reaction pot. Each of these model compounds precipitated from solution and was isolated by vacuum filtration. Compound **2** was purified by sublimation of excess catechol starting material, while models **3** and **4** could be purified by washing with acetonitrile to remove any unreacted starting materials. Elemental analysis is notoriously poor at evaluating exact mass for boronic acid containing compounds; therefore, ^{1}H NMR analysis was used to assess purity of the boronate linked materials.

The synthesis of oligomers began with the bifunctional monomers benzene-1,4-diboronic acid (**5**) and THB (**6**).[21] The oligo(dioxaborole) **1** was generated via a one step condensation reaction as described above for the model compounds (Figure 2). The product began to precipitate from solution almost immediately and was isolated by filtration and washed with dry acetonitrile, affording an off white solid in nearly 70% isolated yield. The resulting product had limited solubility in most organic solvents and decomposed in basic aqueous media.

Full characterization of oligomeric materials provides an attractive option to better understand bonding and structural ordering in polymeric and framework materials based on boronate formation. The bis(dioxaborole)s, **2** and **3**, as well as anhydride **4**, serve as useful examples of well-characterized models, both in solution and in the solid state, that can be used to interpret oligomeric boronate spectra, thereby facilitating the understanding of polymer formation and structure.

Spectral Characterization of Models and Oligo(dioxaborole)s. It has been previously reported that for simple mono-functional compounds, ^{1}H NMR in chloroform is quite useful to differentiate between the free acid (~7.7 ppm), anhydride (8.2−8.3 ppm), or esterified (7.9−8.1 ppm) boronate species based on the chemical shift for the protons on the aromatic ring ortho to the boron.[1] These downfield shifts are often attributed to extended conjugation through the planar ester/anhydride and/or through geometric constraints enforced on the boron thereby increasing the boron Lewis acidity.[22] In this discussion, we attempt to sort through, pull together, and update existing boronate-associated spectral trends. A detailed comparison of key diagnostic indicators for ^{1}H NMR and infrared spectroscopic analyses has been severely lacking and is provided herein, identifying what is truly important to best define the nature of the integral linkages in boronate assembled materials. A cautionary note is also attached given the high environmental sensitivity for many of these boronate containing compounds as represented by solvent dependent spectral outcomes.

Bis(dioxaborole)s are conjugated diboronate esters, and for these more complicated di- and oligomeric boronates, the spectra are more complex and highly solvent dependent. For example, Figure 3 shows the ^{1}H NMR spectra for both bis(dioxaborole) models, **2** and **3**, in deuterated chloroform and in dimethyl sulfoxide (DMSO).[23] The obvious change in all of these spectra is the disappearance of the resonances for the hydroxyl protons for the ester products compared to the starting materials (see Supporting Information). For model **2** in chloroform (Figure 3a), the aromatic protons ortho to the boronate ester (on the boron side) are shifted downfield to 8.2 ppm ($\Delta\delta \sim 0.5$ ppm). This is a more substantial downfield shift compared to the simple mono-esters (typically ~ 8.0 ppm; $\Delta\delta \sim 0.3$ ppm) because there are two electron deficient boron substituents on the phenyl ring and therefore this shift is nearly identical to the chemical shift observed for simple anhydrides. However, in DMSO, these ester ortho protons shift upfield from the acid by 0.3 to 7.4 ppm (Figure 3b). Here, resonance and geometric implications observed in chloroform are negated by coordination between the free *p*-orbital on the boron and the Lewis basic solvent, likely deplanarizing the boron and thereby accentuating the electron donating nature of the diol. For model **3**, protons ortho to the boron have a chemical shift similar to the mono-ester at 8.1 ppm in chloroform ($\Delta\delta \sim 0.3$ ppm, Figure 3c) because there is only one electron withdrawing group on the ring. Again in DMSO, an upfield shift is observed for diester **3** over the acid of ~0.1 ppm (Figure 3d) due to deviation from planarity and donating affects of the diol. For both ester models and in both solvents the diol containing portion of the molecules display chemical shifts for the ortho protons

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(22) Hall, D. G. In *Boronic Acids*; Hall, D. G., Ed.; Wiley-VCH: New York, 2005; Chapter 1 and references therein.

(23) Spectra were referenced to solvent: for those collected in chloroform, solvent = 7.26 ppm; for those collected in DMSO, solvent = 2.49 ppm.

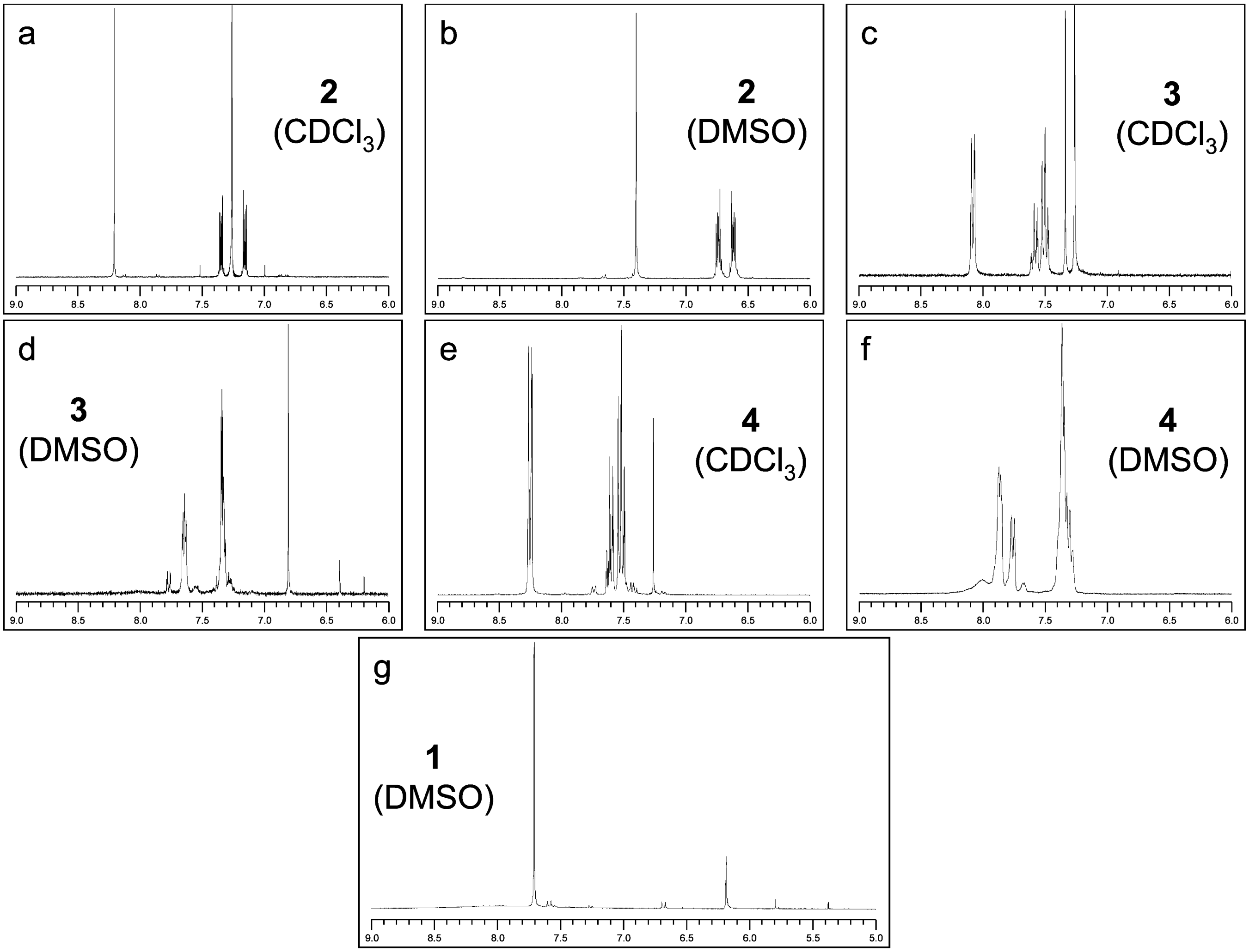

Figure 3. ^{1}H NMR spectra of bis(dioxaborole)s **2** (a) and **3** (c) in chloroform and **2** (b) and **3** (d) in DMSO; boroxine **4** in chloroform (e) and DMSO (f) and oligo-borole **1** (g) in DMSO. All spectra are referenced to solvent (chloroform = 7.26 and DMSO = 2.49 ppm).

consistent with the simple monoesters, that is, shifted downfield, though to varying extents (compared to free diol, **2** shifts ~ 0.4 ppm while **3** shifts < 0.1 ppm). This is likely due to the consistent electron withdrawing nature of the boron compared to a proton, regardless of solvent coordination.

An ever-present concern when working with boronic acids relates to the tendency of these compounds to self-condense[1a,2c,24] resulting in the formation of a boronate anhydride consisting of a six-membered ring of alternating boron and oxygen atoms, also referred to as a boroxine, such as compound **4** depicted in Figure 2. This anhydride formation may result in branching or cross-linking between chains when generating polymeric boronates. The acid, semi-anhydride, and anhydride are most commonly in equilibrium making it difficult, if not impossible, to obtain a spectrum of any of these compounds pure.[1a] In chloroform, anhydride **4** shows the expected downfield shift for the ortho protons ($\Delta\delta$ ~ 0.6 ppm compared to free acid) to 8.3 ppm (Figure 3e). The small doublet observed near 7.7 ppm corresponds to free acid which is always present, even in hydrophobic solvents like chloroform. The doublet between 7.9 and 8.0 ppm in this spectrum corresponds to semi-anhydride, where acids undergo single or multiple dehydration reactions without cyclizing. Unlike the diesters discussed above, in DMSO, the ortho protons for the anhydride are still shifted downfield ~ 0.2 ppm (~7.9 ppm, Figure 2f) though much less than in chloroform. This downfield shift in a coordinating solvent is likely related to the pseudo-aromaticity of the boroxine.[22] Furthermore, while it is still probable that solvent is coordinated to the boroxine ring, it is more likely that only one of the boron atoms is coordinated to DMSO, as has been shown previously for other Lewis basic compounds.[25] Note that even using “anhydrous” DMSO, there is still a great deal of acid present in the sample, indicated by the doublet at 7.7 ppm for the ortho protons and the broad singlet at 8.0 ppm for the hydroxyl protons.

Oligomeric materials such as **1** have signals not only for the main chain but also for end-group moieties, increasing the complexity of the spectra. Furthermore, these unsubstituted oligomers suffer from low solubility in common solvents such as dichloromethane and chloroform, and as such, a spectrum in these solvents could not be obtained. In

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(24) Gilman, H.; Santucci, L.; Swayampati, D. R.; Ranck, R. O. *J. Am. Chem. Soc.* **1957**, *79*, 3077−3081.

(25) (a) Kua, J.; Fletcher, M. N.; Iovine, P. M. *J. Phys. Chem. A* **2006**, *110*, 8158−8166. (b) Kua, J.; Iovine, P. M. *J. Phys. Chem. A* **2005**, *109*, 8938−8943. (c) Perttu, E. K.; Arnold, M.; Iovine, P. M. *Tetrahedron Lett.* **2005**, *46*, 8753−8756.

DMSO, only the shorter oligomeric chains were soluble and it is likely that higher molecular weight materials were formed but were not soluble. Subsequent NMR analysis is based solely on this soluble fraction. An ^{1}H NMR spectrum of the oligomer is shown in Figure 3g (see Supporting Information for starting material spectra). As with diesters **2** and **3**, the most obvious change between starting material and product spectra is the disappearance of the hydroxyl resonance around 8.0 ppm in the starting materials. Closer inspection of this portion of the ^{1}H NMR spectrum of the oligomer shows a broad peak centered around 8.1 ppm corresponding to the terminal hydroxyl groups. End-group analysis, using the integration ratio between the main chain resonances and the terminal hydroxyl groups, was used to determine an approximate chain length of about four to seven units (recall this is representative of the soluble fraction). The terminal aromatic hydrogens of the diboronic acid (7.6 and 7.3 ppm) and bis-diol (5.4 ppm) can be used in a similar fashion to further confirm the proposed chain length. The chemical shifts of the aromatic protons for the starting materials are the same as the signals for the main-chain oligo-ester product. It could be argued that in fact no ester was formed or at least none was dissolved, yet the end group analysis contradicts this. It is possible that these extended π-systems stack in a manner that causes anisotropic shielding of these aromatic protons. This stacking is observed for the model bis(dioxaborole)s and predicted for the oligomers in the solid state (see below). This would also explain why the terminal aromatic resonances are found upfield from starting materials. Variable concentration studies to probe this suggested intermolecular association showed no change in chemical shift but suffered from degradation of the soluble oligomer as it was diluted due to hydrolysis of the boronate esters and provided no additional information about the proposed stacking motif. If a drop of water was added to the DMSO, the oligo-ester was hydrolyzed to afford clearly observable mixtures of the starting materials (see Supporting Information).

To further investigate boronate formation in these materials, we turned to other NMR active nuclei. The limited solubility and/or stability of the diesters and oligomers precludes ^{13}C NMR as an effective method for comparative analysis. Additionally, rapid quadrupolar relaxation associated with ^{11}B−^{13}C coupling results in a broadened signal for the *ipso*-carbon, and therefore this signal is most often lost in baseline noise and not observed in the ^{13}C spectrum for phenylboronic acids.[26] ^{11}B NMR analysis is most useful to evaluate the hybridization around boron[1c,27] and was used to confirm that there is no coordinative cross-linking between main-chain esters and free terminal hydroxyls[16a] in solution and in the solid state.[18b] The ^{11}B NMR of diesters **2** and **3** in chloroform shows a single peak between 30 and 32 ppm, indicating the presence of only sp^2 boron in solution.[27] Using the method developed in our laboratories to compare solution and solid state ^{11}B NMR,[18b] compounds **2**, **3**, and **1** all showed chemical shift values between 29 and 31 ppm, in the solid state, which are consistent with solution based measurements for trigonal planar boron. This result suggested that there were no additional interchain coordinating interactions that cross-link compounds in the solid state.

Analogous to the NMR analysis described above, the most obvious spectral change to look for in the infrared, suggesting the formation of a dehydration product, is the disappearance of the broad peak in the 3200−3400 cm^{-1} range, indicating the disappearance of the hydroxyl moieties found in the starting materials[2b−d,16a] (see Supporting Information). This perturbation on its own, however, cannot account for the formation of ester or anhydride. For model bis(dioxaborole)s **2** and **3**, as well as for anhydride **4**, the complete disappearance of this −OH stretch is observed (see Supporting Information). The oligomeric materials, however, contain terminal hydroxyl groups, and while the intensity of the −OH stretch is greatly diminished, it is still present. Others have also reported attenuation of the band in this region upon formation of porous COFs.[19]

Many literature accounts reference strong bands in the 1300−1350 cm^{-1} range as evidence for certain types of boronate linkage formation (Figure 4,↑).[2b−d,19a] For example, it has been observed that this often broad peak will sharpen and split into two upon ester formation.[19a] Likewise, Blau and co-workers were able to define particular shifts in this region for boron containing rings as compared to acyclic boronates.[2b] Yet this intense peak is attributed to the B−O stretch and is present for boronic acids, esters, and anhydrides alike, with only subtle variations between the forms. Great care must be taken when attempting to interpret the meaning of the absorption bands in this region, and better structural indicators exist.

There is a body of literature from 1958 to 1960[2b−d] that debates the importance of absorption peaks between 650 and 1400 cm^{-1} for the differentiation between boronic acids and anhydrides with little mention of characteristic ester peaks. Santucci and Gilman cite the disappearance of a peak around 1025 cm^{-1} as indication of anhydride formation.[2d] Our laboratory[19a] and others[2c] have observed that there are two sharp and relatively strong absorption bands between 1000 and 1050 cm^{-1} for most boronic acids, and one is attenuated upon anhydride formation. Furthermore, we have observed that one of these bands is also greatly diminished upon ester formation, yet no trends are obvious to distinguish between whether anhydride or ester product is formed from this analysis (Figure 4, ▲).

Snyder et al. have reported[2c] that a better indicator for anhydride formation is the appearance of a strong and sharp band centered around 680−705 cm^{-1} (Figure 4c, Θ). From our analysis we agree that upon anhydride formation an intense peak is observed in this range. However, for some esters, including those derived from tetrol **6**, there is also a sharp, intense peak found in this region of the spectrum (Figure 4b, Θ). A better indicator for anhydride formation is the appearance of a strong and sharp peak between 570

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(26) (a) Pople, J. A. *Mol. Phys.* **1958**, *1*, 168−174. (b) Axelson, D. E.; Oliver, A. J.; Holloway, C. E. *Org. Magn. Reson.* **1973**, *5*, 255−256. (c) Odom, J. D.; Hall, L. W.; Ellis, P. D. *Org. Magn. Reson.* **1974**, *6*, 360−361.

(27) (a) Tetrahedral boron exhibits a chemical shift of 0 ppm with respect to $BF_3 \cdot OEt_2$ (defined as 0 ppm), and trigonal boron displays shifts closer to 30 ppm. (b) Noth, H.; Wrackmeyer, B. In *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1978; Vol. 14.

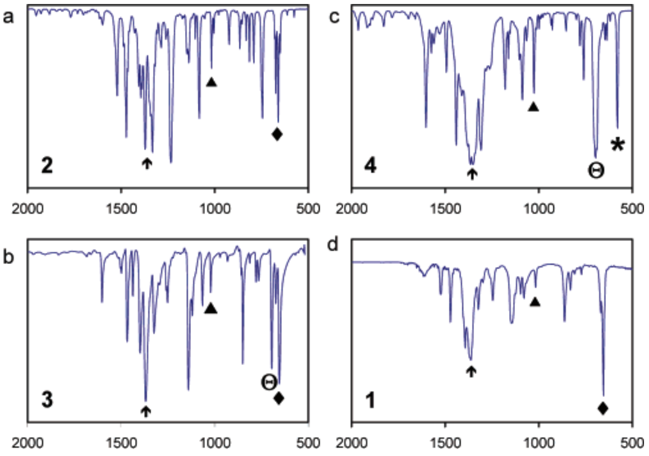

Figure 4. Infrared spectra for (a) bis(dioxaborole) **2**; (b) bis(dioxaborole) **3**; (c) anhydride **4**; and (d) oligo(dioxaborole) **1**. Symbols: (↑) broad intense B−O stretch near 1350 cm^{-1} present in all species; (▲) peak between 1000 and 1050 cm^{-1} found in esters and anhydrides; (Θ) peak between 680 and 740 cm^{-1} indicating anhydride and THB linked esters; (◆) intense peak between 640 and 680 cm^{-1} indicating ester formation; and (*) intense peak near 580 cm^{-1} indicative of anhydride.

and 580 cm^{-1} (Figure 4c, *). While some catechols have weak absorption bands in this region most boronic acid building blocks have none. Only the anhydride exhibits a strong and sharp absorption peak in this portion of the spectrum, and this is clearly different from any bands attributable to catechol. As can be seen in Figure 4d, this peak associated with anhydride formation is absent in the oligo(dioxaborole) spectrum.

While there are numerous examples for using IR to characterize boronic acids and anhydrides, there is little literature precedence of how ester formation compares.[2f] For ester-linked products, we have reported diagnostic bands in the 640−680 cm^{-1} range (Figure 4).[19a] While phenylboronic acids typically have weak and broad absorption bands in this region, ester-linked materials characteristically show two or three intense, sharp peaks (Figure 4a,b,d, ◆). Bis(dioxaborole) **3** exhibits three new peaks in this range in addition to the peak centered near 695 cm^{-1} (discussed above). Diboronic acid **5** displays a relatively intense and broad absorption band in this region, but upon ester formation to afford bis(dioxaborole) **2** and/or oligomer **1**, the band sharpens and intensifies. Even simple mono-esters tend to show two or three new sharp peaks between 640 and 680 cm^{-1} (see Supporting Information). On the other hand, while anhydrides display an intense peak near 700 cm^{-1}, only weak absorption bands are observed between 600 and 680 cm^{-1} and these are typically shifted to lower wavenumbers then what is observed for ester-linked materials.

From these results it is suggested that caution be exercised when assessing the spectral response for oligo-and poly(boronate)s. There are literature examples that cite a downfield shift in the ^{1}H NMR for ester or anhydride formation but do not consider additive electronic affects or the solvent influence. Likewise, when assessing the FTIR results it is common practice to simply refer to the B−O stretch near 1350 cm^{-1} as indication of ester or anhydride formation. Again care must be taken to interpret the full spectral signature for the product, looking not for one particular absorption band but instead interpreting a series of absorption bands to better tell the full story. With this detailed analysis, researchers can confidently predict linear or branched polymers along with the appropriate linkage motif.

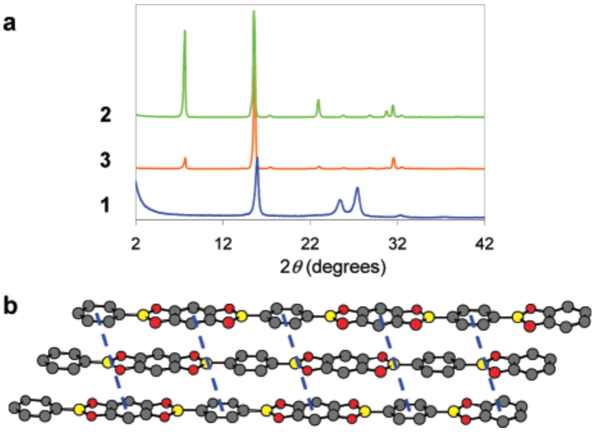

Figure 5. (a) PXRD data for bis(dioxaborole)s **2** and **3** and oligo(dioxaborole) **1**. (b) Minimized structure for penta(dioxaborole)s using AMBER force field in Macromodel. The blue dashed lines indicate the phenyl−boron−phenyl stacking preference observed in small molecule crystal structures.

Lessons Learned: Spectral Characterization Summary. Given the inconsistencies in the changes in chemical shift in the ^{1}H NMR between mono-, di-, and polyesters as well as similarities with anhydride and solvent dependencies, the researcher must be careful in interpreting this type of data and should always corroborate any bonding and structural predictions with other characterization methods. Alternatively, due to the lack of information provided in ^{13}C and ^{11}B NMR spectroscopies, these methods also offer limited information about differentiating between the formation of ester- and the formation of anhydride-linked materials. As a complementary and more definitive analysis method, FTIR provides more information about the type of linkage formed. Even though these are the most commonly sited regions for defining boronate bonding motifs, care must be taken in interpreting bands in the 1300−1350 cm^{-1} and 1000−1050 cm^{-1} range because these peaks are present in most boronate linkages. For differentiating anhydride from ester, the most diagnostic peaks are near 580 cm^{-1} for the anhydride and between the 640−680 cm^{-1} range for esters. Regardless of the apparent clarity for assigning functionality associated with these absorption bands, it is still important to use these analyses in conjunction with other characterization methods. Coupled with the above-described NMR analysis, infrared measurements have proven to be quite useful in reliably differentiating between ester or anhydride formation.

Solid-State Structural Characterization of Model and Oligo(dioxaborole)s. We have previously demonstrated the planarity and supramolecular assembly of bis(dioxaborole)s such as **2** and **3**,[18] including the propensity of these compounds to π-stack in an offset manner, sandwiching the electron deficient boron between electron rich phenyl rings of adjacent layers, forming a phenyl−boron−phenyl sandwich. Alternatively, two-dimensional boronate-linked sheets have been shown to stack in a registered manner placing electron deficient boron atoms in a columnar arrangement throughout the assembly.[19] Given the geometric and structural similarities between bis(dioxaborole)s and oligo(dioxaborole)s, it is expected that oligomeric and polymeric materials would assemble in a manner similar to the smaller bis(dioxaborole)s. Figure 5a shows the PXRD for bis-

(dioxaborole)s **2** and **3** as well as oligomer **1**. As expected the bis(dioxaborole)s have nearly identical PXRD patterns displaying significant peaks at 7.63, 15.60, 22.90, and 31.5° 2θ, corresponding to *d* spacings of 11.58, 5.69, 3.87, and 2.84 Å. The diffraction pattern of the oligomer has prominent peaks at 15.90, 25.40, 27.40, and 32.4° 2θ which equivocates to *d* spacings at 5.55, 3.50, 3.25, and 2.76 Å. Consistent with the model compound assignments, the largest *d*-spacing, at 5.55 Å, is most likely attributable to the main chain repeat pattern. The peaks at 3.50 and 3.25 Å are related to the arene−arene π-stacking distance. These results suggest an off-set π-stacking orientation for the oligomeric chains (Figure 5b) similar to the model bis(dioxaborole)s, **2** and **3**. These distances are also consistent with molecular modeling done using the AMBER force field[28] in Macromodel.[29]

Conclusion

In summary, we report the spectral and structural comparison of linear oligo(dioxaborole)s to a pair of smaller model bis(dioxaborole)s and contrast with the anhydride bonding motif. Structural features found in the small molecule analogues were used to interpret data for the larger oligomeric systems. The formation of an extended oligomeric structure through a series of boronate ester linkages was supported by ^{1}H NMR and IR analysis. Planarity of the oligomer and model dioxaboroles was shown by solid state ^{11}B NMR and supported by PXRD and molecular modeling. The ability to use information obtained from small molecule boronate esters in the structural analysis of macromolecular structures creates a foundation for developing and analyzing self-assembling functional polymers and COFs. However, caution must be exercised when evaluating the spectroscopic signatures related to certain boronate containing species because they are not always obvious and are highly dependent on molecular structure and environmental factors such as solvent. Future efforts will use these fundamental lessons to focus on the synthesis and analysis of functionalized conjugated polymers and the development of extended network materials based on boronate ester linkages.

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Supporting Information Available: Complete ^{1}H NMR, FTIR, and ^{13}C NMR spectra for all starting materials and products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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